To what extent can C Isotopic analysis help substantiate natural attenuation of chlorinated ethenes in groundwater?

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Platform, Panel, and Poster Abstracts

The abstracts assembled in this document represent all platform and poster presentations and panels scheduled as of April 28, 2015. This collection is provided for the use of Symposium registrants who wish to plan which sessions and presentations to attend. **We suggest you download this collection for use before and during the Symposium.** Previously, CDs of the abstracts were distributed to registrants as they arrived at the Symposium, but we have discontinued that practice because many people have told us the laptops and tablets they travel with do not have disc drives.

In the outline below, clicking on the day for a panel or for the platform or poster section of any session will take you to the first abstract in that set. The 61 breakout sessions and 3 panel discussions are grouped under major topics to make it possible to browse related sessions. **Setting your screen to display the full page will make browsing more convenient.** Each abstract has a footer that indicates in which platform or poster session the abstract is scheduled and on which day that session will be conducted. The footer in the final abstract in each session has a link back to the Table of Contents. You may also use the FIND feature to search the text of all abstracts for a term or an author's last name. For the exact times of platform sessions, panels, and poster presentations, see the Final Program booklet posted at **www.battelle.org/biosymp**.

Many of these abstracts will appear in the proceedings, which will be assembled after the Symposium and distributed in digital format to all technical program registrants. Each presentation given at the Symposium will be represented by either the paper submitted by the authors or, if no paper was submitted, by the abstract. The proceedings also will include the presentation files for most platform talks, subject to the speakers' approval.

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TRACKS & SESSIONS

Platform	Posters	TRACK A. Bioremediation Technologies
Tues	Tues Eve	A1. Aerobic and Anaerobic Biodegradation of Organic and Inorganic Contaminants
Tues	Tues Eve	A2. Advances in Biological Oxidation of Chloroethenes and Other Priority Contaminants
Tues	Tues Eve	A3. Phytoremediation
Tues	Tues Eve	A4. Mycoremediation
Weds	Tues Eve	A5. Engineering Biogeochemical Transformation
Weds	Tues Eve	A6. Microbial Fuel Cells
Weds	Weds Eve	A7. Combined Remedies for VOCs
Weds	Weds Eve	A8. Combined Remedies for Other Contaminants
Thurs	Weds Eve	A9. Successes and Failures of Bioaugmentation and Biostimulation
Thurs	Weds Eve	A10. Cometabolic Bioremediation

Platform	Posters	TRACK B-1. Evaluating and Mitigating Vapor Intrusion
Tues	Tues Eve	B1. Chlorinated Compound Vapor Intrusion
Tues	Tues Eve	B2. Petroleum Hydrocarbon Vapor Intrusion
Tues	Tues Eve	B3. Innovative Tools for Evaluating Vapor Intrusion Risk
Tues	Tues Eve	B4. Vapor Intrusion Mitigation Methods

Platform	Posters	TRACK B-2. Munitions Response
Weds	Tues Eve	B5. Munitions Response Site Management Strategies
Weds	Tues Eve	B6. Bioremediation of Munitions Constituents

Platform	Posters	TRACK B-3. Biodegradation of Emerging Contaminants
Weds	Weds Eve	B7. Emerging Contaminants: Chromium
Weds	Weds Eve	B8. Emerging Contaminants: Other Metals
Thurs	Weds Eve	B9. Emerging Contaminants: Perfluorinated Compounds
Thurs	Weds Eve	B10. Emerging Contaminants: 1,4–dioxane
Thurs	Weds Eve	B11. Other Emerging Contaminants

Platform	Posters	TRACK C-1. Managing Petroleum Hydrocarbon Sites
Tues	N/A	PANEL. TPH—What is the Right Cleanup Level?
Tues	Tues Eve	C1. Remediation of Hydrocarbon Spills
Tues	Tues Eve	C2. Advances in Free-Product Recovery
Tues	Tues Eve	C3. Advances in Oxygenate Remediation
Weds	Tues Eve	C4. Petroleum Hydrocarbon-Related Molecular Diagnostics
Weds	Tues Eve	C5. Chemical Fingerprinting and Forensics
Weds	Tues Eve	C6. Aerobic Processes for the Remediation of Petroleum Hydrocarbon Sites

Platform	Posters	TRACK C-2. Biodegradation and Remediation of Crude Oil in Different Environments
Weds	Weds Eve	C7. Remediation of Heavy Hydrocarbon-Contaminated Soils
Thurs	Weds Eve	C8. Bioremediation in Marshes and Deep-Sea Environments
Thurs	Weds Eve	C9. Biodegradation and Remediation of Crude Oil in Cold Regions

Platform	Posters	TRACK C-3. Biological Processes in Unconventional Oil and Natural Gas Development
Thurs	N/A	C10. Biological Processes in Unconventional Oil and Natural Gas Development

Platform	Posters	TRACK D-1. Advances in Natural Attenuation
Tues	Tues Eve	D1. Tools for Assessing MNA
Tues	Tues Eve	D2. Natural Attenuation Processes
Tues	Tues Eve	D3. MNA for Achieving Site Goals

Platform	Posters	TRACK D-2. Advanced Tools for Assessing Bioremediation
Weds	N/A	PANEL. Sampling Groundwater Monitoring Wells: Is What's in the Pipe Representative of the Formation?
Weds	Weds Eve	D4. Fate and Transport of Biofuels
Weds	Weds Eve	D5. Compound-Specific Isotope Analysis
Weds	Weds Eve	D6. Molecular Biological Tools
Thurs	Weds Eve	D7. Advances in Monitoring and Optimization Techniques
Thurs	N/A	D8. Mass Flux and Mass Discharge
Thurs	Weds Eve	D9. High-Resolution Site Characterization

Platform	Posters	TRACK E-1. Sustainable Site Management Strategies
Tues	Tues Eve	E1. Optimizing Existing Systems
Tues	Tues Eve	E2. Risk Management Strategies
Tues	Tues Eve	E3. Licensed Site Remediation Professional Programs: Successes and Challenges

Platform	Posters	TRACK E-2. Green and Sustainable Remediation (GSR)
Tues	N/A	PANEL. Do GSR Frameworks Adequately Represent Ecosystem Services and Natural Resources?
Weds	Weds Eve	E4. Best Practices in GSR
Weds	Weds Eve	E5. Incorporating GSR into Remedy
Weds	Weds Eve	E6. Sustainable Remediation Assessment Tools
Weds	N/A	E7. International Perspective on GSR

Platform	Posters	TRACK E-3. Bioremediation in International Settings
Thurs	N/A	E8. International Challenges and Applications for Site Characterization and Bioremediation
Thurs	Weds Eve	E9. Bioremediation in Latin America
Thurs	Weds Eve	E10. Case Studies and Lessons Learned Applying Bioremediation Internationally

Platform	Posters	TRACK F-1. Bioremediation Implementation Practices
Tues	Tues Eve	F1. Strategies for Bioremediation Performance Assessment
Tues	Tues Eve	F2. Biobarrier Installation and Management
Tues	Tues Eve	F3. Amendment Delivery Strategies
Tues	Tues Eve	F4. Advances in Amendment Formulation
Weds	Tues Eve	F5. Ex Situ Biological Treatment

Platform	Posters	TRACK F-2. Application of Bioremediation to Complex Sites
Weds	Weds Eve	F6. Biodegradation in Fractured Bedrock Sites
Weds	Weds Eve	F7. Biodegradation in Complex Geological Sites
Weds	Weds Eve	F8. Managing Large and Dilute Plumes
Thurs	Weds Eve	F9. Bioremediation of Deep Contamination
Thurs	Weds Eve	F10. Bioremediation of Sediments
Thurs	Weds Eve	F11. Climate Considerations Associated with Bioremediation

Chemically-Enhanced Microbial Degradation of Recalcitrant Chlorinated Compounds

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Background/Objectives. Many of the persistent organic pollutants (POPs) addressed by the Convention of Stockholm are chlorinated compounds (such as Lindane, Mirex and Kepone). While several factors (such as bioavailability) can play important roles in blocking biodegradation, often the first step of the degradation pathway is rate limiting. Thus, while the degradation might be thermodynamically favorable, the slow kinetics can inhibit our exploration of possible biodegradation pathways and the effect of degradation on the microbial community of the impacted ecosystem.

Approach/Activities. The approach used here was to apply a range of different chemical conditions (oxidizing and reducing) in order to favor the biodegradation of a range of POPs. A range of metalic salts with different standard potentials were added to polluted soil incubations to alter the redox and metal catalysts. Chemical and biological degradation was monitored by gas chromatography/mass spectrometry.

Results/Lessons Learned. The metallic salts acted as catalysers for degradation of chlorinated molecules, and thus, affected the potential biodegradation mediated by the soil bacterial community. The changes in the microbial community were monitored by both RISA fingerprinting and phylogenetic microarray. These results were correlated to the biodegradation rates and metabolite types in order to identify potential pollutant degraders. Due to their redox properties, metallic salts might help the biodegradation process by initiating the first steps of the degradation process. Thus, a combination of two processes could be involved: biotic and abiotic. The chlorinated molecules can be chemically degraded by metallic salt leading to the production of by-products that are biologically degradable. Biotic mechanisms could be explained in two ways:

-by-products produced by metallic treatment select for metabolite-degrading bacteria.
-methanogenic and sulfito-reductive bacteria are metallo-enzyme rich organisms that are stimulated by metal salt supplements.

Potential degrading bacteria for different chlorinated xenobiotic compounds can be selected by the use of metallic rich soil particularly iron rich soil. This potential can be enhanced by the addition of different organic substrates.

Success of Mulch to Treat Chlorinated VOCs in a 170-Day Bench Scale Study

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Background/Objectives. The primary objective of this study was to evaluate mulch as a potential in-situ treatment technology for chlorinated solvent contaminated groundwater at former marine terminal. The groundwater contains significant concentrations of chlorinated solvents, primarily vinyl chloride and cis-1,2-dichloroethene (cis-1,2-DCE) at concentrations over 200,000 µg/L. The secondary objective was to identify and evaluate bacterial and fungal colonies in the groundwater treated with mulch. The selected mulch is a commercial brand, available at Home Depot and OSH stores in order to be able to obtain a large and consistent supply for field application.

Approach/Activities. Four sets of reactors were prepared and consisted of 1) Baseline, 2) Control, 3) Azide and 4) Mulch. The reactors contained a three to one (3:1) ratio of groundwater to mulch. The reactors were prepared for triplicate sampling at 5 time periods: 4, 8, 12, 18, and 24 weeks after setup. The Control and Azide reactors were used validate the results of the mulch reactors. Groundwater from each reactor were collected and analyzed for volatile organic compounds (VOCs), *dehalococcoides*, total bacteria, sulfate, sufide, and arsenic for evaluation. During the study, a white cotton-like substance grew in many, but not all reactors. The white substance was analyzed for bacterial and fungal colonies. Separately, the groundwater and mulch were individually analyzed for bacterial and fungal speciation and counts. These results were compared and it was determined that the growth of bacteria and fungus was due to the combination of mulch with the contaminated groundwater.

Results/Lessons Learned. The concentrations of vinyl chloride and cis-1,2 DCE were reduced dramatically after 12 weeks from 90,000 µg/L to 10,000 µg/L and were further reduced to concentrations less than 3.5 µg/L at 24 weeks. The groundwater contained bacteria, including *dehalococcoides*, and mulch contained both bacterial and fungal colonies. The addition of mulch to contaminated groundwater increased the number of *dehalococcoides* bacteria, total bacteria, and grew fungus.

The duration of the bench scale study is a critical component as well as the triplicate sampling at each time interval. The bench scale duration of 170 days provided long-term results showing that degradation of vinyl chloride and cis-1,2-DCE is possible to cleanup levels for this site. Providing three concentrations for each set of reactors at each time interval provided enough data to validate the degradation. The Control and Azide reactors remained intact throughout the study while the mulch reactors degraded. Although the site is not a drinking water source, bacterial and fungal growth can be harmful to human and ecological health and therefore needs to be controlled and evaluated during field application. Mulch has been utilized in permeable reactive barriers installed at Air Force Bases but the potential bacterial and fungal growth has not been studied. Once all the mulch is utilized by the bacteria and fungus, it is expected that the bacteria will return to background levels and the fungus will die since it does not occur naturally within the site groundwater. Additional testing will be conducted prior to full-scale implementation to study the long-term growth and decay of bacteria and fungus.

In Situ Congener Study Supports Anaerobic PCB Dechlorination

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Background/Objectives. A former electrical manufacturing site has polychlorinated biphenyls (PCBs) in groundwater and saturated soil beneath the former facility buildings following building demolition and soil excavation. Groundwater PCB concentration trends over a five year period suggest intrinsic biodegradation, with some wells downgradient of the facility buildings' footprint appearing enriched in less-chlorinated PCBs. A treatability study in bench-scale microcosms containing site groundwater samples found that total PCB concentrations were reduced by approximately 41% as a result of amending the groundwater with nutrients and electron donor (biostimulation), plus a PCB-degrading bacterial culture (bioaugmentation). Total PCB reduction was approximately 41% in the biostimulated/bioaugmented microcosms. A field-scale study using Bio-Trap® In Situ Microcosms was employed to evaluate biostimulation of indigenous microbes and combined biostimulation/bioaugmentation under site conditions. The performance goal was established as at least a 25% reduction in total PCB concentrations relative to natural attenuation at the end of a 90-day study period.

Approach/Activities. A three-unit Bio-Trap® In Situ Microcosm Assembly (Microbial Insights, Inc., Knoxville, Tennessee) was deployed directly into a site monitoring well and incubated for 90 days. The Bio-Trap® contained a control unit (no additives), a biostimulated unit (nutrient and electron donor addition), and a biostimulated/bioaugmented unit (biostimulation plus addition of a PCB-degrading bacterial culture). Each Bio-Trap® was deployed with passive diffusion samplers. To validate microbial degradation mechanisms, groundwater samples were analyzed for PCB congeners in addition to PCB homologs. PCB homolog data quantifies the number of chlorines on the biphenyl ring, while PCB congener data provides information on the structural position of the chlorines.

Results/Lessons Learned. Both biostimulation and combined biostimulation/bioaugmentation significantly decreased total PCB concentrations and shifted the PCB profile to less chlorinated, less toxic homologs. Total PCB concentrations were reduced by 57% in the biostimulated microcosms, and 22% in the biostimulated/bioaugmented microcosms. The congener data demonstrated a shift to non-coplanar, less dioxin-like, less toxic PCBs. The tetra- and penta-CB congeners with meta and para chlorines available to microbes were preferentially dechlorinated. These congener concentrations were reduced by 68% in the biostimulated microcosms, and 53% in the biostimulated/bioaugmented microcosms, providing a second line of evidence supporting biodegradation pathways consistent with microbial reductive dechlorination. These results support the feasibility of using enhanced reductive dechlorination to manage PCB migration in overburden groundwater.

Advanced Field Testing to Support Monitored Natural Attention of a Methylene Chloride Groundwater Plume in Bedrock

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Tamzen Macbeth (CDM Smith, Helena, MT, USA)

Background/Objectives. A detailed characterization effort, including matrix diffusion assessment, contaminant passive flux meters (PFM), compound specific isotope analysis (CSIA) and metagenomics of bacterial populations, was conducted to build a conceptual site model to support monitored natural attenuation (MNA) and a technical impracticability (TI) waiver within a contaminated groundwater plume. The site, located in New Jersey, is underlain by the Passaic bedrock formation consisting of sandstones, siltstones, and shale. The site was used for pharmaceutical manufacturing and a leaking underground storage tank system used for methylene chloride (aka dichloromethane or DCM) resulted in a source of DCM groundwater contamination.

A groundwater extraction system operated from 1995 to 2009 to contain the dissolved phase contaminant plume. However, bench scale studies demonstrated very high intrinsic biodegradation rates with contaminant mass removal rates nearly equivalent to the extraction system. Therefore, the system was shut off permanently in 2009 and additional studies were initiated to verify natural attenuation is achieving a stable and/or retracting DCM contaminant plume. While high contaminant levels persist, overall concentrations in the source area remain relatively stable, with a downward trend in the dissolved phase plume. In addition to the evaluation of biodegradation, other parameters were measured at the site to evaluate phenomena such as sorption and diffusion to support natural attenuation modelling efforts.

Approach/Activities. Over 120 bedrock matrix core samples were collected, extracted and analyzed for DCM concentrations. A subset were analyzed for physical properties. The CSIA evaluated DCM carbon and chlorine isotopes within samples collected from 8 locations within the source area and throughout the dissolved plume. PFMs were used to measure the ambient groundwater flux and contaminant mass flux from a bedrock aquifer at 3 well locations at multiple depth intervals targeting fracture zones. The microbial samples were collected from 10 wells and sent for 16S rRNA gene analysis to identify and quantify microbial populations. Results from 16S rRNA gene analysis were subject to co-variate analysis to investigate how the community is affected by varying DCM concentrations and environmental conditions.

Results/Lessons Learned. Significant contaminant matrix diffusion into the porous bedrock was demonstrated within the source area zone. However, within the downgradient contaminant plume matrix diffusion was limited to the fracture zones and had only migrated very small distances into the rock matrix. CSIA was used to demonstrate DCM removal through biodegradation; constrain the DCM mass removal processes; and estimate the fraction of mass biodegraded. Metagenomics analysis identified DCM biodegrading populations, verified biodegradation mechanisms at the site and was used to select biodegradation rates. PFMs were used to determine groundwater velocities within fracture zones responsible for advective transport of DCM from the source area to the plume. In addition, the contaminant mass fluxes and discharges were evaluated from the fracture intervals. Results of these innovative characterization techniques were integrated in developing parameters for groundwater modelling to evaluate the predictive life of the source and dissolved phase plume under a monitored natural attenuation remedy.

Bioremediation via Soil Mixing to Address Chlorinated Ethenes and Ethanes at a Brownfield Site with High Organic and Metal Soils

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Background/Objectives. Environmental investigation, associated with proposed redevelopment of an approximately 40,000-square-foot brownfield along the High Line Park in the West Chelsea neighborhood of Manhattan, New York, identified chlorinated solvent (tetrachloroethene [PCE], trichloroethene [TCE], cis-1,2-dichloroethene [cis-1,2-DCE], vinyl chloride [VC], and 1,1-dichloroethane [DCA]) contamination in shallow groundwater. The site is located over a former river bed that was filled in the late 1800s. A conceptual remedial plan including in-situ chemical oxidation (ISCO) and in-situ enhanced bioremediation (ISEB) was developed to satisfy remediation requirements of the New York State Department of Environmental Conservation (NYSDEC) and the New York City Office of Environmental Remediation (OER). Regional investigation performed by NYSDEC indicated that the chlorinated solvent contamination was a neighborhood-wide issue and the agency expressed interest in addressing the site contaminants with aggressive remediation.

Approach/Activities. A bench-scale study was performed to confirm applicability and determine design parameters for the ISCO implementation. The bench study tested the soil oxidant demand (SOD) and effectiveness of permanganate and alkaline-activated persulfate. Treatability study results found very high SOD (>150 grams oxidant per kilogram soil). The high SOD is associated with high organic content and oxidizable metals. ISCO was ruled out due to the quantity of oxidant required to overcome SOD before addressing the chlorinated contamination. ISEB/bioaugmentation was selected as the sole technology to address site contaminants.

The presence of daughter products including cis-1,2-DCE and VC and microbes (*Dehalococcoides* and *Dehalobactor)* capable of degrading chlorinated compounds suggest that complete degradation of chlorinated ethenes and ethanes was possible at the site. However, the naturally-occurring biodegradation may be stalling at cis-1,2-DCE and DCA. To address this potential issue, bioaugmentation including the addition of carbon substrates and microbes was recommended. Due to an expedited redevelopment schedule, bioremediation treatability studies could not be performed.

ISEB was implemented at the site beginning in September 2014. The implementation included direct-mixing emulsified vegetable oil (EVO), lactate and two microbial cultures (SDC-9 and TCA-20) into the low permeability clay site soils. The combination of EVO (50%) and lactate (50%) was selected to overcome the high concentration of oxidizable metals. Soil mixing ensured an even distribution of organic substrate and bioaugmentation culture in the low permeability soil.

Results/Lessons Learned. The ISEB field implementation will be completed in early 2015 and results will be available before May 2015. The key findings from this project will include: 1) bioremediation as an effective method to address urban contamination at a Brownfield site, 2) soil mixing as a means to deliver bioremediation substrate, 3) reductive dechlorination effectiveness in the presence of elevated soil metals, and 4) the competition for complete reductive dechlorination between chlorinated ethenes and ethanes.

Bioremediation of a Dissolved Ammonia and Nitrate Plume through In Situ Reduction

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Rachel Peters and Trevor Carlson (Federated Co-operatives Limited,
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Background/Objectives. A retail petroleum site in central Alberta, Canada has been in operation since the 1930’s, and has a history of widespread petroleum hydrocarbon (PHC) contamination in both soil and groundwater. Previous attempts to enhance the biodegradation of the PHC contaminants using alternative electron acceptors through the addition of nitrogen based liquid fertilizer resulted in a reduction in PHC concentrations and plume area. However, incomplete utilization of the electron acceptors resulted in the creation of a nitrate and ammonia plume. The site has sandy lithology and is naturally aerobic, which indicates that natural carbon sources are low, and anaerobic denitrification is unlikely. The goal of the investigation was to facilitate the in-situ reduction of nitrate and ammonia through the addition of an electron donor solution, in this case ethanol. It was anticipated that the nitrification of ammonia would decrease the dissolved oxygen concentrations and produce anaerobic conditions. Subsequently, denitrifying bacteria would utilize nitrate as an electron acceptor during anaerobic respiration, through which nitrogen gas would be produced. Alternatively, we may see simultaneous reduction of both ammonia and nitrate via the anammox process.

Approach/Activities. Carbon source amendment to create in-situ anaerobic conditions is most commonly achieved through the addition of a high fructose corn syrup, molasses, or similar product. The proposed use of ethanol was considered for the site due to its low viscosity and high availability, as well as the simplicity of the carbon source. A mass balance calculation was completed to quantify the volume of ethanol required to complete nitrification and denitrification. Consideration was also given to overcoming potential scavenger electron acceptors such as iron (Fe^{3+}) and carbon assimilation during de-oxygenation for biomass production. Approximately 19,000 L of 15% ethanol solution was direct injected into injection wells throughout the plume area via a gravity feed system. A pre-injection, baseline groundwater sampling event was completed approximately one month prior to injections and a post injection sampling event was completed approximately six weeks post injections, with further sampling events scheduled.

Results/Lessons Learned. The oxygen reduction potential (ORP) decreased to a reducing environment throughout the plume area following the injection of ethanol. PHC concentrations remained relatively static between the sampling events. Ammonia concentrations were reduced throughout the plume area by greater than 99%, with the majority of wells reporting non-detectable or near non-detectable concentrations. Nitrate concentrations were reduced throughout the plume area by greater than 67%. A 21% rebound in nitrite concentrations was measured and expected, as nitrite is produced through the denitrification of nitrate. Additional groundwater monitoring and sampling events are planned for the site four and eight months post injection to confirm the initial post injection results and to document any trends in ORP, ammonia, nitrate and nitrite concentrations. Overall, the in-situ denitrification program using ethanol as a carbon source amendment has proven to be a successful method for the bioremediation of in-situ ammonia and nitrates in groundwater.

Back to Contents

Use of Anaerobic Reductive Dechlorination and Cement/Ferrous Iron System for the Remediation of Chlorinated VOCs

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Background/Objectives. This study relates to the use of anaerobic reductive dechlorination and the presence of a cement/ferrous iron system to address soil and groundwater contamination at a site in Indianapolis, IN that was identified as having impacted soils and groundwater by chlorinated solvents.

Researchers have observed decreases in CVOC (Chlorinated Volatile Organic Compounds) concentrations related with the simultaneous existence of cement and iron in the groundwater. PCE (tetrachloroethylene) degradation by Fe(II) in the presence of cement hydration products has been observed in batch slurry reactors. Cement was found to catalyze or participate in CVOC degradation reactions over a pH range of 10.5-13.8 and the degradation kinetics can be described by a pseudo-first-order rate.

Approach/Activities. An excavation was initially performed at the aforementioned site, which was followed by backfilling of the subsurface with crushed brick and cement from a demolished building. A monitoring well was afterwards installed in the middle of the area and that is where the remedial event was performed. The objective of the remedial design was to promote the conditions in-situ necessary for accelerated dechlorination via both abiotic and microbial processes. The remedial program was designed to mitigate off-site migration, treat sorbed and dissolved contamination, and create subsurface conditions that are ideal for biological reductive dechlorination through pH control, addition of organic hydrogen donors, and vitamin and nutrient supplements.

Results/Lessons Learned. The injected remedial mixture was very effective in decreasing the CVOC concentrations, with TCE (trichloroethylene), cis-1,2-DCE (1,2-dichloroethylene) and vinyl chloride concentrations decreasing by 93%, 97%, and 92% respectively. However based on the groundwater field parameters, most notably pH values of approximately 11.88 pH units, biologically-based reductive dechlorination conditions do not appear to be favorable. Therefore, it is assumed that the decreases in CVOC concentrations were significantly affected by the presence of cement in the area combined with the iron source that was injected during the treatment process.

Case Study: Evaluation of a Bioremediation Process through the Injection of Emulsified Vegetable Oil (EVO)

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Background/Objectives. Activities for environmental characterization have been performed in this industrial area located in São Paulo state - Brazil, since 1997, when a preliminary study was conducted to identify potential areas of concern. During a confirmatory investigation the presence of chlorinated organic compounds were identified in the groundwater, mainly trichloroethene (TCE). The results obtained during these activities were used as a basis for conception and installation of a bioremediation system using emulsified vegetable oil (EVO). The objective of this study is to evaluate the data and results obtained between 2008 and 2011, when two injection events of emulsified vegetable oil (EVO) in the hot-spot area of the site were performed.

Approach/Activities. Based on the conceptual site model, a pilot test was performed in the target area in order to validate the proposed remediation technique. Two main activities were evaluated during the test being: induced flow simulation and efficiency of EVO to accelerate the biodegradation process through reductive dechlorination reactions.

After that, an injection system composed of 10 pairs of injection wells, 5 extraction wells and a mixer area were installed in the site.

Two campaigns for injection of EVO solution were conducted between February and April 2010 and between July and September 2011. After each injection, two groundwater monitoring campaigns were conducted at the system influence area for assessment of the performance of the bioremediation process (3 and 6 months after the injection periods).

The analytical parameters analyzed during the campaign included volatile organic compounds (VOC), total organic carbon (TOC), dissolved gases, physic-chemical parameters and inorganic parameters of concern.

Results/Lessons Learned. Natural attenuation parameters indicated the viability of the biodegradation process at the site. Reductive dechlorination reactions were corroborated through the decreasing concentrations of TCE, and increasing concentrations of daughter compounds over time. After the second injection the reduction of vinyl chlorine concentrations indicated the completion of the chlorinated compounds degradation which directly correlates with the final sub product formation (ethane and ethene).

The total mass reduction over this period was about 82%, compared to the baseline mass. Despite the significant mass reduction, the concentrations of TCE were above the remediation goal in one specific area after the second injection, indicating the necessity of complementary remediation actions.

Living Cells of *Stenotrophomonas maltophilia* PM102 as Natural Bioreactors for Chlorinated Hydrocarbon Remediation

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Background/Objectives. Trichloroethylene – a volatile, non-flammable polychlorinated-hydrocarbon proves to be a tough challenge for microbial bioremediation, due to its low water solubility and persistency in soil and groundwater. TCE has gradually found its way in almost every corner of this World, mainly through its application as an industrial solvent and metal degreaser, owing to its excellent solvent properties. According to WHO, TCE is even present in the air we breathe. US-EPA reports TCE as the most frequent groundwater contaminant in its National Priority List. Overexposure to TCE may lead to skin dermatitis, failure of central and peripheral nervous system, hepatocellular carcinoma, cardiac arrhythmias and leukaemia. The great genetic and metabolic diversity of *Stenotrophomonas maltophilia* has been exploited for the bioremediation of monocyclic hydrocarbons, chlorinated pesticides, DDT, RDX, atrazine, keratin, geosmin, p-nitrophenol, etc. However, we were the first to report trichloroethylene degradation activity in the genus Stenotrophomonas. The bacteria isolated from Burnpur industrial-belt (Asansol, West-Bengal), in our laboratory designated: PM102 was novel in the sense it could grow on TCE as the sole carbon source.

Approach/activities. In our laboratory-based research work, we have tried to unfold some of the characteristics of the bacterium at the molecular level that account for its TCE degradation mechanisms. The isolate was identified by 16SrDNA sequencing. Detailed structure was studied with SEM. TCE degradation by the PM102 isolate was monitored with Fujiwara test and Mohr method of argentometry. Total protein profile was studied and Rabbits were immunized with the TCE induced proteins from the PM102 isolate to generate specific antibody. This antibody was immobilized on epoxy-activated sepharose 6B to purify the proteins from the isolate PM102 grown with TCE as the sole carbon source. The purified peptides were analysed with MALDI-TOF-mass-spectrometry. Genetic investigations revealed two genes when the PM102 DNA was amplified with primers specific for the toluene dioxygenase TodC1 gene of *Pseudomonas putida* F1. A novel mono-oxygenase was characterised from the isolate PM102 and verified with zymogram analysis. Biotransformation products were studied through FTIR-spectroscopy.

Results/Lessons learned. The isolate PM102 was 99% homologous to *Stenotrophomonas maltophilia* based on 16S rDNA based identification (NCBI GenBank accession number JQ797560). Proteomic investigations revealed five TCE inducible proteins of 90.25, 51.61, 38.83, 35.14 and 20.47 kDa. Enhancement of TCE degradation by the bacterium was achieved through a three-tier strategy: first, TCE degradation was monitored in presence of other aliphatic and aromatic hydrocarbons like toluene, benzene, chloroform, glucose and phenol. Increase in TCE degradation by living cells of the PM102 isolate was seen when benzene was present as a co-substrate besides TCE. This same property was documented at the enzymatic level i.e., activity bands appeared to be more prominent in the zymogram when the protein-gel was immersed in benzene as the substrate. The second strategy involved enhancement of the PM102 mono-oxygenase activity in presence of copper as a cofactor. The third strategy was to immobilize the living cells of PM102 in calcium alginate beads. This also increased cell viability and reusability and could be exploited for in-situ bioremediation through designing of column-based bioreactors. The natural association of *Stenotrophomonas maltophilia* with plant roots can also be exploited for phytoremediation of contaminated sites.

Functional Metagenomics of Microbial Communities in Groundwater for a Methylene Chloride Plume and Source Area in Bedrock

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Background/Objectives. Microbial community analysis was performed on groundwater samples from a mature remediation site. The site is a former pharmaceutical manufacturing facility that employed an underground storage tank for methylene chloride (aka dichloromethane or DCM). An undetermined quantity of DCM was released from the tank and piping system over several years. The site is located in central New Jersey and is underlain by the Passaic bedrock formation of sandstones, siltstones and shale, with competent bedrock as shallow as 10 feet below grade. The tight bedrock formation has low yielding (0.5 to 2.5 gallons per minute) wells.

A groundwater extraction system operated from 1995 to 2009, but DCM concentrations remain several orders of magnitude above clean up goals. Bench scale biodegradation studies demonstrated the capability to intrinsically biodegrade DCM at approximately the same rate as removal by the extraction system. A biodegradation monitoring study was initiated in 2009 to observe DCM and biogeochemical concentrations. While high contaminant levels persist, overall concentrations in the source area remain relatively stable, with a downward trend in the dissolved phase plume. This has been attributed to native microbial communities at the site. This study used metagenomics to focus on the structure and functional potential of microbial communities in these groundwater environments.

Approach/Activities. This study examined four quarterly groundwater sampling events starting in October 2013. Samples were collected from 10 wells per event and sent for 16S rRNA gene analysis to identify and quantify microbial populations, including putative DCM degraders, present in site groundwater. Results from 16S rRNA gene analysis were subject to co-variate analysis to investigate how the community is affected by varying DCM concentrations and environmental conditions. In addition, functional/shotgun metagenomics was used to build upon microbial community data, which involves random sequencing of microbial community DNA to identify and quantify the relative abundance of individual genes present.. This expresses the timing and regulation of complex microbial processes, including responses to changing environmental conditions.

Results/Lessons Learned. This work is ongoing with the first batch of metagenomic data expected in late 2014. The results is expected to show which biodegradative pathways are present, and which nutrients and conditions are important for degradative metabolism. This metagenomic data will be used in generating predictive models to estimate biodegradation rates. Preliminary co-variate analysis shows strong correlation between several known DCM degrading bacteria and DCM concentration. This correlation is also seen between DCM concentrations and some previously unclassified bacteria, which suggests these novel bacteria may be involved in DCM degradation as well. Comparative functional metagenomics (i.e. comparing the relative abundance of genes involved in degradation at higher contamination wells compared to those with lower contamination) will reveal if the microbial community has adapted to using DCM as a carbon source.

Bioremediation of Source Zone and Migrated Plumes

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Background/Objectives. The former Unocal distribution facility in Wichita, KS, blended and packaged bulk chemicals for industrial customers. As a result of historical operations, tetrachloroethene (PCE) was released to the groundwater at the site. Since 1989, several remedial technologies have been implemented at the site to treat chlorinated volatile organic compounds (cVOCs) in the groundwater, including soil vapor extraction, pump & treat, excavation, bioremediation, and phytoremediation. Despite the many remedial activities conducted, the contaminated groundwater has migrated approximately ¼ mile from the primary source area to adjacent properties.

During annual groundwater monitoring conducted in 2013, PCE and its daughter products were present at concentrations over 10,000 μg/L. Nitrate concentrations within the contaminated groundwater were generally low; however, sulfate was present at concentrations over 1000 mg/L in some portions of the plume. The formation of carbon dioxide, methane, and ethene as well as the presence of *Dehalococcoides* sp. (*Dhc*) in the on-site portion of the plume indicated that reductive dechlorination was ongoing; however, little to no biodegradation was apparent in many off-site portions of the plume. The monitoring data also indicated that the total organic carbon (TOC) levels were limited across the site.

Approach/Activities. To mitigate further expansion of the plume and reduce cVOC concentrations, a phased treatment approach is being implemented at the site. A Bio-Trap® treatability study was implemented in December 2013 to determine the effectiveness of various amendments to promote enhanced reductive dechlorination (ERD) at the site. The biological and chemical amendments tested in the Bio-Trap® study included emulsified vegetable oil (EOS®); the proprietary electron donors HRC® and EHC®; and a commercial feedstock with and without zero-valent iron (ZVI). Based on the treatability study results, it appeared that biostimulation using any of the electron donor amendments tested facilitated continued degradation of cVOCs present in groundwater at the site, although observations noted that the commercial feedstock product had an intrinsic sulfate demand and degraded more rapidly than the others. Based on its attributes of possessing a high ratio of hydrogen produced to product weight coupled with a high percentage of ZVI by weight, EHC® appeared to be the most desirable product for stimulating both biodegradation and chemical reduction. Therefore, EHC® and EHC® Liquid were the amendments selected for injections at different areas across the site, depending on site-specific geochemical conditions and contaminant concentrations.

Results/Lessons Learned. The first round of injections began in July 2014. A total of approximately 29,500 pounds of EHC® (injected as a 30% slurry) and 1,850 gallons of EHC® Liquid (diluted to make a 5% solution) were injected among six barriers and one injection grid using a total 165 injection points over a one month period. Baseline monitoring was conducted in June 2014 prior to the injection event and the first two performance monitoring events were conducted in November 2014 and March 2015. The results indicate the amendments are conditioning the aquifer to promote reductive dechlorination.

Anaerobic Biodegradation of Lindane by Mixed Dechlorinating Consortia

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Lindane, the γ isomer of hexachlorocyclohexane, is a persistent organic pollutant that was extensively used in agriculture as an insecticide. Lindane contaminated sites have been identified throughout the globe; the French overseas department of Guadeloupe, for example, has significant areas contaminated with Lindane. Given its moderate hydrophobicity, Lindane is found sorbed to soil and sediments and bioaccumulates in higher organisms. Under anaerobic conditions, Lindane biodegradation has been studied with pure and mixed cultures. Monochlorobenzene (MCB) and benzene have been reported as main end products. Unfortunately, MCB and benzene are non-desirable toxic end products. Recently, the sustainable anaerobic bioconversion of MCB to benzene and benzene to methane and carbon dioxide was reported (1). Although microorganisms from the genus *Clostridium, Desulfovibrio,* and *Dehalobacter* have been implicated in Lindane degradation, the diversity of microorganisms responsible for the anaerobic biodegradation of Lindane remains to be further explored. Also, the enzymes responsible for the reductive dechlorination of Lindane have yet to be identified. Lindane-degrading consortia, enriched from soil and sediments samples from Guadeloupe, are currently being studied in order to: (1) characterize the microbial community and identify potential bacterial genus involved in the dechlorination of Lindane, (2) investigate the dechlorination pathway of Lindane in these consortia, and (3) evaluate the full bioconversion of Lindane to methane and carbon dioxide by combining a Lindane-degrading consortium with a MCB/benzene-degrading consortium.

To characterize the microbial community of the Lindane-degrading consortia, 16S rRNA gene sequencing was performed. In order to investigate the potential intermediates of Lindane degradation, time-course samples from a lab-scale Lindane-degrading consortium are being analyzed by gas chromatography – mass spectrometry (GC-MS). To address the third objective, microcosm experiments will be performed with a combined inoculum from the Lindane-degrading and MCB/benzene-degrading consortia. Lindane degradation is being monitored by GC-MS after liquid-liquid extraction with hexane. MCB and benzene are being monitored by headspace GC-FID (flame ionization detection).

Samples from the Lindane-degrading consortia revealed that 50 – 70% of the microorganisms present in these consortia belong to the phylum Proteobacteria, Firmicutes, and Chloroflexi, which have been previously implicated in Lindane degradation. The genus *Clostridium, Dehalobacter, Dehalococcoides,* and *Geobacter*, known dechlorinating groups, were in high abundance. The end-products of Lindane degradation in these consortia are MCB and benzene. Currently, the GC-MS screening of intermediates is being performed. The results from the GC-MS study and the preliminary findings of the combined experiment will be discussed during the symposium. ADDIN RW.BIB

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Hydrodechlorination of TCE by Pd and H_2 Produced from a Copper Foam Cathode in a Circulated Electrolytic Column at High Flow Rate

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Background/Objectives. Pd-catalytic hydrodechlorination of trichloroethylene (TCE) by cathodic H_2 produced from water electrolysis has been recently reported. For a field in-well application, the flow rate is generally high. In this study, the performance of Pd-catalytic hydrodechlorination of TCE using cathodic H_2 is evaluated under high flow rate (1 L/min) in a circulated lab-scale column. We use a Pd-containing lab-scale column with various electrode materials such as cast iron and MMO anodes, and a copper foam cathode under the high flow rate for degradation of TCE in ground water by a circulated electrolytic system. For the potential field application, a cost-effective and sustainable *in situ* electrochemical process using a solar panel as power supply is proposed.

Approach/Activities. An iron anode and a copper foam cathode are used as the electrodes to enhance TCE hydrodechlorination because iron anode produces reducing conditions and copper foam cathode hydrodechlorinates TCE directly in addition to producing H_2. Presence of ferrous ions results in precipitates, which gradually cover the surface of electrodes and decrease the removal rate of contaminants. In systems using the iron anode, it is assumed that the high flow rate would favor the remediation process since it would flush out precipitations and prevent clogging.

Results/Lessons Learned. Under the conditions of 1 L/min flow rate, 500 mA current, and 5 mg/L initial concentration, TCE removal efficacy using iron anodes (96%) is significantly higher than using mixed metal oxide (MMO) anodes (66%). Two sets of experiments with iron anode and two types of cathodes (MMO and copper foam) in the presence of Pd/Al_2O_3 catalyst under various current intensities were conducted to evaluate the effect of cathode materials on TCE removal efficacy under a flow rate of 1 L/min. The removal efficiencies are almost the same for both cathodes under the same conditions, with more precipitation generated using copper foam cathode. Packing Pd pellets into the column with both iron anode and copper foam cathode improves the removal rate to 90% for all the currents applied except 62 mA, which produces less precipitates. For the potential field application, a cost-effective and sustainable *in situ* electrochemical process using a solar panel as power supply is proposed.

Back to Contents

Engineered Aerobic and Anaerobic Biooxidation at Two Manufactured Gas Plant (MGP) Sites in Florida

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Background/Objectives. Biological oxidation of dissolved-phase petroleum hydrocarbons (including MGP-related compounds) occurs naturally or via engineered applications when suitable microbial populations and geochemical conditions are present in the aquifer. During bio-oxidation, microorganisms utilize hydrocarbons as electron donors in the presence of available electron acceptors. Aerobic treatment mechanisms are thermodynamically favored but are limited by the low solubility of oxygen in groundwater and the rapid consumption of oxygen by competing scavengers. Anaerobic treatment mechanisms that utilize sulfate and/or nitrate are advantageous because of high solubility in groundwater, natural abundance in the subsurface, and lack of natural sinks or scavengers.

Approach/Activities. Engineered applications of aerobic and anaerobic bio-oxidation were completed at two MGP sites located in Florida (inland and coastal). At the inland site, a groundwater recirculation system delivered dissolved oxygen and nitrate to promote biological oxidation of the dissolved plume primarily consisting of benzene and naphthalene. After 2.5 years of operation, cleanup objectives were achieved in 95% of the treatment area. Isolated areas remained that required additional treatment due to ineffective delivery of electron acceptors. Geochemical data indicated that sulfate concentrations (<5 mg/L) were significantly less than background concentrations (~200 mg/L). Multiple sulfate injections were completed as a polishing step to promote anaerobic bio-oxidation in the remaining areas. In addition, qPCR was used to confirm an increase in sulfate reducers with the appropriate functional genes.

At the coastal site, water-gas tar DNAPL is being degraded by natural source zone depletion (NSZD) processes at a rate significantly faster than it can be hydraulically recovered, but the DNAPL remains a source of dissolved-phase VOCs and polycyclic aromatic hydrocarbons (PAHs) to groundwater migrating offsite. A 9-month biosparge pilot study was completed at the site boundary to enhance aerobic biological oxidation of VOCs and PAHs to supplement DNAPL NSZD processes, reduce offsite mass flux, and achieve treatment criteria. A portion of the biosparge system was positioned within the DNAPL tar source area to promote contaminant weathering and further reduce the time that the tar is a source to groundwater.

Results/Lessons Learned. At the inland site, contaminant concentrations significantly decreased under sulfate reducing conditions. The rate of naphthalene degradation was less than benzene even though microbial diagnostics showed a significantly increased population of sulfate reducers with the functional gene to oxidize naphthalene. At the coastal site, aerobic biological oxidation with biosparging decreased the concentrations of VOCs and PAHs to the target criteria and resulted in clean groundwater migration offsite. These results demonstrate the applicability of NSZD concepts to MGP remediation and highlight multiple methods of effective electron acceptor delivery that can be used to achieve remediation success.

Assessing the Contribution of Ethene-Oxidizing Bacteria to Aerobic Cometabolism of Vinyl Chloride at Contaminated Sites

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Background/objectives: Vinyl chloride (VC), a known human carcinogen, can be generated in chlorinated solvent contaminated groundwater via anaerobic reductive dechlorination of chloroethenes and chloroethanes. If the VC plume escapes strictly anaerobic conditions and encounters oxygen, a variety of aerobic bacteria could potentially co-metabolize VC in groundwater provided there are other growth supporting substrates present (e.g. methane and ethene). Although cometabolism of VC by methanotrophic bacteria is well-known, the contribution of ethene-assimilators (i.e. "etheneotrophs") to aerobic VC cometabolism has not been well delineated in field situations, but could be significant. This is because etheneotrophs are obligate aerobes can operate at low oxygen concentrations, co-metabolize VC in the presence of ethene, and can also adapt to VC as a growth substrate. Our objective is to better understand the relative contribution of etheneotrophs to VC natural attenuation at contaminated sites.

Approach/activities: Etheneotroph functional genes key to VC and ethene biodegradation are *etnC*, which encodes the alkene monooxygenase (AkMO) alpha subunit and *etnE*, which encodes the epoxyalkane:coenzyme M transferase (EaCoMT). Methanotrophic functional genes include those encoding particulate methane monooxygenase (*pmoA*) and soluble methane monooxygenase (*mmoX*). We can investigate the abundance and activity of etheneotrophs and methanotrophs at VC-contaminated sites where the geochemical conditions are favorable for VC oxidation by collecting groundwater and/or sediment samples, extracting DNA and RNA, and applying quantitative PCR (qPCR) that targets these key functional genes (and their transcripts via reverse transcription (RT)-qPCR). To date, groundwater samples have been obtained and subjected to qPCR from several VC-contaminated sites in North America and Australia that contain varying levels of VC, ethene, and methane. We have also extracted RNA from groundwater samples and applied RT-qPCR for both etheneotrophs and methanotrophs at two sites (in MA and VA). This allows us to assess whether these microbes are actively expressing functional genes involved in VC oxidation. Recently, VC and ethene enrichment cultures were prepared with groundwater from a chloroethene-contaminated site in Alaska. A metagenomics study was initiated to track the changes in the microbial community that resulted from VC and ethene enrichment.

Results/Lesson learned: Application of etheneotroph qPCR to DNA from several VC-contaminated sites confirmed etheneotroph presence (*etnC*/*etnE* abundance ~10^3-10^7 genes/L of groundwater). Generally, methanotroph functional genes were relatively more abundant than etheneotroph functional genes in these samples. These functional genes were more abundant at a site that also had high VC and ethene concentrations relative to the other sites. Evidence of *etnC*/*etnE* expression in selected groundwater samples was obtained via RT-qPCR. Expression of *pmoA/mmoX* was also detected in samples from two different sites. At one site etheneotrophs appeared to be more active than methanotrophs at the time of sampling, while at a second site the RT-qPCR data suggested that etheneotrophs were not as active. The metagenomics study indicated enrichment of *Nocardioides*, *Mycobacterium* and *Pseudomonas* sp. in response to VC and ethene. Continued application of etheneotroph qPCR and RT-qPCR as well as metagenomics techniques at chloroethene-contaminated sites will facilitate improved understanding of their relative contribution to VC oxidation in the field.

Land Application of Sulfate for the Treatment of a Petroleum Hydrocarbon Source

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Background/Objectives. Biodegradation at sites impacted with petroleum hydrocarbons (PHCs) is usually limited by the availability of electron acceptors (e.g., oxygen, nitrate, or sulfate). Electron acceptors are commonly added to the groundwater system to enhance the rate of mass removed by biodegradation. Since sulfate reduction accounts for the majority of PHC mass removed by anaerobic processes, the addition of soluble sulfate to stimulate anaerobic biodegradation is an attractive concept. While this approach is usually effective, it is moderately expensive using traditional delivery methods, and hence more economical but yet robust approaches are required. When the target treatment zone is shallow and the geological conditions are favorable, the application of sulfate salt at the ground surface is an appealing alternative that does not require the installation of an expensive delivery system.
To improve our understanding of some of the issues surrounding the land application of sulfate, a pilot-scale experiment was performed under relatively controlled conditions to assess the ability of this delivery approach to treat a PHC source zone. In addition, we also focused on identifying the major migration pathways, assessing spatial and temporal distribution of PHCs and sulfate, and quantifying the longevity of sulfate at key locations within and downgradient of the PHC source.

Approach/Activities. This pilot-scale experiment was performed in the sandpit area at the University of Waterloo Groundwater Research Facility at CFB Borden located near Alliston, ON. A multicomponent PHC source zone (3 m x 3 m) was emplaced in 2012 between 1 and 3 m below ground surface inside a sheet pile walled experimental gate. Simulation tools were used to design an optimal sulfate dosage system that would satisfy the reagent delivery and remediation requirements. Three episodes of sulfate release (5 m^3 of 5-20 g/L Na_2SO_4, and 0.3 g/L $(NH_4)_2SO_4$) at the ground surface were conducted over an 8-month period. A host of multilevel monitoring wells in conjunction with a real-time resistivity data collection system was employed to continuously track sulfate patterns and migration. Treatment performance was evaluated based on changes in sulfate concentration in the plume and PHC mass discharge across a downgradient monitoring fence line. Results from compound specific isotope analysis (CSIA) and biomarker tools were combined with the conventional monitoring data to assess enhanced sulfate reduction of the PHCs.

Results/Lessons Learned. Data collection and analyses efforts are currently ongoing; however, the results of sulfate monitoring showed the real-time resistivity system allowed the collection of high resolution data. By the time of the presentation we expect to have the entire data set assembled and will be able to provide a coherent picture of the utility of the land application of sulfate and its ability to treat this PHC source.

Field Application of Iron Oxide Nanoparticles as Electron Acceptor for the Enhancement of Microbial BTEX Degradation

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Background/Objectives. Sulfate, nitrate, and oxygen are commonly applied electron acceptors for the *in situ* stimulation of microbial BTEX or PAH degradation. Iron oxides can also serve as electron acceptor for the microbial oxidation of organic contaminants via microbial iron reduction. However, iron oxides occur as non-soluble, dry powder; or as gel-like sludge at best. An injection into contaminated aquifers for bioremediation purposes has therefore not been considered so far. In addition, conventional iron oxides show only low reaction rates compared to liquid electron acceptors, because of their low surface area and high crystallinity.

Approach/Activities. Our objective was to overcome the limitations of iron oxides in bioremediation. Our approach to this was using *nanoparticles* of iron oxides. At nano-scale, several advantages for application open up. Iron oxide nanoparticles (NPs) are known to have a much higher reactivity in microbial iron reduction reactions, and reactivity can be further enhanced by modifying their large surface area. They can be stabilized in colloidal suspensions, thus enabling their migration through porous media like soils. Yet their stability can be tuned specifically to a desired degree, depending on the respective aquifer geochemistry, so that an adsorption of the NPs after injection is guaranteed. So by injecting iron oxide NPs, a deposit of electron acceptor can be created within contaminant plumes. There, high microbial degradation activity should take place, and a rebound of contaminant can be avoided. We investigated our idea in a range of lab experiments, and finally in three different field site applications.

Results/Lessons Learned. We managed to produce a stable colloidal iron oxide nanoparticle suspension at industrial quantities, at reasonable costs. This suspension fulfilled the demands for colloidal stability, mobility in soils, stability of the injected deposit, and reactivity towards BTEX. It is eco-toxicologically safe. We applied 5, 20 and 50 m^3 of our suspension to three different contaminated sites. The injections were successful, creating a radius of influence of 2 to 3 m per injection well, with homogenous iron oxide distributions, and minimal increases of the groundwater pressure levels. After injections, the NPs showed no renegade leaching over months, but stayed within the ROI. The hydraulic aquifer conductivity in contrast was not significantly diminished. High-resolution monitoring data of one year indicated a strong increase in microbial iron reduction, a change of the microbial community towards iron reducers, and a decrease of contamination.

In summary, we propose the use of iron oxide nanoparticles as a novel, and field-tested tool for BTEX bioremediation.

Back to Contents

Hybrid Biological, Nanoscale Zerovalent Iron, and Electron Beam Treatment for Industrial Waste Streams

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Background/Objectives. The focus of this study is the treatment of recalcitrant wastewater generated by industry and the development of hybrid approaches, which combine advanced oxidation processes with biological treatment for disposal. The performances of a range of treatment approaches were tested against several waste streams separately and in different sequential combinations. Sequential hybrid biological, nanoscale zero-valent iron and electron beam irradiation treatment lead to synergistic detoxification of a metalworking fluid and a textile dyeing wastewater streams, as determined by various toxicity surrogates. Though research has been done on these technologies individually; they have received far less attention when combined as a hybrid system comprising biological, nZVI and e-beam treatment. This is surprising as in combination they have the potential to achieve synergies by being coupled together, reducing typical e-beam energy requirements by removing labile components using biological processes and nZVI's potential of absorbing, co-precipitating and reducing compounds. Employing a combination of treatments overcomes the limitation of each individual approach.

Approach/Activities. This work was undertaken as part of a PhD course at the University of Oxford on a laboratory scale. Current technologies, such as reverse osmosis or ultra filtration are particularly costly and capital intensive due to the complex nature of industrial wastewaters. Added to this their high pollutant loads and propensity to foul membranes makes the process very energy intensive. Biological treatment of complex wastewaters is an excellent alternative, as it requires little energy to run and is effective at removing high loads. On their own, biological degradation processes are susceptible to shock loads and not very efficient when it comes to degrading toxic and recalcitrant wastewaters. However, some of these limitations can be overcome by coupling biological treatment with more vigorous advanced oxidation processes. Two particularly promising technologies are treatment using nanoscale zero-valent iron (nZVI) and electron beam (e-beam) irradiation to treat, detoxify and recover resources from industrial wastewater. In particular, a large theoretical and empirical body of evidence has shown that nZVI has its place in environmental remediation applications and it is the most widely studied reductant in environmental applications. Being a strong reducing agent, nZVI is able to degrade a wide range of organic and inorganic pollutants and metals in real industrial waste streams. E-beam irradiation treatment is also recognised as being very effective for treating refractory organic wastewaters and has been investigated on a range of waste streams. Its high efficiency and throughput offers promising economics, although compared to other technologies, i.e. ozonation, UV/H_2O_2 and photocatalytic oxidation, has received far less attention.

Results/Lessons Learned. The results show that metalworking fluids and textile dyeing wastewaters have scope for a hybrid treatment as they are detoxified synergistically, but each waste had its own specific treatment requirements in terms of effectiveness. Treatment efficiency depends on the initial concentration and the nature of the stream. A variety of established measures such as chemical oxygen demand, biological oxygen demand, suspended solids, total organic carbon, pH and colour removal measured by optical density, are employed for evaluating the toxicity and bioavailability changes after treatment of industrial wastewaters. To allow for a more versatile and complete evaluation of toxicity from an environmental perspective, these are combined with toxicity surrogates such as biological respiration, growth curves, plate counts, flow cytometry and a combination of bacterial biosensors that express activity in the form of fluorescence; constructing a comprehensive novel model for monitoring bioremediation and detoxification of industrial wastewaters.

Back to Contents

Phytoremediation of Salt and Hydrocarbon-Impacted Soils Using Biochar Augmentation

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Background/Objectives. Phytoremediation has gained acceptance as a cost-effective, green technology to replace dig and treat methods of remediation. Salinization of soils can often occur concurrently with hydrocarbons in oil producing and processing areas. Rhizoremediation is the process whereby microorganisms degrade soil contaminants in the area surrounding the root system. Plants including ox-eye daisy (*Leucanthemum vulgare),* and alfalfa (*Medicago sativa)*, have shown promise as rhizoremediators of heavy hydrocarbons (e.g. polycyclic aromatic hydrocarbons (PAHs)). Biochar which is produced by the thermal decomposition of organic matter, sequesters carbon dioxide, improves plant growth and assists in phytoremediation. This project will demonstrate the use of rhizoremediation and biochar to concurrently remediate hydrocarbons and reduce the effects of a saline environment on plants.

Approach/Activities. Greenhouse studies using hydrocarbon and salt impacted soils have been initiated. Alfalfa, yellow clover, tall wheat grass (*Agropyron elongatum*), Nuttall's alkali grass (*Puccinellia nuttalliana*), and inland salt grass (*Distichlis spicata*) were grown in soils with and without 2.5% (w/w) biochar. Soils were monitored for hydrocarbon contamination levels over a three month period. Plant growth and health were measured throughout the studies and compared to controls.

Results/Lessons Learned. Full soil and biochar characterization is critical to successful remediation. Source and production of biochar affect sorption and other key properties. Biochar augmentation has been demonstrated to improve growth in the field at a local salt-impacted site. A comparison of plant health and growth between the different species and contaminants used in the greenhouse will be presented, and the effects of biochar on hydrocarbon degradation will be discussed.

Phytoremediation of PAHs: Designing for Success

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Background/Objectives. Phytoremediation of soils impacted with PAHs continues to increase in popularity. The appeal of phytoremediation lies in its inexpensive and relatively non-invasive implementation. Of particular interest with regard to remedy evaluation criteria, phytoremediation scores high as a green and sustainable remedy as well as providing multiple secondary benefits not realized through excavation, thermal, or other applicable PAH remedies.

Yet despite its potential benefits, the real value of phytoremediation can only be achieved if it successfully accomplishes its remedial goals. In a recent evaluation of 20 phytoremediation projects that included a control area, less than half of the sites reported significant declines in petroleum hydrocarbon concentrations in planted areas compared with those observed in control areas. These case studies underscore the importance of an informed design and the need for better understanding of phytoremediation's limitations as well as its benefits.

Approach/Activities. A proper design should account for technological limitations of the remedy and the specific nature of the contaminants, such as the recalcitrance of PAHs. Aromatic compounds including PAHs are not as amenable to biodegradation as lighter weight and more soluble hydrocarbons. It has been suggested that PAHs only degrade through co-metabolic reduction and this process requires the presence of aliphatic hydrocarbons, which are often absent from highly weathered impacts.

To demonstrate factors that should be evaluated during design, two full-scale field studies will be presented. One site is a former foundry in Illinois with PAH impacts in the upper three feet of soil. The design incorporates native prairie grasses and trees. A second case study in the coastal plain of North Carolina used a mixture of black and white willow trees to address PAHs in the upper six feet of soil.

The design approach for each site will be presented to highlight factors considered in plant selection, spacing, installation, and maintenance. These include: past species performance in lab or field demonstrations, degree of hydrocarbon weathering, constituents of concern and potentially limiting compounds, depth of impacts, monoculture versus multiple plant species and types, potential for phytotoxicity, climate and growing season length, soil type, estimating time to reach goals, irrigation, aeration of the vadose zone, fertilization, and maintenance requirements.

Results/Lessons Learned. While phytoremediation is not an appropriate remedy for every site, it can be an effective and low cost remedy at many sites if properly designed and implemented. As demonstrated with the two case studies and supplemented with similar supporting results in the literature, the limitations and potential pitfalls can be avoided by a thorough analysis of site conditions and impacts.

Study of the Possibility of Phytoremediation of Hydrocarbon-Contaminated Soil in the Area of Abandoned Steel Production Plant “Poldi”

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Background. High concentrations of toxic pollutants in soils near populated areas may cause the death of plants or reduce their production and what is more the spread of contaminants can endanger the health of people in nearby residential areas. Source of contamination is mostly of anthropogenic origin - from industrial activities (ie. mining, processing and treatment of ores, industrial production). Even if the industrial activity was completed, the site remained contaminated. These locations are usually called brownfields and their recovery is very costly and time-consuming. In the Czech Republic there are many sites with old ecological burdens (sites are listed in the register of contaminated sites on Ministry of Environment) and that is why cheaper and effective methods are in concern. Phytoremediation can be a way to prevent the spread of contamination, while recover a site. Plants can effectively reduce the contamination of brownfields by immobilization of the contaminants in the soil or by accumulation of contaminants in their tissues.

Approach. Our project is aimed at improving a brownfield in city Kladno. The area of Poldi (about 500 ha) is an old steel producing facility. Forges, whose history dates back to the mid 19th century, decided to build its own coking plant at the time of the Second World War. It went into operation in 1944, and then it expanded. Downturn occurred during the 80 years of the last century and coke production finally ended in 1988. Ecological burdens are caused mainly by processing of co-products of coke production, which were tars or oils. Knowledge of toxicology and environmental aspects will help enhance the protection of human health and the environment. Primarily, we focused on soil sampling and identification of pollutants. Next, we made a selection of suitable plant species for stabilization/decontamination of the site. Plant species were selected based on their resistance to contaminants as well as accumulation ability.

Results. Results showed that organic contamination on site is very variable. Average concentrations in soil were i.e.16282 mg/kg of C10-C40, 547 mg/kg benzo(a)pyrene, 1665 mg/kg naphthalene, 0.97 mg/kg PCB, and TEQ BaP was 744 mg/kg. An effect of contaminants on biomass production and root system were measured. For field experiments *Populus* sp. were selected, for laboratory testing *Brassicaceae* sp. seeds were used. Firstly, an effect on seed germination and root growth in first stadium of development was tested. Secondly, a test of cell viability was used. Finally, the effect of soil on biomass production, pigment analysis and root morphology was detected as well as accumulation of PAHs.

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Extraction of Chloride from a Cement Kiln Dust (CKD) Landfill with Halophytic Grasses

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Background/Objectives. Soil salinity is an issue of growing concern, and remediation strategies are limited. Salinity can occur naturally, or as a result of landfilling high salt content waste material, such as cement kiln dust (CKD), which is a waste product from cement manufacturing. CKD landfills often become marginalized lands no longer capable of maintaining vegetation. A number of phytotechnologies can be implemented to improve vegetation cover and aesthetic appeal, while also extracting salts from the soil. These technologies include the application of biochar (a carbon amendment found to improve soil quality in degraded soils) and the careful selection of halophytic plant species. This research is based at a saline-sodic CKD landfill located at the operating Lafarge Cement Plant in Bath, Ontario, Canada.

Approach/Activities. CKD soil was amended with 10% biochar in greenhouse studies and six halophytic grass species were selected for germination and transplant trials. Successful species included *Puccinnellia nuttalliana*, *Spartina pectinata*, and *Agropyron elongatum*. These species were then planted *in situ* in control as well as 5% biochar amended plots and monitored over a growing season for chloride uptake. Species were compared based on their ability to phytoextract chloride from the soil. Excretion, as a salinity tolerance mechanism, was quantified and evaluated from a remediation perspective. In addition, a temporal study was conducted to determine the chloride phytoextraction potential of the resident colonizer *Phragmites australis* at the site.

Results/Lessons Learned. Biochar was found to enhance germination potential of halophytic grasses. *Puccinnellia nuttalliana* and *Spartina pectinata* both have potential to be used for re-vegetation at the site. *Phragmites* australis was found to be a successful species for re-vegetation and phytoextraction of chloride, however to a lesser extent than *S. pectinata* which has the ability to both accumulate and excrete excess chloride, eliminating the need for plant harvest. Salt tolerance and survival of halophytic species is critical to report in conjunction with salt tolerance mechanisms to ensure the most effective remediation/re-vegetation strategy of salinized lands is achieved.

In Situ Remediation of Aromatic Amines Using an Engineered_Phytoremediation^{SM} System (EnPhySys^{SM})

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Background/Objectives. A limited scale *Engineered_Phytoremediation*^{SM} system is being implemented at a former waste oil recycling facility in the Southern U.S. where soil and groundwater have been impacted by 2,4/2,6-toluenediamine (TDA). Groundwater contamination occurs approximately 18 feet below ground surface (bgs). The *Engineered_Phytoremediation*^{SM} technique combines conventional phytoremediation mechanisms (e.g. phytodegradation and rhizodegradation) with groundwater hydraulic containment utilizing *TreeWell*® units within an engineered remedial approach. The limited scale *Engineered_Phytoremediation*^{SM} system was designed to overcome difficult characteristics in a small portion of the site including windthrown trees and uptake of only shallow perched water by the existing trees.

Approach/Activities. The *Engineered_Phytoremediation*^{SM} system involved installation of twenty-five (25) *TreeWell*® units by (1) drilling 40-inch diameter boreholes to the zone of interest, (2) backfilling the borehole with a locally sourced and custom mixed sandy loam soil, (3) planting the tree within the *TreeWell*® unit, and (4) closing the *TreeWell*® units and adding a gravel crown. Ten of the *TreeWell*® units had Regenesis' Oxygen Release Compound (ORC®) added to the backfill. The addition of ORC® in the *TreeWell*® provides an aerobic environment for TDA biodegradation. Sweetgum and Cypress trees, two native plant species, were selected based on their deeper root systems and substantial canopy. Transducers were installed into select *TreeWell*® units to monitor groundwater elevation trends. The design and implementation phases were accomplished in 2013. In addition to monthly tree assessments, a pre-existing network of monitoring wells and piezometers is used to evaluate system performance and groundwater cleanup.

Results/Lessons Learned. Phytoevaluations conducted to-date show a maturing tree population with rooting networks that have reached the water table. The similar water elevation trends between the *TreeWell*® units and the site monitoring wells indicate that the units are hydraulically connected to the target sandy water bearing zone. Groundwater monitoring data including site COC concentration and groundwater elevation as well as *TreeWell*® assessment parameters will be presented.

Back to Contents

Growth and Survivability of Poplar Trees Exposed to LNAPL Bench Scale Pilot Test

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Background/Objectives. L-5 Landfill (SWMU 7) was the historical disposal site for steel foundry waste and refinery wastes. L-5 is located adjacent to a river and was addressed under Corrective Action (CA). As part of CA, a mechanical subsurface liquid collection system was installed within L-5 to maintain an inward gradient from the adjacent river to prevent the formation of seeps in the river. To evaluate the use of poplar trees to provide natural hydraulic control within the landfill, bench scale pilot testing was conducted with the objective of determining impacts of LNAPL and impacted groundwater on their growth and survivability.

Approach/Activities. Three bare-root hybrid poplar clones were planted on-site in containers, DN-34, NI-88 and NE-58. Three groups containing each of the clones were established. Monitoring and watering was conducted weekly as follows: Group A – landfill subsurface water and LNAPL, Group B – landfill subsurface water without LNAPL, and Group C – non-impacted water obtained from the river. A subset of trees had LNAPL injected directly into the soil to ensure contact with the root system. In addition, poplar trees were maintained over the winter and monitored for growth during the following growing season.

Results/Lessons Learned. Of the three test groups, trees watered with landfill subsurface water without LNAPL (Group B) exhibited the best growth, followed by the trees watered with water from the river (Group C). This indicates that the landfill impacted water would not have a negative impact in tree growth provided LNAPL is not present. The trees that had LNAPL added (Group A) exhibited significantly less growth, although this group also exhibited less growth during the acclimation period when all of the groups were watered with river water. None of the trees that had LNAPL added to the water or injected in the soil exhibited signs of stress during the initial growing season.

Of the three clone varieties, the DN-34 clone exhibited significantly better overall growth than the other two clones. In the group of trees exposed to LNAPL, the MI-88 and NE-58 clones exhibited significantly better growth than the DN-34 clone. This indicates that the DN-34 clone may be more suitable for the local climate and site conditions but that the MI-88 and NE-58 clones may be more tolerant of the presence of LNAPL. After one growing season, it appeared that the presence of LNAPL may result in slower growth but not fatality in the quantities applied. However, the data on tree viability collected during the winterization portion of the pilot test indicates that trees that had LNAPL applied were less likely to survive the winter. Trees that received the greatest amount of LNAPL application (applied to both soil and water) were the least likely to survive. In addition, trees that were winterized with mulch were more likely to survive than trees that did not have freeze protection. The DN-34 clone exhibited the best overall growth in both the control group and the trees that had LNAPL application. Based on these observations, it was recommended that the DN-34 clone be utilized for full scale application.

Field/Greenhouse Studies of Phytoremediation with California Native Plants for Soil Contaminated with Petroleum Hydrocarbons, PAHS, PCBS, Chlorinated Dioxins/Furans, and Metals

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Background/Objectives. Phytoremediation is a promising method for remediating contaminated soil, but its effectiveness depends on contaminant properties and concentrations, soil characteristics, plant species and microbial populations. At many sites it is important to select plant species which are native or naturalized to the site so that phytoremediation plantings do not upset the local ecosystem. The objective of this Department of Energy (DOE) funded research was to determine the efficacy of California native plants for remediating soil contaminated with a wide variety of organic and inorganic compounds.

Approach/Activities. Native and naturalized California plant species were screened for their phytoremediation potential for the cleanup of soil contaminated with petroleum hydrocarbons (PHCs), poly-aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated dioxins/furans, and heavy metals (collectively the contaminants of interest [COIs]). This screening was followed by controlled greenhouse experiments to further evaluate the phytoremediation potential of the best candidates. Field specimens and soils used for this study were collected from the former Energy Technology Engineering Center (ETEC) at the Santa Susana Field Laboratory in Southern California that was operated by the DOE. Soils at this site contain all of the COIs. Nine plant species were screened in the field: Purple Needlegrass (*Nassella pulchra*), Blue Elderberry (*Sambucus nigra*), Laurel Sumac (*Malosma laurina*), Mule Fat (*Baccharis salicifolia*), Palmer's Goldenbush (*Ericameria palmeri*), Summer Mustard (*Hirschfeldia incana*), Narrowleaf Milkweed (*Asclepias fascicularis*), Coyote Brush (*Baccharis pilularis*), and Thickleaf Yerba Santa (*Eriodictyon crassifolium*). In the field three samples of each species growing in contaminated soil and one of each species growing in uncontaminated soil were harvested for analysis. The roots, foliage, and soil around the roots were sampled separately and analyzed for the COIs. Coyote Brush, Mule Fat, and Purple Needlegrass were selected and grown in site soil in greenhouse microcosms. Five replicates of each microcosm type were incubated for 211 days. Chelating agent (EDTA) and fertilizer were separately added to sets of microcosms to test for the effects of these treatments. Three control treatments were tested: sterilized (gamma irradiation) soil planted with Purple Needlegrass, unplanted soil, and sterilized unplanted.

Results/Lessons Learned. In the field screening, some uptake of PAHs, chlorinated dioxin/furans, silver, cadmium and lead were observed, while PCB or mercury uptake was not observed. In the greenhouse microcosms, soil concentrations of dioxin/furans were reduced by about 20% in 7 months by planting with Coyote Brush ($p=0.036$, $p=0.022$). Soil PCB concentrations decreased similarly in planted microcosms and unplanted sterile microcosms, indicating no significant effect of plants on PCBs. The TPH results are inconclusive due to suspected laboratory anomalies caused at least in part by interference from natural organic material. Further investigation is ongoing. All of the metals were taken into the roots of plants to some degree, with Purple Needlegrass showing the most promise for metal extraction as it showed some of the highest concentrations of metals in roots and was the only species that contained mercury and silver in the foliage. However, none of the plants were hyper-accumulators of metals, and none of the soil metal concentrations significantly decreased in any of the microcosms. Overall phytoremediation of COIs appears to be limited for this site, and would be most appropriate in areas with limited human exposure where long-term remediation would be acceptable.

Effects of Varying Biogeochemical Controls on Anaerobic BTEX Biodegradation in Greenhouse-Scale ABR Systems

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Background/Objectives. An anaerobic bioreactor (ABR) constructed from engineered mixtures of peat and sand can provide an environment to foster the use of microbial degradation processes to eliminate high concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX) from groundwater. This method is an economical, energy efficient, and environmentally sound approach to create a near-natural and more sustainable *in situ* water treatment method for volatile organic compounds when compared to conventional treatment processes. The objective of the research is to develop a design approach for ABR systems that can incorporate different terminal electron acceptor processes into the process, creating a versatile platform for degrading groundwater contaminants using this sustainable process. In this study, a greenhouse-scale ABR was constructed to treat 10 mg/L of BTEX while simultaneously adjusting the terminal electron accepting processes in the bed.

Approach/Activities. This study was conducted using three greenhouse-scale ABR systems packed with a peat-sand bed mixture with regulated temperature, sunlight and humidity in a growth chamber. The systems were initiated in an unplanted condition and loaded in an upflow mode with 10 mg/L of each BTEX contaminant. Laboratory analysis of the groundwater along the flowpath determined the base degradation rates of BTEX and the initial nutrient components within the columns after an acclimation period. Genomic DNA in the peat-sand bed mixture was extracted from various depths in the mesocosms and next generation sequencing of 16S rRNA in V4 region will be used to characterize the microbial diversity within the systems. Sulfate (~500 mg/L SO_4^{2-}) is currently used as the electron acceptor to evaluate BTEX degradation, following a 5-month methanogenic study (no added electron acceptor). Wetland plants will be planted in two of the three columns to generate an anaerobic-aerobic interface at the rhizosphere and enhance BTEX aerobic biodegradation around the plant roots. 1,4-dioxane will be evaluated as a co-contaminant to BTEX contaminated groundwater.

Results/Lessons Learned. Measurements to date revealed that BTEX is degrading anaerobically through the ABR system to below the USEPA maximum contaminant levels standards in groundwater when loaded at rates of 1.93 g BTEX/m^2/day with water loading of 193 L/m^2/day. Methanogenic conditions (no added electron acceptor) removed ~90% at the loading rate above with 10 mg/L being the design contaminant in the BTEX mixture. The preferential compound with the highest percentage removal is toluene, followed by xylenes, benzene, and then ethylbenzene. Each of these compounds degraded primarily within the bottom half of the ABR beds. Currently, sulfate reducing conditions are being applied to the ABR beds and the data shows an increase in the percentage of BTEX removed in the beds from 90% removal to approximately 95% removal of BTEX. The preferential compounds have shifted during sulfate reducing conditions with the highest percentage removal compound of benzene, followed by toluene, ethylbenzene, and then xylenes. The results of the on-going laboratory study will be amended by the addition of wetland plants and 1,4-dioxane in the upcoming months. Next generation sequencing will track the changes in microbial populations during electron acceptor process transitions. The laboratory studies and analysis will be completed well in advance of the May 2015 conference.

Germination of *Lepidium sativum* as a Method to Measure the Removal of Herbicides in Soil

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Background/Objectives. Herbicides are well known environmental pollutants that are used extensively in the agriculture sector to remove weeds. However, many of them are known to persist in the environment resulting in harm to both man and environmental ecosystems. One of the ways in which herbicides and pesticides in general can be dealt with in agriculture is to consider implementing the so called “Active post-harvest decontamination of pesticide treated soil”. In this study, an attempt is made to decontaminate a herbicide treated soil. The objective of the study is to evaluate the effectiveness of using L sativum germination as a monitoring tool in the removal of a herbicide from contaminated soil.

Approach/Activities. 2,4 Dichloro Phenoxy acetic acid (2,4 D) will be used as a model pollutant in the study. In addition, a variety of strains with the genetic capability of using 2,4 D will be used. L sativum germination will be used together with chemical analysis to monitor the removal of 2,4D from the soil. A sandy loam soil will be contaminated with 2,4 D and the efficiency of removing the pollutant will be assessed in a variety of treatments in which the different strains with the capability of degrading 2,4D are added. A control will be a treatment in which no bioderaders are added. The removal of 2,4 D will be analysed using HPLC as described by Top et al (1999).

Results/Lessons Learned. The results of this study can lead to the use of bioindicators as an alternative monitoring instrument which can complement chemical analysis. L sativum was useful in monitoring the removal of 2,4D from the soil. The germination of L sativum increased with the reduction of 2,4D in the soil. The germination levels of L sativum were much higher in treatments in which 2,4D degraders were added, whilst germination was not noticeable in the control.

Evaluation of Soil Microbial Communities as Influenced by Crude Oil Pollution

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The impact of petroleum pollution in a vulnerable Niger Delta community ecosystem was investigated by making a reasoned assessment of interactions in a first generation phytoremediation site of a crude oil freshly spilled agricultural soil. A community-level approach for assessing patterns of sole carbon source utilization by mixed microbial samples was employed to differentiate spatial and temporal changes in the soil microbial communities. Genetic diversity and phenotypic expressions were also measured for a more holistic perspective. The 5'-terminal restriction fragments generated after Csp digestion of 16S rRNA gene correlated with observed DNA concentrations in the community profile and revealed loss of diversity with pollution. Crude oil pollution significantly reduced the phosphomonoesterases and respiratory activities and values were pH dependent. There were no expressed dehydrogenases activity in initial spill site but were enhanced with phytoremediation. Factor analysis of predictors and independent variables indicates that respiratory, alkaline phosphatase and β-glucosidase activities could be used to explain underlying factors. Positive soil–microbial plant interactions were observed.

Background/Objectives. This study seeks to evaluate the influence of crude oil pollution in soil microbial community and the effects of phytoremediation on such ecosystem

Approach/Activities. Field trial. The study area consists of a two – week old crude oil spilled (and burnt afterwards) soil in Oshie community in the Niger Delta region of Nigeria. This community is a host to a major oil company in Nigeria. Eye witnesses suspects sabotage as the cause of spill. 20cm depth soils from this site were randomly collected and bulked following a field survey and set up in a phytoremediation pot experiments (in replicates of three) using *Vigna subterranea, Hevea brasilensis, Cymbopogom citratus* and *Fimbristylis littoralis* were designed. An agricultural soil in the same region with history of no pollution constituted control regimes. Chemical and physical characterization of control and polluted soils were performed before the start of the experiment. After 90d with watering, based on need, plants were harvested and rhizopheric soils were collected for laboratory analyses. These were transported in ice chests to Institute of Agrophysics Poland for analysis. Different soil regimes from planted and unplanted, polluted and unpolluted variants were subjected to preparations for various analyses

Results/Lessons Learned. From data obtained from this study, there were marked shift in the genotypic structure of soil microbial assemblage with crude oil pollution and diverse interactions were observed after a phytoremediation experiment. CLPP generally, revealed significant changes due to contamination in metabolic diversity of mixed microbial communities. Limtations to this study may include PCR bias with DNA extractions, quantificationsome less dominant microorganisms in the community might not be detected without fractionation. Also, the substrate concentration in the well of the BIOLOG plate may be much higher than that usually found in such parched environment.

Back to Contents

Microcosm Tests for Natural Attenuation, Biostimulation, and Bioaugmentation of Soils Contaminated with PCBs, Dioxins, PAHs, and Petroleum Hydrocarbons

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Background/Objectives: Weathered petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), dioxins, and polychlorinated biphenyls (PCBs) (collectively the contaminants of interest [COIs]) have persisted at the Santa Susana Field Laboratory (SSFL) in southern California for over 40 years in some cases. Remediation through monitored natural attenuation, *in-situ* biostimulation, and/or bioaugmentation may help to reduce COI concentrations at the site. The objective of this DOE-funded study is to estimate potential biodegradation rates of COIs in SSFL soils via natural attenuation, and determine the potential for biostimulation and bioaugmentation using a laboratory-scale microcosm study.

Approach/Activities. Several types of soil microcosms were established: one set of microcosms was run without amendments to estimate natural attenuation rates at the site; biostimulation was tested by addition of nitrogen and phosphorus rice hulls, and biosurfactant (soya lecithin), another set was augmented with the fungi *Phanerochaete chrysosporium*; and gamma-irradiated microcosms served as sterilized controls. Soil samples were collected and analyzed for dioxins, PCBs, PAHs, and total petroleum hydrocarbon (TPH) after 0, 4, and 9 months of incubation. Initial microcosm soil contamination was primarily heavily chlorinated PCBs and dioxins, weathered petroleum hydrocarbons, and PAHs with 3-5 aromatic rings.

Results/Lessons Learned. Dioxin and TPH concentrations decreased slightly in the microcosm soils, but none of the other COI concentrations were reduced significantly over 244 days of incubation. The petroleum hydrocarbons were primarily longer-chain hydrocarbons in the C21 to C40 equivalent carbon range, and thus it is likely that the lighter hydrocarbons were already biodegraded at the site leaving the more recalcitrant longer-chain hydrocarbons. However, mass spectrometer analyses suggest that natural organic material contributed a significant fraction of what was measured as TPH, and thus residual petroleum compound concentrations are lower than implied by the TPH concentrations. Larger PAHs (3-5 rings) comprise the majority of the residual PAH soil contamination. Given that concentrations of these PAHs have not decreased significantly during the duration of the study, it is likely that these larger PAH contaminants are somewhat recalcitrant and will take a longer time to biodegrade. It is not surprising that little or no PCB biodegradation was observed because the PCBs were found to be highly chlorinated, and bacterial biodegradation of these highly chlorinated compounds is reported to occur only under anaerobic conditions. Soil vapor analyses at the site indicate highly aerobic conditions in the soil and the experimental microcosms were maintained under aerobic conditions. Fungi have been reported to mediate PCB and dioxin biodegradation under aerobic conditions, but the microcosms bioaugmented with the fungi *Phanerochaete chrysosporium* did not show any measureable biodegradation of PCBs. The slight decrease in chlorinated dioxin concentrations may have been due to fungal degradation because dioxins also typically require anaerobic conditions for bacterial degradation, while fungi may be capable of dioxin biodegradation under aerobic conditions. A companion study showed the presence of bacteria and fungi capable of degrading the COIs, but the high degree of weathering may have limited biodegradability. Contaminant sequestration in the soil may have also limited biodegradation, but even microcosms augmented with a surfactant (soya lecithin), which would be expected to solubilize sequestered COIs, did not show significant biodegradation.

Forest Residues Transformed by White Rot Fungi and Disinfested by Photolysis

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Background/Objectives. Colombia's lumber industry produces large quantities of organic waste approximately 5 million tons of dry matter per year. The sawn wood industry stands out as being a big producer of residues approximately 50% during this stage; mainly, sawdust. Accumulation of this lignocellulosic materials in large quantities present a disposal problem generating deterioration of environment but also in loss of potentially valuable material that can be used. Several novel markets for lignocellulosic residues have been identifies recently. The use of fungi in low cost bioremediation projects might be attractive given their enzymatic hydrolysis of lignocellulose. White rot fungi, are capable of degrading lignocellulosic biomass due to their ligninolytic systems. Delignification is of significance to reduce the biomass recalcitrance. The objetive of this study is to determine the ability of colonization and biotransformation sawdust residues by white rot fungi.

Approach/Activities. Sawdust residues obtained from a plantation forest of rosy trumpet tree (*Tabebuia roseae*) and eucalyptus (*Eucalyptus pellita*) from plantations located in Villanueva, Casanare and Monterrubio, Magdalena (Colombia). These residues was characterized chemically, (ratio C/N), cellulose, hemicellulose and lignin percentage. Biotransformation process was evaluated to scale of laboratory with mixture of residues (1:1) using white rot fungi (WRF) *P. ostreatus*, *T. versicolor*, *G. lucidum* and *P. crhysosporium* (1:1:1:1). The solid-state fermentation was carried out in a 750 mL glass bottle with 35 g of sawmill residues with an initial moisture of 80%, the system was a continuous sterile air supply and incubated at 23 °C during 75 days. Was studied measuring the ratio C/N, production of CO_2 and enzyme activity lacasse, manganese peroxidase (MnP) y endoglucanase after 15, 30, 45, 60 and 75 days. At the end of the biotransformation process observations was made by electron microscopy. Finally the residue transformed was disinfested by a photolytic reactor using lamps of low pressure mercury (wavelength 254 nm) for 24 hours. To determinate the concentration of white rot fungi serial diluted and plated on agar wheat bran extract, previously and subsequently the photolytic process.

Results/Lessons Learned. In regards to chemical characteristics, residues shown high C/N ratio (139) related to high carbon content of lignin 38.8%, cellulose 40.1% and hemicellulose 8.54%. Low content of lignin and higher content of cellulose and hemicellulose as the most suitable for the white rot fungi biotransformation process. For the solid-state fermentation with WRF, C/N ratio decreased from 351 to 161, then remains steady between days 30 and 75, and decrease 63.8 %. Maximum laccase and MnP activity was found 56.97 U/g and 0.37 U/g after 45 days of treatment, likewise, the maximum CO_2 production after 45 days of treatment (4.8 mg CO_2/g), endoglucanase activity showed two peaks at 45 (5.8 U/g) and 75 (6.2 U/g) days. The sawdust of T. roseae and E. pellita characterized by the presence of vessels, fibers and tracheids, structural spaces allowing hyphal colonization, also, penetration by WRF. Finally, in the solid matrix the WRF decreases by 25.22% after photolytic treatment.

Correlating Fungal Occurrence and Diversity to Contaminant Profile at the Atlantic Wood Industries Superfund Site

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Background/Objectives. Due to their recalcitrance, the remediation of heavy hydrocarbons in soils is often limited to excavation and *in-situ* stabilization. While traditional bacterial bioremediation has been investigated, this approach has had limited success because often bacteria lack enzymes which can degrade large molecules. On the other hand, common wood-degrading fungi have been identified which are capable of initiating the degradation of these same large recalcitrant compounds using non-specific enzymes. In the current study, the application of mycoremediation (i.e., fungal bioremediation) is investigated as a first step towards the degradation of polycyclic aromatic hydrocarbons (PAHs) through biostimulation. The site of interest is a 48-acre site on the industrialized waterfront of Portsmouth, VA which was contaminated by wood preservation activities that took place from 1926-1992. More than 30 different PAHs have been detected in the soil. In addition, the site is known to have dioxins, metals, and pentachlorophenol present.

Approach/Activities. Various soil samples were obtained from the Atlantic Wood Industries Superfund site with varying degrees of PAH contamination and screened for fungal taxa known to degrade site contaminants using both culture and non-culture based approaches. In total, five soils and two buried wood-chip deposits of varying pollutant level were sampled. The soils and wood-chip deposits were plated using traditional culturing methods to assess the culturable fungal fraction. The resulting isolates' were identified based on the internal transcribed spacer (ITS) gene. To assess the non-culturable fraction of fungi, total soil genomic DNA was extracted and either the more conserved small or large subunit gene region was amplified via PCR. Amplicons were subjected to Illumina next generation sequencing. Quantitative Insights into Molecular Ecology (QIIME) and R were used to transform the raw sequences. Finally, the Ribosomal Database Project's Classifier tool assigned taxonomy to the non-culturable organisms. In addition, PAH concentration profiles were obtained for each sample using gas chromatography combined with electron impact mass spectrometry (GC/EIMS).

Results/Lessons Learned. Total PAH concentrations across the locations sampled ranged from 40 µg/g to over 96,000 µg/g. Fluoranthene appeared in all samples at 10-20 percent of the total. Phenanthrene appeared in five of the locations at 15-30 percent of the total. One location was less dominated by the few PAHs named and was more evenly contaminated by PAHs including benzo(a)pyrene, benzo(e)pyrene, chrysene, and benzo(bkf)fluoranthene. Culturing efforts resulted in six isolates of soil fungi corresponding to the *Trichoderma*, *Geotrichum,* and *Mortierella* genera. The non-culture based approach revealed clear differences between the microbial communities present in the contaminated soils and controls. The most common fungal genera were within Ascomycota, Basidiomycota, with a few belonging to Zygomycota. Statistical analyses including ANOSIM and NMDS are underway to identify correlation between fungal genera and specific PAH identity and concentration. In the long term, it is anticipated that the results of this analysis will eventually be integrated into a larger biostimulation treatment approach.

Evaluation of Cellulolytic and Hemicellulolytic Activity of a Bacterial Consortium Inoculated in Bark of *Pinus caribaea*

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Background/Objectives. The development of pine forest chain in the eastern plains region in Colombia has increased in recent years. This chain generates lots of lignocellulosic residues, which degrade very slowly; The degradation of waste as pine bark results in products that can be used as plating substrates plant propagation; on the other hand, the production of biofuels from these wastes has become an attractive option; However lignocellulose has a very rigid and complex structure, therefore, the conversion is costly because of the need for extensive pretreatment and relatively large amounts of cellulases for effective hydrolysis. Although lignocellulolytic fungi can secrete high amounts of enzymes, the production of the bacterial enzyme may be advantageous due to their rapid growth and increased tolerance to environmental stress. Thus a biotechnology strategy lignocellulosic waste degradation is solid state fermentation, inoculating bacteria having an enzyme complex capable of degrading the structural components. Therefore, the aim of this study was to assess the production of cellulolytic and hemicellulolytic enzymes in a bacterial consortium on pine bark Villanueva Casanare Colombia.

Approach/Activities. A consortium of 4 strains asylee bark of *Pinus caribaea* (Gram positive bacilli and actinobacteria) exhibiting carboximetilasa activity (cellulase, 1,4-β-D-endoglucanase) (CMCase), 1,4-β-glucosidase (EC was inoculated 3.2.1.21), cellobiohydrolase CBH (EC 3.2.1.91) and endo-xylanase (EC 3.2.1.8) in piles of pine bark in the town of Villanueva Casanare Colombia. Cellulolytic and hemicellulolytic activity was assessed quantitatively from a crude extract obtained from samples of cells every 15 days over a period of 66 days, additional parameters were evaluated as percentage of CO_2, temperature, humidity, pH and chemical composition Initial and the end of the inoculated cell stack and controlling.

Results/Lessons Learned. In the first 15 days of fermentation, for batteries with bacterial inoculation and control (no inoculation) was evidenced increase in temperature and percentage of CO2. To stack inoculated with bacteria, the endoglucanase enzyme activity peak was evident at day 45 of fermentation being 5.1 U / L. As for β-glucosidase activity, peak activity for inoculated for the stack to the stack monitoring during the first 15 days, with 13.60 U / L and 8.17 U / L respectively was observed. The cellobiohydrolase activity, zero or near zero for two batteries held for the first 30 days of fermentation. Following this, an exponential increase in activity was evident on day 45 being the peak of expression of the enzyme which was 3.89 U / L and 3.51 U / L for monitoring battery and inoculated with bacteria respectively. For endoxylanase enzyme, a peak of activity was evident on day 30, with 25.90 U / L and 23.38 U / L for bacteria and control cells respectively. I observed is the decrease in C / N ratio from 48 to 44 and from 52 to 45.65 for the control and the battery stack respectively inoculated. In conclusion evidenced increased expression of cellulolytic enzymes and on the stack hemicellulolytic inoculated with bacteria in relation to the control stack, still, these enzyme activities may be affected by the recalcitrant nature of wood related to the content of lignin and cellulose.

Back to Contents

Review: Fungal Biotreatment of Petroleum Contamination

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Background/Objectives. Interest in the biotreatment of petroleum contamination has existed for last years. In the Arabian Gulf Region also in Saudi Arabia, less attention has been paid to the microbial bioremediation of petroleum contamination. In Saudi Arabia, petroleum widespread environmental and continuously pollutants that are amenable to removal by biotreatment.

The present review might give a data base in microbial biotreatment of petroleum contamination for some future studies in Saudi Arabia as well as in the Arabian Gulf Region.

Approach/Activities. Most of the Eastern Regions of Saudi Arabia, including the coastal area bordering Kuwait, Bahrain and Qatar became polluted with petroleum during the Gulf War (1990), results from a 1991 rapid assessment survey to investigate the extent of resulting from the massive spillage of petroleum and the burning of oil well pollution in the Arabian Gulf was restricted to approximately 400 km from the sources, oil contamination as a floating tar balls were investigated from the Arabian Gulf to the Arabian Sea, ecology of seagrasses in Northeastern Saudi Arabia after Gulf War was examined for the direct result of the Gulf War oil spill, mean concentrations of total hydrocarbons were 2.95,4.14 and 3.29 ugl-1 in Saudi Arabia and Qatar respectively , high concentrations were measured at the Northern coasts of Qatar were found to be affected directly by water advected through the water circulation in this area , petroleum contamination following the 1991 Gulf War was organized to determine contamination by petroleum that entered the Gulf and oil field in Kuwait.

Results/Lessons Learned. While environmental biotechnology benefits is broadly based in variety of environmental protection, restoration, and agriculture industrial practices, for a decade it has been most commonly linked with bioremediation, rehabilitation and waste treatment technology.

A Comparative Study of the Effects of Biosurfaction, Non-Ionic and Ionic Surfactants on the Biological Degradation of Oil Sludge During Composting of Contaminated Soil

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Background/Objectives. A comparative study of three surfactants including one non ionic, one ionic surfactant and biosurfactant generated by a bacillus sp was carried out to determining their effect on the degradation of oil sludge during composting with wastes from sugar cane industry and treated with a 1.0% solution of Arkopal-100 (a commercial surfactant) under laboratory conditions.

Approach/Activities. Soil amended with 1000 g kg^{-1} of crude oil sludge was mixed with 10% solution of Arkopal-100 and then mixed with sewage sludge (4:1 w/w) before mixing with wood chips (2:1 w/v). The mixtures were incubated for 24 weeks at ambient temperature in rectangular glass troughs in the laboratory. Three other experiments were set up with similar mixture described above but with one not containing surfactant, the not containing sewage sludge and the last, designated as control not containing both surfactant and sewage sludge. Composts were turned weekly and moisture level was maintained at 70% moisture holding capacity by using the 1.0% Arkopal solution. The pH, temperature, CO_2 evolution total petroleum hydrocarbons (TPH) and concentration of selected polyclic aromatic hydrocarbons (PAH) in the composts were measured every four weeks. Microorganisms present in the composts were isolated at the start, at 12 weeks and at the end of the experimentation. The organisinms were purified and characterized by molecular techniques using 16S rDNA gene. Reduction in TPH and PAHs was determined by solvent extraction and GC/MS.

Results/Lessons Learned. Temperature in all the treatments except the control exceeded 50^{O}C by the 5th week of incubation before starting to decline. The pH in most treatments generally dropped from about 7.3 to 6.2. CO_2 evolution rose from about 18.78 µg/dwt/day at the start to about 435.5 µg/dwt/day by the 7th week before become relatively stable. There was no significant change in the profile of the microorganisms present at the different stages of the composting process except for some basidiomycetes that started growing in almost all experiments towards the end of the experimentation. The dominant species identified were *Acinectobacter, Rodococcus, mycobacterium, Pseudomonas, Bacillus*, *Arthrobacter* and *Staphylococcus* species. The fungi identified included *Pleurotus*, which appeared towards the end of the experimentation, *Penicillium* and *Aspergillus sp*. and TPH was reduced by 92% in the treatment containing sewage sludge and surfactant and by between 75 and 81% in all other treatments except the control which showed a reduction of 44.2%. Measurement of PAH concentrations showed reduction of between 75 and 100% in the treatments. There was no significant different between reduction in all the treatments except for the control which showed a reduction of between 18 and 42%. The results showed that a careful blend of surfactant and sewage sludge could be employed to enhanced TPH reduction in compost bioremediation of crude oil sludge.

Bioremediation of Petroleum Hydrocarbons by Mangrove Fungi from Red Sea Coast of Saudi Arabia

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Background. Pollution of land and water by petroleum compounds is a matter of growing concern necessitating development of methodologies including microbial biodegradation to minimize the impending impacts. Red Sea being treaded extensively for transport of oil is substantially polluted due to leaks, spills and occasional accidents.

Objectives. This paper aims to (a) explore the degradative capability of three fungal strains *Cladosporium sphaerospermum, Eupenicillium hirayamae* and *Paecilomyces variotii* isolated from the petroleum-contaminated mangrove sediments using Petroleum oil as the sole carbon source, (b) to compare fast degradation among strains and their consortium and (c) the extracellular enzyme system involved.

Materials & Methods. Tidal water, floating debris and soil sediment was collected from mangrove stands on three polluted sites along the Red Sea coast of Saudi Arabia and forty five fungal isolates belonging to 14 genera were recovered from these samples. Three of these isolates were found to be able to grow in association with petroleum oil as sole carbon source under *in vitro* conditions. These isolates were identified as *Cladosporium sphaerospermum, Eupenicillium hirayamae* and *Paecilomyces variotii*, using 18S rDNA gene analysis. Gain in biomass under each treatment and the corresponding control was recorded and difference between gain in treatment and control was considered to be due biodegradation activity of the fungus. After 30 days incubation, enzyme level in the medium was assayed for controls and treatments. Volumetric and gravimetric estimation of CO_2 evolved for each isolate together with corresponding control during 4-week incubation was performed using sturm test. As a separate treatment, consortium of the three above isolates was also tested for biodegradation activity

Results. The Isolates *Cladosporium sphaerospermum, Eupenicillium hirayamae* and *Paecilomyces variotii*, as well as their consortium were selected among all the isolated strains for their faster growth rate and relatively higher petroleum oil bioremediation ability. As compared to the controls, these fungi accumulated significantly higher biomass, produced extracellular enzymes and liberated larger volumes of $CO_{2.}$ These observations were authenticated by gas chromatography-mass spectrophotometry (GC-MS) analysis, which elucidated that many high mass compounds present in the oil before treatment either disappeared or showed diminished level and some smaller molecules turned up *de novo* after treatment with the fungal isolates.

Conclusion. These observations confirming that these strains could be interesting to use in future field tests.

Back to Contents

Biogeochemical Transformation of Trichloroethene in Engineered Iron Sulfide Systems

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Background/Objectives. In situ biogeochemical transformation involves biological formation of reactive minerals (e.g., iron sulfides, magnetite) that can destroy chlorinated solvents such as TCE without accumulation of toxic intermediates such as vinyl chloride (AFCEE et al., 2008). This process has promise for active remediation and post-remediation management of large-dilute plumes. It can be implemented in a number of configurations including biowalls, bioreactors, injection/recirculation systems, and post-remediation natural attenuation. Unfortunately, the process is often implemented in the field in an ad hoc manner. A better understanding of the factors controlling the process is needed.

Approach/Activities. Laboratory column studies, a critical evaluation of full-scale systems, rejuvenation of under-performing biowalls, and an ESTCP demonstration of the process were conducted to increase our understanding and to develop engineering guidance for the process. The column studies system systematically evaluated various factors affecting the process. The critical evaluation of full-scale systems was conducted to identify specific conditions that resulted in different levels of performance. The rejuvenation study elucidated certain underlying mechanisms leading to activity loss over time. Finally, the ESTCP demonstration was designed to directly compare biological and biogeochemical processes.

Results/Lessons Learned. Column study results demonstrated that an optimal combination of sulfate consumption, residence time, electron donor, and iron oxides resulted in an abiotic pattern of TCE removal without accumulation of daughter products. Analysis of full-scale systems provided results consistent with the column study: high volumetric sulfate consumption rates and geochemical conditions that promoted nucleation of small-diameter, high surface area minerals favored an abiotic pattern of TCE removal. Rejuvenation of poorly-performing biowalls demonstrated that passivation of iron surfaces can occur but can be overcome. The results taken together indicate that biogeochemical transformation is a dynamic process that involves competing processes of reactive mineral formation and de-activation. Optimization of VOC removal requires design and operation of the biogeochemical transformation promote a sustained rate reactive mineral formation. This presentation will provide the audience with an understanding of the critical factors that promote biogeochemical transformation along with practical tools that can facilitate technology implementation.

Laboratory Study of Iron Amendments Used to Facilitate Reductive Dechlorination of TCE in High Sulfate Groundwater

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Background/Objectives. High sulfate conditions present particular challenges for application of enhanced in-situ bioremedation (EISB) of chlorinated compounds. Sulfate reducers compete with dechlorinating bacteria for electron donor and sulfate is reduced to hydrogen sulfide (sulfide), which at high concentrations is toxic to bacteria or inhibits biological processes such as electron donor fermentation and reductive dechlorination. Ferrous iron, either as an amendment or as produced from ferric iron by iron reducing bacteria, will react with sulfide in solution to produce insoluble iron sulfides, mitigating or removing inhibitory levels of sulfide. The iron sulfides formed may themselves be reactive toward chlorinated solvents. Iron amendments can be added in situations where the soil or bedrock matrix contains insufficient iron and are available in multiple forms, including soluble forms of ferric and ferrous iron and solid forms such as magnetite and hematite. Attributes of an ideal iron source for EISB are compounds that are injectable, stable under storage, non-toxic, safe to handle, contain a high iron content, low-cost, and do not adversely impact the subsurface pH or geochemistry.

Approach/Activities. A laboratory microcosm study was performed to test the efficacy of various electron donors and iron sources for their ability to support the reductive dechlorination of 100 mg/L trichloroethylene (TCE) in a high (600-900 mg/L) sulfate environment using crushed gypsum bedrock and groundwater obtained from an industrial site in western New York. The 140-day study was designed to evaluate combinations of two donors (sodium lactate and emulsified vegetable oil [EVO]), nutrients, and six solid or soluble iron amendments (magnetite powder, ferric sulfate, ferric chloride, ferrous chloride, ferrous lactate, and ferrous sulfate). A factorial experimental design and statistical analyses were utilized to evaluate and compare each combination of donor and iron source. Each treatment was run in duplicate and incubated at 20°C.

Results/Lessons Learned. This study demonstrated that the addition of iron amendments was effective at controlling sulfide concentrations and promoting the complete reductive dechlorination of TCE to ethene. Statistical analysis of the data indicated that magnetite powder supported the most rapid dechlorination of all the iron amendments, with the powder with a smaller particle size and resultant greater surface area the most efficacious. Ferrous sulfate and ferric citrate were also effective at supporting dechlorination. Lactate promoted more rapid biodegradation than EVO in this study, although both lactate and EVO supported complete dechlorination. The magnetite-amended bottles with EVO as the donor were among the best at controlling sulfide levels, where sulfide concentrations did not exceed 2 mg/L. Magnetite may also have other advantages for field application. It meets all the criteria of an ideal iron source stated above and as a solid should remain in place near the injection locations better than more soluble iron sources.

Combining In Situ Chemical Reduction and Biogeochemical Degradation to Treat Chlorinated Ethenes in High Sulfate Aquifers

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Background/Objectives. Historical operation of a dry cleaning facility in Las Vegas (Site) resulted in a release of tetrachloroethene (PCE) to soil and groundwater at the Site producing a CE ground water plume that extends approximately 7,500 feet long, 100 feet wide, and 80 feet deep with reported concentrations of PCE of up to 7,200 micrograms per liter (µg/L). Groundwater beneath the Site is moderately aerobic (~ 4 mg/L dissolved oxygen) and contains sulfate at concentrations ranging from 1,500 to 3,700 milligrams per liter (mg/L).

Previous field pilot tests at similar sites in the area that applied only a biological approach for treatment of the CEs were not successful, resulting in the incomplete degradation of the PCE and accumulation of toxic daughter products. The incomplete degradation was primarily attributed to the elevated concentrations of dissolved sulfate and other geochemical conditions. Based on these unsuccessful pilot tests, biologically mediated enhanced reductive dechlorination was not considered applicable for treatment at the Site.

Recent advancements in the use of iron containing organic substrates have demonstrated that high concentrations of dissolved sulfate can be beneficial to biological CE degradation by enhancing biogeochemical and abiotic degradation processes. During the application of biologically mediated reductive dechlorination, iron and sulfate reducing conditions are established resulting in the generation of dissolved ferrous iron and sulfide. Although sulfide can inhibit biological activity, naturally occurring bioavailable iron is usually present at sufficient concentrations to sequester low concentrations of sulfide thereby allowing continued biological degradation of the CEs. At sites with very high sulfate concentrations however, the amount of naturally occurring iron is often insufficient to remove sulfide from solution. At such sites the ISCR provides a direct abiotic pathway by supplying zero valent iron. ISCR also can provide ample ferrous iron to sequester the sulfide. This secondary process forms reactive minerals such as mackinawite (FeS) and pyrite (FeS_2). CEs have been demonstrated to degrade by the β-elimination pathway upon contact with these reactive minerals as well as zero valent iron. This pathway is preferable to the biological hydrogenolysis pathway because it does not produce toxic daughter products.

Approach/Activities. The applicability of ISCR in high sulfate groundwater was demonstrated in bench tests using soil and groundwater from the Site. Parallel microcosms were prepared in triplicate. In one microcosm set, a zero valent iron and solid organic carbon containing substrate EHC ®; PeroxyChem) was applied. In a second set, a soluble organic and soluble iron containing substrate (EHC®-Liquid; PeroxyChem) was applied. PCE was adjusted to 1,700 µg/L and magnesium sulfate was added to bring the sulfate concentration to 2,300 mg/L. A CE degrading microbial culture (SDC-9™, CB&I) was added at concentration of $1x10^8$ cells/Liter. Samples were collected and analyzed on a regular basis and concentration of sulfate, nitrate, sulfide, iron, CEs, and dissolved gasses.

Results/Lessons Learned. The bench tests demonstrated that the organic component of both ISCR products produced rapid reduction of sulfate to sulfide. Contemporaneously, the iron supplied by the ISCR substrates was demonstrated to rapidly remove sulfide from solution thereby eliminating the potential for biological inhibition. The precipitation of iron sulfide resulted in combined biological and abiotic degradation of the PCE. The test demonstrated that ISCR is a highly effective treatment for CEs in high sulfate aquifer by combining multiple degradation pathways.

Bedrock Applications of Biogeochemical Reductive Dechlorination (BiRD)

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Background/Objectives. In situ chemical reduction (ISCR) treatment of groundwater containing dissolved chlorinated aliphatic hydrocarbons (CAH) and other high oxidation state contaminants by zero valent iron (ZVI)-based abiotic approaches has become common and has led to an increase in both remedial efficiency and site closures. A class of sites where abiotic dominated treatment approaches have lagged are those where affected groundwater is located in bedrock. The colloidal nature of most ISCR amendments complicates amendment delivery and has led to limited use of the otherwise often successful treatment option. Colloidal amendments are prone to falling out of solution, limiting the extent of delivery and potentially clogging bedrock fractures and dissolution channels, which in turn could lead to the diversion of affected groundwater to previously unaffected areas or areas of relatively low impact.

Combining biological and abiotic processes to form reactive minerals in situ using the biogeochemical reductive dehalogenation and metals stabilization (BiRD or BiRDS) technology can circumvent the need to use colloidal amendments for ISCR. A range of engineering options, including soluble reactants, are available to generate ferrous sulfide based in situ reactive zones within fractured bedrock. With care during BIRDS design, the desired precipitation can be limited to coatings along fracture walls that are a few tens of nano-meter thick, which should not significantly influence fracture conductivity.

Approach/Activities. BiRD has been applied at two fractured rock sites; a large pilot-scale source area treatment near St. Louis, Missouri, and a phased full-scale treatment in eastern Pennsylvania. Both sites involve CAH source zones in overburden and dissolved phase plumes in the underlying fractured bedrock, which is limestone in both cases. In situ microcosm (ISM) studies were performed at the Missouri site to demonstrate efficacy using conventional and environmental molecular diagnostics (EMD) before initial field implementation in June of 2013. Field implementation at the Pennsylvania site commenced after extensive geophysical study in July, 2014. At both sites, dye tracer studies were completed concurrently with BiRD amendment application, and performance monitoring included conventional and EMD analytes.

Results/Lessons Learned. BiRD efficacy was demonstrated in the Missouri site ISM by decreases in CAH concentrations, corresponding ^{13}C isotopic enrichment, and the generation of acetylene. Field scale amendment delivery, by temporary direct push emplacement to the top of bedrock at the Missouri site and by permanent bedrock wells and an infiltration gallery installed at the top of bedrock at the Pennsylvania site, demonstrated effective soluble amendment delivery at both sites.

At the Missouri site CAH concentrations have decreased by an average of 50 percent through August 2014 as compared to concentrations measured in baseline samples. The data show evidence of stimulating primarily abiotic degradation pathways (parallel CAH compound degradation along the beta-elimination pathway) in some samples and concurrent degradation along abiotic and bio-mediated (sequential parent to daughter CAH compound degradation by hydrogenolysis) degradation pathways in other samples. CAH concentrations at the Pennsylvania site collected one month after amendment application (August, 2014) show favorable trends and will be supplemented by quarterly sampling data.

Evaluation of Engineered and Natural Biogeochemical Transformation at Multiple Chlorinated Ethene Sites

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Background/Objectives. Total molar concentration reductions, observed first-order decay rates, and biogeochemical data will be presented for multiple project sites where biogeochemical and biological transformation was included as part of the remedial design. The evaluation will include observed data from multiple sites at Travis Air Force Base (AFB) in California and Tinker AFB in Oklahoma, as well as one confidential industrial site in California. Each site included addition of an organic substrate to stimulate enhanced in situ biodegradation. Subsequently, anaerobic sulfate- and iron-reducing conditions suitable for supporting abiotic degradation of chlorinated ethenes were also generated. Large decreases in chlorinated ethene parent compounds with little daughter product formation, as well as corresponding abiotic geochemical indicators offer compelling evidence of the occurrence of biogeochemical transformation. Different types of biogeochemical indicator data will be used to present a multiple line of evidence approach to demonstrate a combination of biotic and abiotic degradation is occurring at these sites.

Approach/Activities. Biogeochemical transformation approaches at Travis AFB and Tinker AFB included combinations of emulsified vegetable oil (EVO) injections and installation of in situ mulch bioreactors. Iron pyrite was added to the in situ bioreactors at Travis AFB to support abiotic degradation of trichloroethene (TCE). At Tinker AFB, geochemical amendments were not added. Instead, the natural, iron-rich soils were relied upon for the production of iron sulfides to support abiotic degradation of TCE. At an industrial site in California, delivery of EVO to stimulate in-situ biodegradation of chlorinated ethenes appears to have fortuitously generated iron sulfide minerals that achieved some degree of chloroethene degradation.

Biogeochemical indicator data for the Travis AFB and Tinker AFB sites includes groundwater geochemistry parameters and acetylene data, as well as magnetic susceptibility and iron sulfide sediment data. At the confidential industrial site, geochemical data, acetylene, and compound-specific isotope analysis (CSIA) data were evaluated to determine if abiotic degradation is occurring due to iron sulfide minerals.

Results/Lessons Learned. Total molar concentration reductions of chlorinated ethenes as high as 99 percent and f_{abiotic} ratios approaching 1 have been observed at source area treatment sites presented in this study. The observed concentration reductions, biogeochemical and biological indicator data, and observed first-order decay rates will be presented for each site. Additionally, lessons learned will be presented regarding the process used to select reagent doses, as well as usefulness of specific types of data collected for evaluation of biotic and abiotic degradation at these sites.

Back to Contents

Enhanced In Situ Biogeochemical Pilot Study of a Chlorinated Ethene Plume

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Background/Objectives – More than 85% of Air Force (AF) installations are contaminated with chlorinated ethenes. Several of these installations have large and dilute chlorinated ethane plumes comprised of trichloroethene (TCE) and dichloroethene (DCE) in deep alluvial aquifers and fractured bedrock. OU 1 Site 19 is an aerobic aquifer contaminated with TCE. This project aims to demonstrate and validate in situ biogeochemical (ISBG) reactions in the subsurface at Edwards Air Force Base (AFB), OU 1 Site 19 which contains a large and dilute TCE plume in a deep (> 60 ft bgs) aerobic aquifer. ISBG is a technology relying primarily on reduced reactive iron minerals to abiotically transform chlorinated ethenes. The reduced reactive mineral, in this case, iron monosulfide (FeS), will be formed by the injection into the subsurface and recirculation of sulfate and an electron donor.

Approach/Activities As a research demonstration this project utilizes initially fast reacting amendments (lactate and magnesium sulfate) that will rapidly form the FeS that will be used to transform the TCE. This was followed by slow release amendments (emulsified vegetable oil and gypsum) to make the transformation process more sustainable. The injection wells however became clogged and fouled with gypsum and sulfate reducing bacteria. After doing a cost benefit analysis the decision was made to conduct direct injection instead of rehabbing the wells.
A second attempt at the injections will be conducted by direct injection using a sonic rig. The amendments that will be injected are emulsified vegetable oil, magnesium sulfate, and iron sulfate. Adding additional iron sulfate ensures there is enough iron available to react with the sulfide to form iron sulfide. The contamination at Edwards AFB is 60 to 80 ft bgs, deeper than is possible to treat with a biowall. This project will demonstrate that ISBG can be sustained by the injection of liquid and or slurry amendments at deep depth in a dilute plume. A recirculation approach will be used to distribute the amendments throughout the treatment area. Groundwater will be extracted from down gradient extraction wells and injected into upgradient nested injection wells at three different depths.

Results/Lessons Learned. The lessons learned from this pilot study include:

- Fast reactive amendments like lactate and iron sulfate were better for enhancing ISBGT at this site
- Geology must be considered when selecting injection method. Although this site was characterized by alluvium groundwater flow rate varied significantly from depth to depth.
- Direct Injection vs Recirculation will be discussed
- A slow releasing sulfate amendment for liquid injections is needed.

The above lessons learned and supporting figures will be discussed.

Biogeochemical Reductive Dechlorination (BiRD) Bench Study: TCE Plume in Tampa Limestone

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Background/Objectives. Historical solvent usage at a Tampa, Florida Brownfields site led to Trichloroethylene (TCE) impact to groundwater present in limestone of the Tampa Member of the Arcadia Formation. The horizon of impact where TCE concentrations exceed the State water quality guidelines (GCTL) is approximately 20 to 130 feet over several acres. Within this interval the groundwater flows through variably weathered limestone with discrete layers of less weathered limestone representing preferential pathways for groundwater and TCE migration. Hydrogenolysis (sequential dechlorination) is taking place; trans-1,2 Dichloroethylene (DCE) and cis-1,2 DCE as well as Vinyl Chloride (VC) have been detected in increasing concentrations with increasing distance of subsurface transport from the source area. Groundwater remediation planning is focused on enhanced reductive dechlorination and monitored natural attenuation. To support remedial planning, a bench-scale treatability study was commissioned to evaluate the efficacy of biogeochemical reductive dehalogenation and metals stabilization (BiRD or BiRDS) technology to significantly reduce TCE concentrations at relatively low overall cost and without accumulation of DCE isomers and VC. Other options to achieve a similar outcome exist but are thought to involve more complex operations and/or costs.

Approach/Activities. The bench study was prepared using limestone and groundwater collected from two specific horizons where the bedrock weathering is observed to be less and TCE and degradation products are clearly present. The approximate 25 feet deep horizon is referred to as Shallow and 45 feet is referred to as Deep. The study involved six batch microcosm lines with four serum bottles per line dedicated to destructive testing at four of five milestones post build (Time = 0, 41, 71, 91, and 120 days). Each 250-milliliter (ml) glass bottle contained approximately 150 grams of limestone and 150 ml of groundwater with a small volume of distilled water and a 20 ml headspace. The screw-on cap had a PTFE - coated septa. TCE mass contained in the groundwater was sufficient to avoid artificial spiking. The microcosm lines included a live-control (deep), organic carbon amendment (shallow), and two shallow lines and two deep lines with the following amendments: organic carbon, sulfate, and iron. Across these latter four lines the ratios were constant but four separate dosage levels were evaluated. Baseline and post-BiRD development mineralogical and morphological condition of the limestone was evaluated for total iron (acid digestion/ICP) and using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), as well as Transmission Electron Microscopy (TEM).

Results/Lessons Learned. The whitish solid phase turned black in all bottles except the live control indicating formation of ferrous sulfides. Preliminary review of 120-day analytical results indicates that TCE concentrations have declined to near zero in each microcosm, including the carbon amendment microcosm where background sulfate and iron are significant. DCE isomers formed in some cases and not in others. VC, ethane, and ethane were not detected. In general, observed kinetics for TCE are similar to that expected for abiotic processes (half-lives on order of 30 days). Over 95 percent reduction was achieved by 41 days for the two microcosms with the highest dosage application. Organic and sulfate substrate utilization and iron reduction (and re-oxidation) from the ferric iron amendment was quite variable across the microcosms. While biological transformation cannot be ruled out completely, abiotic processes dominant and perhaps even led to reverse chlorination in one of the two high dosage microcosms. The full data set, conclusions, insights, as well as influence on remedial planning will be covered.

DNAPL Source Zone and Dissolved Phase Plume Treatment: ZVI and BiRDS Combined Remedy Strategy

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Background/Objectives. Historical use of solvents containing chlorinated aliphatic hydrocarbons (CAH) has resulted in uncontrolled releases of the solvents into the environment at tens of thousands of locations across the United States. At many of these locations the solvents have entered the subsurface, resulting in zones within the soil, sediment, or bedrock hosting Dense Non-Aqueous Phase Liquids (DNAPL) comprised primarily of the CAH. The CAH mass redistributes from the DNAPL over time and spatially extensive plumes of dissolved phase CAH mass often results. These DNAPL source zones and groundwater plumes may represent a threat to human and environmental receptors and in many cases must be actively characterized and managed through hydraulic control or some form of treatment. Current treatment practice is trending towards in-situ remediation with specific treatment technologies applied to the DNAPL and high concentration adsorbed mass zone (together referred to as the source zone) and others applied to the dissolved phase plume (which includes moderate to low concentration adsorbed mass). Integrated or combined remedy approaches are of significant interest to the environmental remediation community but there are few examples where different treatment technologies have been overtly integrated in space and time for comprehensive source-plume treatment and remediation.

Approach/Activities. An integration strategy for CAH source-plume active treatment will be presented that involves combining in-situ chemical reduction (ISCR) technology and in-situ biogeochemical transformation (ISBGT) technology, specifically zero valent iron (ZVI) for source zone treatment and biogeochemical reductive dehalogenation and metals stabilization (BiRD or BiRDS) for treating the dissolved phase plume. The strategy can also apply to heavy metal/metalloid and mixed organic and metal/metalloid pollutant situations.

Results/Lessons Learned. This integration strategy is in early stages of insertion into decision documents and field-testing. The ZVI provides primary and secondary functionality whereas the primary function is to rapidly reduce CAH mass and the secondary function relates to geochemical modifications involving pH and ferrous iron that are supportive of BiRDS reactive zone development but especially extended treatment performance. Some of the finer points will be covered.

Abiotic Reduction of Polychlorinated Hydrocarbons by Bioreduced Iron Oxide

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Background/Objectives. Chlorinated aliphatic hydrocarbons (CAHs) are common groundwater pollutants and pose a significant threat to human health as suspected carcinogens. According to a national survey, certain CAHs are frequently detected volatile organic compounds in US aquifers. As per National Council Report (2012), at least 126,000 sites in the US have residual contamination, and CAHs are among the main organic pollutants found at those sites. An inexpensive approach of handling complex site contaminated with CAHs can be by monitored natural attenuation. This work investigates abiotic degradation of CAHs by common iron oxide minerals commonly present in aquifers that may contribute of natural attenuation processes in contaminated aquifers. It is well known from recently published work that certain chemically precipitated Fe^{2+}-containing mineral phases (e.g., magnetite, green rust, iron sulfide, etc.) can facilitate abiotic (chemical) transformation of highly chlorinated hydrocarbons to less chlorinated species by reductive dechlorination. In this study, we will examine if common iron oxide minerals that may be microbially *'bioreduced'* under Fe^{3+}-reducing and sulfate-reducing conditions can also facilitate similar abiotic transformation of highly chlorinated hydrocarbons to less chlorinated species.

Approach/Activities. Bench-scale studies are in progress with *Shewanella putrefaciens CN32,* a Dissimilatory Iron Reducing Bacteria (DIRB), to bioreduce laboratory-synthesized hydrous ferric oxide (HFO) containing reactive Fe2+ species in batch microcosms with lactate as electron donor. The degradation potential of various CAHs such as carbon tetrachloride (CT), 1,1,2,2,-tetrachloroethane (1,1,2,2-TeCA) and trichloroethene (TCE) were investigated with bioreduced HFO, and the production of daughter products were monitored frequently for 2-3 months. The reaction kinetics of CT degradation with 10 mM initial HFO were compared with and without an electron shuttle, anthraquinone-2,6-disulfonate (AQDS).

Results/Lessons Learned. This study began in January 2014, and preliminary results show that CT, 1,1,2,2-TeCA and TCE may degrade by reductive dechlorination. While CT and 1,1,2,2-TeCA degraded quickly with a half-life of a few hours, TCE degraded much more slowly with half-life of a few weeks. We plan to examine degradation potential of various CAHs with common iron oxide minerals that may express activity upon getting microbially *bioreduced'* under Fe3+-reducing and sulfate-reducing conditions.

Back to Contents

Bioelectrochemically Enhanced Remediation of Hydrocarbon-Contaminated Soil: Amplification from Bench to Pilot Scale

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Traditional chemical or biological approaches for hydrogen-contaminated soil remediation are facing problems of significant energy consumption and low efficiency caused by low permeability and lack of electron acceptors. Here we present a new bioelectrochemical system (BES) with electrodes served as a nonexhaustible electron acceptor for *in situ* bioremediation of hydrocarbon-contaminated soil. The deployment of BES not only eliminates aeration or supplement of electron acceptors as in contemporary bioremediation but also significantly shortens the remediation period and produces sustainable electricity, which maybe used to power real-time sensors.

Tubular BESs with spiral sandwiched electrode assembly and different anode materials (carbon cloth, graphite granule and biochar) were inserted into raw water saturated soils containing petroleum hydrocarbons (around 12 g/kg-dry soil of total petroleum hydrocarbon (TPH) for enhancing *in situ* remediation. Air cathodes (activated carbon cloth or stainless steel mesh) use oxygen in air as electron acceptor to consume electrons from degradation of hydrocarbons on the anode. The electrode tube dimensions are L 20 cm × D 3.5 cm and L 23 cm × D 15 for bench and pilot BESs, respectively, which target 2.4 L and 50 L volumes of soil with maximum radii of 5 cm and 34 cm to reach outside soil edges. Control reactors were operated under same conditions but with open circuit. TPH concentrations were measured using gas chromatography. Microbial metabolism and community structure of soil and anode biofilm were analyzed by enzyme activities and high-throughput pyrosequencing, respectively.

For bench-scale BESs, TPH removal rate almost doubled in soils close to the anode (63.5−78.7%) than that in the open circuit positive controls (37.6−43.4%) during a period of 64 days. The maximum current density ranged from 73 to 86 mA/m^2. For pilot-scale BESs, 82.1–89.7% of TPH was degraded after 120 days across 1–34 cm radius of influence (ROI) from the electrode modules. This represents a maximum of 241% increase of biodegradation compared to control. The current production correlated with the TPH removal, reaching the maximum of 70.4 mA/m^2. The maximum ROI, deducting influence from the baseline natural attenuation, was estimated to be more than 90 cm beyond the real soil edge (34 cm), and exceed 300 cm should a non-degradation baseline be used. The ratio of the projected ROI to the radius of BES electrode module was 11–12. Residual TPH has a strongly positive correlation with hydrocarbon-degrading microorganism numbers, dehydrogenase activity, and lipase activity and a negative correlation with soil pH, conductivity, and catalase activity. Distinctive microbial communities were identified at the anode, in soil with electrodes, and soil without electrodes, suggests that a unique constitution of microbial communities may play a key role in BES enhancement of hydrocarbons biodegradation in soils. Research results suggest that bioelectrochemical *in situ* remediation can be carried out in large field scale.

Life Cycle Environmental and Cost Assessment of Microbial Electrochemical Cells and Conventional Technologies for Wastewater Treatment at Forward Operating Bases

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Background/Objectives. In the past decade, US military operations have relied heavily on forward operating bases (FOBs) to accomplish missions abroad. FOBs provide unique challenges to safe supply and disposal of water and wastewater. To address these challenges, the US military is exploring emerging technologies for on-site water and wastewater treatment. One suggested technology is the application of microbial electrochemical cells for wastewater treatment and production of electricity or hydrogen peroxide (H_2O_2) at the FOB. While electricity can be directly reused to run systems at the FOB, H_2O_2 can be utilized to treat or disinfect gray water to non-potable reuse standards, minimizing the total amount of water that must be shipped to the FOB. Life cycle assessments (LCA) and life cycle cost (LCC) assessments are conducted to quantify the environmental and cost impacts over the useful life of different products, services, and activities. When the LCC is combined with results from the LCA, a holistic picture of both environmental and cost burdens is realized. The objective of this project is to perform a LCA and LCC analysis of different wastewater treatment options ranging from the status quo to different MFC configurations for various sizes of military FOBs.

Approach/Activities. The sizes of the FOBs assessed in this study will include company (70-250 soldiers), battalion (300-1,000 soldiers), brigade (2,000-5,000), and division (10,000-20,000 soldiers). In total there are six alternatives that will be assessed for both LCA and LCC impacts at each of the FOB sizes. The three main alternatives include conventional black water and gray water treatment for FOBs of varying size, as well as MFC treatment including electricity production and MFC treatment including H_2O_2 production.

Results/Lessons Learned. To date, the impacts for the battalion size have been quantified. Preliminary results indicate that MFCs have the potential to increase the potential for water reuse which can in turn decrease soldier casualties by lowering the amount of required water resupply convoys; however, the difference in life cycle environmental impact from water reuse is less significant. Additionally, preliminary results indicate that for the battalion size, conventional wastewater treatment has the lowest environmental impact whereas the MFC with H_2O_2 has the highest environmental impacts. For all scenarios, the transport of goods to the FOB contributes significantly to overall environmental impacts. Further analysis will determine the life cycle environmental, cost and casualty impacts of all alternatives defined above at the varying sizes of FOBs.

Application of Microbial Fuel Cell to Treat Pyrite-Containing Mine Tailings

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Background/Objectives. Mine tailings generated during the mining process are often heaped around the mines and left untreated. In particular, the pyrite-containing mine tailings lead to the formation of acid mine drainage causing another environmental problems. Microbial fuel cell (MFC) technology can be applied to treat pyrite-containing mine tailings and generate electricity at the same time. Aeration can prohibit formation of biofilm on anode by letting dissolved oxygen (DO) in the anode compartment to be used as a terminal electron acceptor, but it can enhance the treatment of pyrite-containing mine tailings by increasing the oxidation rate. Effect of aeration on performance of an MFC where pyrite (FeS_2) grains are used as substrates and indigenous bacteria as an inoculum is observed.

Approach/Activities. Oxidation of pyrite leads to generation of sulfate ions (SO_4^{2-}), which contributes to the formation of a highly acidic solution, and dark brown $Fe(OH)_3$ precipitates. Under acidic conditions (pH<3) a high reduction potential is required for pyrite oxidation and it can be catalyzed by iron oxidizing bacteria. Indigenous pyrite-oxidizing bacteria isolated from Ilgwang mine (Korea) was used as the experimental inoculum. An air-cathode single-chamber MFC where the anode was inoculated with the indigenous bacteria and pyrite was purged with nitrogen and air to vary DO concentrations. A reactor without bacteria was used a control.

Results/Lessons Learned. The MFC where the DO concentration was maintained in the range of 4-6 mg/L operated in a fed-batch mode generated a maximum current density of 0.01 mA/m^2, while the control generated that of 0.10 mA/m^2. The control yielded better current density, and it implies that DO in the anode was used as an electron acceptor by the inoculum. It is expected that purging with nitrogen and lowering DO will yield better current density.

Leachates From Sanitary Landfill Treated In Microbial Fuel Cell Equipped with a Low Cost Membrane

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Background/Objectives. The metropolitan area of Mexico has a population of nearly 21 million inhabitants. At the end of the 2011 the mega sanitary landfill “Bordo Poniente” where the municipal solid waste was disposed of, was closed. “Bordo Poniente” has a surface area of 300 ha and received about 12, 600 ton/day; it has been in operation for 26 years. In this sanitary landfill, a significant an amount of highly recalcitrant and aggressive leachates is produced. On the other hand, microbial fuel cells (*MFC*s) is a promising technology that could treat wastewater with simultaneous production of bielectricity. Nevertheless, in *MFC*s the proton exchange membrane (*PEM*), in spite of the advantages for cell performance, has a high unit cost and represents up to 40% of the total cost of *MFC*s. Therefore, the aim of this work was to treat the leacheates from an actual sanitary landfill using *MFC*s equipped with a novel, low cost *PEM (LCM)*.

Approach/Activities. Single chamber *MFC*s *(SCH-MFC)* were used to carry out the leacheates treatment. The actual leachates used as substrate and treated through *MFC*s have a high values of pH, Conductivity (mS/cm) and *COD* (g/L); 8.3, 36.7 and 12.3, respectively. It actual leachates were mixed with an inoculum previously enriched in Fe (III) reducing bacteria, then the final *COD* was 2 g/L. Regarding the *PEM*s, a comercial membrane (Nafion 117 (*NF-117*)) was equipped in the *MFC* to compare the *MFC* performance against a low cost membrane. Graphite flakes with surface area of 0.28 m^2 were used as anodic material in both *MFC*s. The batch operation was carry out along 15 d and divided in two periods; 0 to 8 and 8 to 15 d. The main response variables analyzed along the long batch process were the average volumetric power (P_V), *COD* removal (η_{COD}), and the current intensity (I_{MFC}).

Results/Lessons Learned. In the first period of the batch operation (0 to 8 d), the P_Vs observed were 9 and 4 W/m^3 for *MFC* equipped with *LCM* and *NF-117*, respectively. In the second period (8 to 15 d), the R_{ext} were set at 47 and 82 Ω in the *MFC*s equipped with *LCM* and *NF-117*, respectively. The average P_Vs obtained were 20 and 6.8 W/m^3 for the *MFC*s equipped with *LCM* and *NF-117,* respectively*.* The cells removed up to 30 – 40% of the organic matter of the leachate. By the one hand, the *MFC* equipped with *LCM* was 10% higher than *MFC* equipped with *NF-117* in terms of η_{COD}*.* The *MFC* equipped with *LCM* delivered power 66% higher than that of the cell equipped with the *NF-117* membrane. Furthermore, cost analysis of the membranes involved showed that the cost of *LCM* was only 0.83% of the *NF-117* cost. It means that the *LCM* was two orders of magnitude more economic than *NF-117*. So, the cost of *MFC* to treat leachates or other organic effluent can be significantly reduced. Also, it is worth highlighting that the *LCM* did not require a pretreatment with hydrogen peroxide and sulfuric acid, as is the case of *NF-117*. Consequently, the manufacture and use of *LCM* avoids the production of hazardous wastes, besides the increased costs of membrane fabrication and conditioning.

Finally, in this work we demonstrated the use of a new *LCM* is associated to a better process performance and is outstandingly more economic than *NF-117.* Besides, the depuration capacity of the *MFC* in terms of the observed η_{COD} was quite attractive, in spite of the relatively short time of operation.

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Back to Contents

Pilot-scale Enhanced Biodegradation of Petroleum Hydrocarbons in Soil by a Bioelectrochemical System

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Background/Objectives. Utilization of bioelectrochemical systems (BES) for bioremediation of petroleum hydrocarbon-contaminated environmental matrices is recent topic being explored by researchers and industries. The common closed configuration of BESs limits the range of the technology to be practical in actual field conditions; therefore, an alternative open configuration has been investigated for increasing biodegradation rates beyond the anode. A tubular pilot BES has been reported to enhance petroleum hydrocarbon biodegradation in water-saturated soils, with biodegradation was observed with increasing time over increasing distances from the BES anode. However, it was not confirmed that the radius of influence (ROI) would increase with distance beyond the container walls. A scaled-up pilot BES test was conducted to determine the ROI for enhancing hydrocarbon biodegradation in soil. Also, the effectiveness of the BES was determined for enhancing hydrocarbon biodegradation in unsaturated soils.

Approach/Activities. A scaled-up acrylic soil reactor was constructed for testing the hydrocarbon biodegradation enhancement performance of a pilot BES. The dimensions of the reactor were 2.0 X 0.3 X 1.0 m (L X W X H) to determine the 2-dimensional range of influence of the BES. The tubular BES was constructed with dimensions of 90 cm X 10 cm dia., and was inserted into the soil reactor filled with petroleum hydrocarbon-contaminated soil that was collected from an industrial site. Water flow through the soil was controlled by a pre-set pump, with the water level pre-determined by outlet position. Samples were collected at different depths and distances from the BES anode and analyzed for total petroleum hydrocarbons (TPH).

Results/Lessons Learned. Monitoring results for TPH in soil indicated that the BES enhanced biodegradation activity. Biodegradation of TPH was observed in both the water saturated zone and unsaturated zone, and biodegradation rates increased over time at increasing distances from the BES anode. Therefore, this increasing range of TPH biodegradation indicated that the ROI increases with time. From the TPH data, soil moisture data, soil characterization, and BES voltage generation, the BES process was modeled to predict BES performance and ROI at varying soil conditions. The results from this test provides important design parameters for a field-scale implementation of the tubular BES at a petroleum hydrocarbon-contaminated site.

Chromium (VI) Detection Using MFC Concept

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Background/Objectives. Heavy metal pollution from industrial wastewater has become a serious problem nowadays. Chromium (VI) mainly used in electroplating process is one of the important contaminant, due to tits high mobility and toxicity. Microbial fuel cell (MFC) is a technology to produce electricity from oxidation/reduction reaction by microbial catalyst. Microbes mainly oxidize organic matters in the anode and, at the same time, oxygen or heavy metals can be reduced in the cathode. Produced voltage is related to the standard redox potential of each heavy metal ions. By applying this concept, chromium (VI) can be detected and quantified by the voltage and the current produced in the MFC.

Approach/Activities. Acetate was used as an organic carbon source. It was oxidized by microbes in the anode. Produced electrons were transported to the cathode through a wire. The transported electrons reduced chromium (VI) ions in the cathode. The voltage of this process was related to the standard redox potential of chromium (VI) and acetate. The amount of the reduced ions was determined by the amount of the produced electrons calculated from the produced current. Therefore, the concentration of chromium (VI) could be calculated by the produced current. According to Nernst's equation, standard reduction potential mainly determined the voltage and the voltage decreased with lower chromium (VI) ion concentration. Standard reduction potential was calculated using Nernst's equation with the voltage and chromium (VI) ion concentration in order to determine the existence of heavy metal ions in wastewater.

Results/Lessons Learned. After the injection of chromium (VI) into the cathode, the voltage corresponding to the difference of the standard redox potential between acetate and chromium (VI) was detected. The voltage decreased slightly with the decrease of chromium (VI) concentration by reduction. The voltage produced by chromium (VI) disappeared when chromium (VI) was completely reduced.

Comparison of Alternative Proton-Exchange Membranes to Replace High-Cost Nafion Ones in Microbial Fuel Cells

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Background/Objectives. Research and development on microbial fuel cells (*MFC*s) has grown exponentially in the last 15 years because of their capability of providing electricity generation from wastes as well as waste treatment. It has been reported that the proton exchange membrane (*PEM*), in spite of the advantages for cell performance, has a high unit cost and represents up to 40% of the total cost of *MFC*s. So, this work compared the performance of *MFC* fitted with alternative, low cost membranes. The control *MFC* was fitted with the classical Nafion membrane.

Approach/Activities. Lab scale single chamber *MFC*s were loaded with sulfate-reducing inoculum as biocatalyst and a semisynthetic leachate typical of dark fermentation of organic wastes. The *MFC*s were equipped with either an agar membranes *M2* (2% agar), *M6* (6% agar), a hybrid membrane made of agar and nafion *MH*, and the control Nafion 117 membrane (*NF*). The “fuel” exhibited a pH of 7.63 and 16.8 mS/cm conductivity. Electrochemical characterizacion of the four cells was performed by the polarization curve method.

Results/Lessons Learned. We found that the internal resistances (R_{int}) were low for all the cells, independently of the type of membrane. The lowest R_{int} corresponded to alternative membranes *M6* and *MH*, Table 1. So, results of R_{int} tend to favour the alternative membranes. The costs of these membranes were only 2.5 to 6% of the cost of the *NF* one, Table 1. However, the powers delivered by *MFC* fitted with alternative membranes were 14 to 25% of the power of the cell equipped with the conventional *NF* membrane. In spite of the reduced power, the alternative membranes still exhibited a higher Power/Cost ratio than that of the *NF* membrane, 0.9 to 4.4. mW/US$ membrane compared to 0.23 mW/US$, Table 1.

Table 1. Summary of characterization results of the microbial fuel cells in our work.

Membrane types	R_{int} [a] **(Ω)**	$P_{v,max}$ [b] **(mW/m^3)**	P_s [c] **(mW/m^2)**	**Cost (US$/m^2)**	**Ratio Power-to-Cost (mW/ US$)**
NF [d]	110.1 ± 0.8	14246 ± 2051	403 ± 58	1733	0.23
M2 **(2% agar)**	112.0 ± 5.3	2146 ± 506	61 ±14	14	4.36
M6 **(6% agar)**	89.8 ± 7.6	2363 ± 427	67 ± 13	41	1.63
MH	88.4 ± 3.6	3353 ± 594	95 ± 12	107	0.89

Notes: [a] Internal resistance of the *MFC*; [b] maximum volumetric power ; [c] maximum surface area density power; [d] Nafion membrane

We should highlight that the alternative membranes do not require the conditioning treatment with hazardous chemicals typical of *NF* membranes. Therefore, there is another competitive edge of alternative membranes in the form of avoided costs of chemicals and hazardous waste disposal.

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Back to Contents

Integrated Treatment Design for Remediation of Chlorinated Solvents

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Background/Objectives. A former dry cleaner site in Värnamo, Sweden, is contaminated with chlorinated solvents (PCE, with breakdown products) at depths of 0-35 mBGL in an area comprising approx. 40 000 m2. A municipal drinking water abstraction well is located 450 m southeast of the site, and is being impacted with low concentrations of chlorinated solvents (particularly cis,1-2-DCE and TCE). To start with the council planned to excavate the source zone 0-8 m and to use a hydraulic containment system for a minimum of 15 years, pumping out and treating 200 m3/day. It was determined that this strategy would result in excessive long term costs and so an integrated remedial design was implemented instead.

Approach/Activities. The remedial strategy finally selected for full scale remediation comprised of SVE/MPE in combination with reductive dechlorination. Soil vapor extraction (SVE) is used in the unsaturated zone and a multi-phase abstraction system (MPE) treat the impacted soil and groundwater in the upper part of the permeable saturated zone to provide rapid mass reduction there. Enhanced reductive dechlorination is used in the low permeable saturated zone using a range of controlled release injectable substrates – targeting high levels of contamination including DNAPL. The offsite receptor is protected by high volume pump and treat, which will ultimately be phased out, once the source area treatment is completed.
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The site presents many challenges to be accounted for in the integrated design; being located above a loop in the River Lagan, part of the site is formed of a steep unstable slope. Here implementation will be completed through multi-level directional drilling. The geology is highly heterogeneous vertically, comprising of sandy-gravel 0-8 mBGL, underlain by a low permeability saturated clay 8-12 mBGL, which is acting as an aquatard, and contains high levels of contamination including DNAPL. Under the clay is a fast-flowing, highly permeable coarse gravel 12-35 mBGL, which is carrying a small portion of the chlorinated solvents beyond the site boundary. The contaminant concentrations rang from 100-2000 mg/kg in the unsaturated zone and 10-100 mg/l (DNAPL) in the clay, hence treatment type and dose have been carefully formulated and targeted. Injection under the slope and river is challenging, and will be done with assistance of directional drilling.

Results/Lessons Learned. Treatment of the unsaturated zone in the original source area started in December 2012 and have removed approx. 800 kg of contaminants. The level of contaminants in the incoming vapor is still about 110 000 µg/m3, but declining. The next phase of the works, comprising vertical and horizontal direct push-injection, will be carried out in December 2014, and will be described in detail in this presentation as well as the results collected January-April 2015. It is estimated that the integrated approach will save at least $4 million, and will provide greater surety of site closure.

Combined Biological and Chemical Technologies for In Situ Remediation of Chlorinated Ethenes at the MARS Site

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Background/Objectives. The remediation of contaminated sites is often a complex matter, frequently requiring the use of several complementary methods. The necessity of multiple remediation technologies is often driven by the presence of multiple contaminant types or in cases where a single method fails to achieve the target values. Similarly, technology combinations might be recommended when contaminants are present in a geologically complicated environment and both the source and the plume remediation are simultaneously needed. The engineering production company MARS in Svratka (Czech R.) has a historical chloroethenes contamination both in the form of the original hotspots, which represents a long-term residual source, and a groundwater plume, which follows a preferential pathway towards a river. The total concentration of chlorinated ethene in the area of the hotspots is above 40 mg/l and within the plume it is on the order of 10 mg/l, significantly above the limits determined by the risk analysis.

Approach/Activities. A geological model of the site was created using EnviroInsite®, groundwater datavisualization software, and a flow model in MODFLOW®, served to optimize the individual remedial technologies proposed. These technologies represent a combination of four reductive methods - i) anaerobic biodegradation using lactates applied to the contamination hotspot, ii) abiotic chemical reductive dehalogenation using nZVI applied subsequent to the biological method, iii) electrochemic reduction using a DC electrical field applied to increase the effectiveness and longevity of the nZVI and finally iv) a passive reactive barrier with gates filled with macroscale Fe to protect the area in the groundwater flow direction. The various methods were subjected to batch and column laboratory tests prior to application. The aim was to assess their applicability under specific conditions and in terms of technology combinations of methods to test their efficacy. The various methods were applied consecutively in the order lactate, nZVI and DC field. The effectiveness of each of the methods was bimonthly monitored over a period of two years using an extensive grid of monitoring points where not only the concentrations of individual chlorinated ethenes were measured but also pH, ORP and conductivity.

Results/Lessons Learned. The site demonstrated that for successful remediation it is often necessary to combine various methods. A combination of oxidation and reduction methods, which has been applied previously at many other sites, is problematic because there are very drastic changes in the conditions in the rock environment. A combination of biological, chemical and electrochemical methods is very effective for significantly reducing the concentration of chlorinated ethenes in environments with complex geology and a poorly defined contaminant source. The use of lactates leads to a significant bioreduction of PCE and TCE to cis-1,2-DCE, which is significantly less biologically degradable and accumulates in the groundwater. The subsequent use of nZVI leads to an even degradation of all of the monitored CHCs. The use of nZVI is also intensified by the application of a DC field, which extends the effectiveness of the nZVI at the site (prevents its oxidation) and increases its range. The methods are complemented by three PRB barriers, which effectively protect the downstream groundwater.

A Treatment Train Approach to a DNAPL Site Remediation Project

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Background/Objectives. A RCRA facility investigation (RFI) completed in April 2004 at a former industrial landfill in central Florida identified a DNAPL source area contributing to the groundwater contamination of multiple aquifers. The lateral extent of groundwater contamination encompassed approximately 5 acres with a maximum depth of approximately 250 feet below land surface. Groundwater remediation has progressed in a phased approached at the site. Initially, approximately 69,000 tons of DNAPL impacted and highly contaminated soils were excavated and removed from site. In 2005 a groundwater extraction system was installed to maintain hydraulic control of the plume and aid in groundwater remediation. In 2006 an in-situ air sparge (ISAS) was installed to treat the shallow impacted-groundwater plume with expansion of the ISAS system occurring in 2009. The combined source removal and ISAS remediation efforts reduced the plume size to less than 2 acres in size with contaminant concentrations being reduced by several orders of magnitude. However, to meet the project redevelopment schedule, additional remedial actions were warranted to reduce remnant source mass and achieve plume stability for risk-based closure.

Approach/Activities. To expedite site restoration, specifically in the deeper aquifers (approximately 100 to 150 feet bls) and a localized area present in the surficial aquifer (approximately 50 feet bls) that was inaccessible to historical excavation activities, AECOM Technical Services completed a supplemental investigation and remedial alternatives analysis (RAA) to evaluate remedies to treat the remaining portion of the groundwater plume. The supplemental instigation and RAA indicated that in-situ chemical oxidation (ISCO) was the most appropriate technology for treatment of the surficial aquifer. Commercial grade vegetable oil was selected for injection into the lower permeable transitional zone between the surficial and deep aquifers. Injection and recirculation of an organic substrate using the existing groundwater extraction system was selected for treatment of the deeper aquifers. From February 2013 to March 2013 approximately 42,000 pounds of hydrogen peroxide activated sodium peroxide were injected into the surficial aquifer. Following injection of the chemical oxidants, approximately 72,000 pounds of emulsified and neat vegetable oil was injected into the transition zone. In October 2014, the existing groundwater recovery system was converted to a recirculation system for substrate amendment.

Results/Lessons Learned. ISCO remedial progress sampling was completed from February 2013 to June 2014 and start up groundwater sampling was completed in October 2014. Sampling results to date confirm remedial objectives have been achieved. This presentation will discuss data evaluation methods, decision points for transitioning into each phase of work, and subsequent contaminant reductions observed following each phase. Lessons learned during the field activities, including modifications implemented during the work completed and plans for future optimization, will be presented.

Update: Successful In Situ Bioremediation Following In Situ Chemical Oxidation for PCE Remediation

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Background/Objectives. The following is an update on bioremediation activities that will result in closure for a historic release of perchloroethylene (PCE) to shallow groundwater from a dry cleaner at a site west of Denver. The subsurface saturated zone is comprised of granite gravels and weathered granite overlying more competent granite bedrock. Shallow groundwater is hydraulically connected to groundwater in deeper fractured bedrock. As the dissolved phase PCE moved north with shallow groundwater the plume took an oval shape.

In-situ chemical oxidation (ISCO) was selected as the remedial technology for use on the site because the of low soil oxidant demand in soils and because the oxidant could be injected and also introduced in a passive manner. After two injection events using potassium permanganate, in December 2008, forty percent sodium permanganate (SP), which has a molecular weight similar to PCE, was decanted into dry wells (dosed) situated in the source area. Selected dry wells were situated in locations near a former dry cleaning machine so that the SP might travel the same or similar path as any PCE potentially released to the subsurface from the machine. SP in shallow groundwater in selected source area wells remained unreacted for almost one year resulting in an order of magnitude reduction of dissolved phase PCE (from 26,000 to 5,000 µg/L) during this period of time. A subsequent dosing event in December 2009 temporarily lowered levels of dissolved phase PCE to 2,900 µg/L in source area wells, however within three months concentrations had rebounded to levels above 7,000 µg/L.

Following the ISCO events, bioremediation was not a consideration based on the belief that the oxidants had likely destroyed most organisms such that the system could not be driven sufficiently anaerobic. However, results from one of the monitoring wells in the network situated downgradient of the source area continued to exhibit the presence of daughter products at molar concentrations greater than PCE, under reducing conditions.

Approach/Activities. In November 2011, a mixture of highly soluble Wilclear Plus® substrate and a slowly soluble substrate, LactOil® soy microemulsion were blended and injected into 22 injection points, two monitoring wells and six dry wells. The injection of the substrate was conducted to drive the saturated zone anaerobic in the main plume area while providing a more slowly soluble substrate for the source area. Two additional targeted injections of this blend of substrate, injected in December 2012 and December 2013, have created reducing conditions for two areas within the plume that had previously not responded.

Results/Lessons Learned. Results from twelve subsequent quarterly monitoring events since reflect a conversion from aerobic to anaerobic environment in the saturated zone, a three to four order of magnitude drop in dissolved phase PCE in the source and downgradient areas, the buildup and then subsequent drop in concentrations of PCE daughter products through vinyl chloride, with steady concentrations of ethene.

Integrating Sustainable In Situ Thermal and Biological Treatment

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Background/Objectives. There is increasing interest in the combined use of thermal and biological groundwater remediation in offering the potential for more sustainable remedial solutions. Micro-organisms that degrade chlorinated solvents such as *Dehalococcoides* are known to be temperature sensitive. Integral to the combination of thermal and biological treatment is therefore the ability of an aquifer to retain or recover a microbial population with appropriate degradation capabilities.

This paper outlines a combined in-situ biological and thermal treatment project, within a fractured bedrock aquifer, with a focus on evaluation of the recovery of a microbial population in an area where in-situ thermal treatment was undertaken. The significance of the results for future combined treatment at other sites is also discussed.

Approach/Activities. Groundwater samples were collected from three monitoring wells (R5, R8 and R11), located within the thermal treatment zone, prior to steam injection (baseline) and on three occasions post cessation of steam injection, at approximate three monthly intervals. Each sample was analyzed for bacteria and functional genes responsible for biodegradation of chlorinated solvents, including *Dehalococcoides*, using *BioFlo*^{TM} sampling equipment to characterize and quantify microbial populations and activity; VOC and natural attenuation parameters were also determined pre- and post-thermal treatment. Additionally, previously installed thermocouples were monitored at the time of sampling.

Results/Lessons Learned. Post treatment consistent with the mass reduction recorded, significant reductions in chlorinated concentrations were noted in the monitoring wells assessed. In terms of microbial numbers, the baseline sampling data showed *Dehalococcoides* to be below the laboratory method detection limit (mdl) in a sample collected from well R11; it was however detected in samples collected from wells R5 and R8 at concentrations of 16.9 and 27.2cells/mL, respectively. Analysis of samples circa three months post steam injection cessation detected up to two orders of magnitude increase in *Dehalococcoides* concentrations in samples R5 and R11, with the remaining sample (R8) showing one order of magnitude decrease of the same.

A comparison of the microbial community compared to contaminant concentrations, geochemistry and temperature has been undertaken. The results of this assessment post treatment indicate that the microbial community has recovered quickly when groundwater temperatures declined to ambient, and demonstrates the feasibility of combining in-situ thermal treatment with reductive dechlorination as a combined technique at this site, and potentially other sites, to address low levels of residual contamination post intensive source treatment.

Implementation of Year-Five Follow-Up Injections at a Large-Scale CVOC Bioremediation and Thermal Remediation Project

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Background/Objectives. Historical releases of chlorinated solvents occurred from a former manufacturing facility in Connecticut resulting in concentrations of chlorinated volatile organic compounds (CVOCs) in source zone groundwater of up to 780 ppm and concentrations of over 20 ppm in the resulting 15-acre downgradient groundwater plume. Source area residual dense non-aqueous phase liquid (DNAPL) and CVOCs were situated in tight soils (till) and weathered bedrock. The majority of the off-site CVOC groundwater plume is located within a forested wetland where the soils are more permeable than in the source area. The primary contaminant of concern was trichloroethylene (TCE) although other CVOCs persisted in groundwater. The final multi-faceted remedial solution was a large-scale project incorporating limited source zone excavation followed by source zone *in situ* electrical resistance heating (ERH), and extensive plume-wide *in situ* bioremediation utilizing enhanced reductive dechlorination (ERD) and bioaugmentation.

Approach/Activities. *In situ* thermal treatment of the saturated zone was proposed as the remedy for the source area combined with *in situ* bioremediation via ERD and bioaugmentation, followed by monitored natural attenuation to address the migrating groundwater plume. The bioremediation system consisted of approximately 600 injection wells installed across multiple biobarriers installed to a maximum depth of 40-feet. Approximately 13,800 gallons of emulsified vegetable oil substrate (EVO) was injected between June 2010 and June 2011 followed by bioaugmentation. Beginning in Spring 2013, approximately two years following the initial phase of treatment, targeted injections were undertaken at 30 new wells in the former thermal treatment area and at approximately 200 locations spread across several areas within the original biobarriers with the goal of reducing recalcitrant pockets of CVOCs and accelerating remedial completion. The ERH system operated from October 2010 through July 2011 and was comprised of 89 electrodes installed in the source area overburden and weathered bedrock. Approximately five years of remediation performance monitoring data, consisting of CVOC concentrations, residual substrate measurements, biogeochemical parameters, mobilized metals, and groundwater temperature has been collected and evaluated. Substrate measurements were performed analytically and geophysically. CVOC distribution and mass flux/discharge was calculated. The monitoring well network has been evaluated for locations where compliance has been attained and where pockets of recalcitrant CVOCs remain.

Results/Lessons Learned. Nearly five years following initial substrate injections, the combined ERD/ERH remedial approach is progressing well despite challenges. It is anticipated that targeted substrate injections will be required in Summer 2015 to treat pockets of recalcitrant CVOCs. The exact locations for substrate addition will depend on current performance data. Geophysical field measurements and biogeochemical parameters will be collected and analyzed in early 2015. Data analytics will be utilized to target injection locations and maximize injection efficiency. This abstract focuses on the evaluation, design, and implementation of year-five supplemental substrate injections and will highlight the basis for the design, design approach, challenges, lessons learned, and changes required from the initial two injection programs.

Back to Contents

Combining In Situ Chemical Reduction and Phytoremediation as an Expedited Closure Strategy in a Low pH/Elevated Sulfate Pinelands Aquifer at a Long-Term New Jersey Superfund Site

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Background/Objectives. In order to accelerate groundwater remediation at a long-standing Superfund Site in the New Jersey Pinelands, an approach was established to supplement previous soil washing and In-Situ Chemical Oxidation remedies, and supplant an eighteen year old groundwater recovery and treatment system (system) using In-Situ Chemical Reduction (ISCR) and Phytoremediation. ISCR bench-scale and pilot testing programs were conducted to evaluate using ISCR to address various Volatile Organic Compounds (VOCs) and heavy metals in a shallow Pinelands aquifer with low pH (4.0 to 6.5 Standard Units [SU]) and high natural sulfate levels (31,000 to 120,000 micrograms per liter [µg/l]). Phytoremediation, including the planting of 880 poplar trees of three different species, was used to manage water budget in the residual source area and to remediate VOCs and metals in shallow groundwater. The significant compounds of concern (COCs) consisted of: tetrachloroethene (PCE); trichloroethene (TCE); 1,1,2,2-tetrachloroethane (1,1,2,2-PCA); 1,1-dichloroethane (1,1-DCA); 1,1,1-trichloroethane (1,1,1-TCA); ethylbenzene; beryllium; and chromium. As a result of residual source area impact and various groundwater hot spots, these COCs continued to exceed the Applicable or Relevant and Appropriate Requirements (ARARs) and projected timeframes for meeting ARARs using the current pump and treat remedy presented overall project end-point and cost concerns.

Approach/Activities. To expedite the remedial timeframe and reduce overall remedial costs for the site, an alternative remedial approach was established and supported by the United States Environmental Protection Agency to include: optimization of the existing system while ISCR and Phytoremediation could be evaluated; baseline monitoring to update site conditions; Phytoremediation to manage source area water budget and supplement source area remediation; ISCR bench-scale testing; and ISCR field implementation. System optimization involved: pH titration testing to determine optimal pH for effective beryllium removal; amending the treatment train to improve metals removal; equipment replacement and maintenance to improve system uptime, throughput and treated water discharge; and system procedural improvements. ISCR bench-scale testing involved the collection, preparation and periodic analysis of four soil/groundwater microcosms that were treated with varying dosages of Peroxychem EHC-M® and pH buffering material. ISCR field implementation consisted of: pre-design testing including Membrane Interface Probe (MIP) and geochemical analyses to identify and characterize relevant implementation areas; EHC® (24,850 lbs) and pH buffering material (magnesium hydroxide) injection in three targeted areas of the site (one residual source area and two groundwater hot spots); applying bacteria inoculum; and a comprehensive post-ISCR injection groundwater monitoring program.

Results/Lessons Learned. The ISCR bench-scale test proved successful for the reduction of metals and chlorinated ethanes but natural sulfate levels were identified as a limiting factor in achieving adequate ORP levels to fully address ethenes. In order to overcome this limitation in the ISCR field implementation, EHC® was used instead of EHC-M® and EHC® dosing rates were established to account for the sulfate-driven demand. Additionally, pH buffering was integrated into the ISCR field application in order to drive pH levels up to a point where bioaugmentation could be applied and maintained. Varying levels of ISCR success were observed in the three areas of ISCR application as follows:

In the residual source area (MW-29S Area), optimal pH and ORP conditions were maintained because the ISCR injection area was sufficiently upgradient from groundwater recovery wells and the phytoremediation plot positively influenced hydraulic gradient throughout the source area. As a result, many COC concentrations were reduced to below ARAR levels and ARAR levels were achieved completely some portions of the source area (e.g., MW-29S).

In one hot spot (R-6 Area), significant abiotic degradation of CVOCs was observed initially but only after the pumping rate for recovery well R-6 was significantly reduced were optimal pH and ORP conditions observed. After the R-6 pumping rate was reduced, significant secondary reductions of COC concentrations to below ARAR levels were observed.

In one hot spot (MW-5S Area), the hydraulic gradient was not modified from normal system pumping conditions and optimal pH and ORP conditions were not achieved. As a result, only limited abiotic degradation of CVOCs was observed.

In areas where hydraulic gradient has been controlled to promote the transformation of the ISCR implementation area to buffered, reducing conditions, ISCR has proven successful in reducing many of the COCs despite the challenging pH and sulfate conditions. An explanation of the overall remedial approach and full evaluation and comparison of the ISCR bench-scale and field implementation results, along with a discussion of the challenges that affected the ISCR approach, will be provided in this presentation. Because it has been proven that ISCR can be successfully implemented at a site with naturally low pH and high sulfate levels, an added ISCR application is currently being designed to address residual ARAR exceedances throughout this site.

Synergy of Trap & Treat BOS® 100® and 3DMe Tackles Large TCE Plume

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Background/Objectives. A large manufacturing facility used vapor degreasing in the 1970s and 1980s that resulted in contamination of soil and groundwater with TCE. Shallow groundwater occurs in unconsolidated soil and weathered bedrock. Bedrock occurs at relatively shallow depths (5 to 18 feet bgs), and consists of shale interlayered with thin beds of siltstone, sandstone and limestone. The overlying unconsolidated material is weathered shale and residual silty clay soil derived from shale. The depth to water in the shallow zone beneath the site varies from less than 2 to about 5 feet bgs, and generally deepens slightly going from south to north. Key objectives are as follows.

1. Prevent migration of high-concentration CVOCs from the source area into surrounding groundwater;
2. Promote degradation of the shallow zone CVOC plume outside of the source area by promoting varying zones of aerobic and anaerobic conditions across the site, allowing for multiple degradation pathways.
3. Monitor the treated area and document the response to biostimulation, to determine suitable reinjection intervals and estimate the time required to achieve groundwater remediation goals.

Approach/Activities. Near the former degreaser area, TCE concentrations in groundwater exceeded 100 ppm and rapid cleanup was required to achieve the primary objective. Pilot testing of Trap & Treat BOS 100® demonstrated the ability of this product to effectively and quickly eliminate the source. BOS 100® is a specialized catalyst manufactured by Remediation Products Inc. and designed for rapid degradation of chlorinated solvents. Biostimulation was selected for treatment of the large dissolved-phase plume beyond the source area and involved injection of Regenesis' 3DMe (a multi-component electron donor containing both quick-release and slow-release components). The 3DMe injections were designed to produce a sequence of anaerobic and aerobic treatment zones in the shallow aquifer to take advantage of mixed microbial behavior and multiple CVOC degradation pathways.

Results/Lessons Learned. Injections were completed in the fall of 2012. Installation of the BOS 100® resulted in rapid reduction of TCE of over 95% with comparable reductions in cis-DCE and vinyl chloride. Spikes in chloride and production of ethene and other hydrocarbon gases demonstrated destruction of CVOCs. As a result, mass flux at the source area is substantially reduced enabling more efficient deployment of 3DME. A supplemental injection of 3DMe was performed in February 2014. As expected, degradation of CVOCs is occurring through multiple pathways with some generation of cis-DCE and vinyl chloride. At this point the biostimulation strategy appears to be working with daughter product concentrations beginning to fall. The current plan is to monitor for a couple of quarters, update the trend analysis, and recast estimates of time to achieve cleanup goals.

Utilization of Remediation Performance Indicators to Select mZVI Powders for Inclusion in an Enhanced *In Situ* Bioremediation Remedy

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Background/Objectives. Microscale zero valent iron (mZVI) powders are increasingly being utilized to treat groundwater impacted by redox-amenable contaminants such as chlorinated solvents either as a stand-alone remedy or in conjunction with other technologies like enhanced in situ bioremediation (EISB). Over the past decade, conventional mZVI powders with a mean particle size of 20 microns to hundreds of microns have been successfully utilized as reactive backfill or deployed using highly energetic injection techniques to treat impacted source areas and groundwater plumes. This treatability study focused on the development of remediation performance indicators (RPI) for ZVI powders with average particle sizes of ~ 5 microns.

Approach/Activities. Three commercially available mZVI powders were studied to compare in their abiotic, iron-mediated transformation of chlorinated ethenes (CEs) and carbon tetrachloride (CT). In the study, triplicate batch reactors containing 10 g/L of mZVI, with mean particle sizes near 5 microns (two samples) and 75 microns (one sample), were reacted with aqueous target contaminants including perchloroethene (PCE), trichloroethene (TCE), cis-dichloroethene (c-DCE), and carbon tetrachloride (CT), each at an initial concentration of 5 mg/L The RPI included: (1) determination of percent reduction for each contaminant; (2) identification of contaminant degradation products; (3) molar chlorine and carbon balances to help discern reductive versus sorptive losses; and (4) development of standard kinetics-related parameters including the pseudo first-order rate constant (k_{obs}), mass-normalized rate constant (k_M), and surface area-normalized rate constant (k_{SA}). The treatability study included sampling intervals at elapsed time intervals of 0, 7, 14, 28, 42, and 56 days.

Results/Lessons Learned. Although all three irons rapidly degraded CT equivalently well, performance differences became more pronounced in the CE series, with k_{obs} varying by one order of magnitude while k_{SA} typically varied more than 2 orders of magnitude. The reactivity trend for all three irons generally followed CT > PCE > TCE > c-DCE, confirming the expected correlation between rate and degree of chlorination. Beyond degradation rates, this study documents significant difference between the mZVIs with respect to other key performance parameters: the rate of contaminant transformation, pH and ORP profiles, and the evolution of reduced hydrocarbon gases such as ethene, ethane, and methane. Although reactivity is clearly a key parameter in the ZVI-mediated transformation of contaminants, it alone may not adequately assess potential efficacy in a combined remediation strategy with enhanced *in situ* bioremediation.

Back to Contents

Combined Remedy Synergies – Examples and Conceptual Road Map

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Background/Objectives. Today, there are many *in situ* remediation technologies used regularly around the world in countries with established clean-up legislation, ranging from extractive (pump-and-treat, thermal), chemical (in situ chemical oxidation / reduction) to biological (enhanced / monitored natural attenuation). That so many options are available is testimony in itself that no one technology is ideal in all circumstances – if that were so, it would follow that that technology alone would be employed. The variety of technologies available is instead a direct reflection of the variety of performance characteristics they each present, be it in the balance of achievable cost vs. time, the degree of intrusion necessary for their furtherance, their optimum concentration range for maximum efficiency, or their suitability to a given geological, hydrological or geochemical setting.

Integrated treatment design is developing as a progressive approach to remediation, incorporating a range of synergistic technologies to achieve site closure, each operating in its own particular area of individual strength. Specifically, the strategy requires pragmatic selection of compatible technologies, such that each compliments the others and operates at its greatest efficiency, ensuring optimum performance and cost-effectiveness throughout the project duration – which can be significantly shortened as a consequence.

Through the deployment of a combination of compatible technologies, which may be drawn from physical, chemical and biological arenas, remediation goals and site closure can frequently be achieved more rapidly, and at lower cost, than through the use of any one approach used alone. This is due to each technology having very different strengths and weaknesses, and through suitable combination – either sequentially, spatially or both – the strengths can be combined and the weaknesses overcome to achieve far better results, more rapidly, and with less expense, than through the use of any of the technologies in isolation.

Approach/Activities. This talk briefly explores the driving pressures and evolutionary background to the widespread single-technology design predisposition still evident across much of the industry, and outlines the technical basis of its inherent shortcomings in the dynamic and heterogeneous context of an impacted aquifer undergoing clean-up. The physico-chemical principles favoring the use of integrated remedial approaches – both spatially and temporally – are summarized, and practical indicators for determining optimal points of inflection of technology change are outlined. The case is presented for incorporation of integrated design considerations with objective technology changeover trigger points into the initial remediation approval process, thereby securing efficiency and cost benefits to all stakeholders.

Results/Lessons Learned. The potential benefits of the concept are illustrated through field examples taken from different aquifer and regulatory settings around the world, offering striking illustrations of both the scale of the potential problem and the magnitude and ease of potential savings achievable through appropriate application of technology integration. It is anticipated that this talk will be of interest to end-users, regulators and professional remediation engineers alike.

Combined Remedy Benefits of Integrated Physical, Chemical and Biological Treatments on a 14 Million Litre Fuel Spill in a Swedish Forest

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Background/Objectives. A series of historic spills from a Swedish military storage depot led to an extensive area of groundwater under forest and commercial property being impacted with petroleum fuels. The largest spill event was an explosion resulting in a loss of life and the release of 14 million litres of petroleum products, of which 6 million litres reached the wider environment, covering an area of approximately 45,000m^2. The problem was enhanced by the difficult terrain, which largely consisted of a hillside moraine and boulder fields covered with dense vegetation. An integrated *in situ* treatment approach proactively combining physical, chemical and biological technologies both spatially and in sequence was selected, with the combined application presenting clear time and cost benefits over the projected use of any one of the technologies used alone.

The principal pollution incident occurred in 1958 following an explosion. 14,000,000 L of gasoline, diesel and jet-fuel were released and flowed down the forested mountainside and into a lake. The initial 1950's clean-up activities included setting the lake on fire, with the remaining free-product 'lake' on shore then covered with soil, left in place and used as a playground.

Approach/Activities. Contemporary remedial options considered have included excavation, multi-phase extraction, *in situ* chemical oxidation (ISCO), bio-sparging and enhanced natural attenuation. Following costing and feasibility evaluations, integration of physical, chemical and biological technologies both spatially and sequentially was been identified as the most cost-effective and flexibly adaptive strategy. Pilot tests of the component parts (selected as compatible) were conducted separately to identify optimal efficiency bands and dosing requirements, and from this, the spatial arrangement of technologies and sequential switch-points for optimal efficiency were determined. The first stage of full-scale application was conducted through winter of 2013-14. Performance validation (at time of abstract; 6 – 8 months) describes concentration reductions of >95% to non-detect through the majority of the areas treated.

Results/Lessons Learned. Identification of optimal bands of application based on pilot study performance and cost-projection enabled each technology to be applied at its maximum efficiency, providing an overall 'treatment-train' synergy. The projected cost of integrated technology application was calculated at between 25 – 55% of the cost of any of the same technologies used alone, representing cost savings of between $1.7M – $6.5M on the overall project. The projected time for completion was also shortened by several years, although the actual extent of this is harder to reliably determine. In the final design, excavation was not required. The remediation left no visible impacts; important both for aesthetics, military security, and macro-environmental impact – the forest was left in place.

This talk provides qualitative and quantitative examples of the cost and practicality benefits that may be secured through proactive technology integration by way of a large, multi-faceted, formal case study. It is anticipated that this talk will be of interest to end-users, remediation practitioners and regulators alike.

In Situ Treatment Train (ISCO, Aerobic and Anaerobic Bioremediation) to Address an LNAPL Source Area

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Background/Objectives. An active power plant experienced a release of fuel oil to shallow groundwater that threatened to impact an adjacent federally protected river in Maryland that feeds into the lower Chesapeake Bay. The impacted area contains several subsurface utilities that would make physical removal (dig and haul) of the soils in the impacted zone difficult and would likely require the shutdown of the plant during excavation activities. A less intrusive remedial option selected for addressing the fuel oil LNAPL was an in situ treatment train that included chemical oxidation, aerobic and anaerobic bioremediation with limited multi-phase extraction. A blend of sodium persulfate and calcium peroxide was chosen based on the combined substrates ability to provide chemical oxidation as well as aerobic and anaerobic biodegradation of the residual fuel oil. A successful pilot test was conducted in December 2008, with full-scale implementation conducted from 2009 through 2011.

Approach/Activities. Approximately 6,000 gallons of an 8% injection solution was injected into the subsurface (approximately 3,000 pounds of persulfate/peroxide) in 3 injection events between 2009 and 2011. Multi-phase extraction was implemented for approximately six months in 2012 to capture LNAPL that was liberated by the substrate injections outside of the treatment zone. Significant decreases in LNAPL and dissolved phase hydrocarbons were observed in several monitoring wells at the Site after the initial injections early in 2009.

Results/Lessons Learned. LNAPL was initially measured at 1.2 feet at the source area monitoring well. Eighteen months after injections, LNAPL was measured at only 0.2 feet in the same monitoring well. Dissolved phase TPH-DRO had been detected at concentrations up to 6 mg/L prior to initiating the injection program. Concentrations in 6 of the 7 performance monitoring points in and around the source area were non-detect for TPH-DRO in May 2011. Groundwater geochemistry was observed to be mildly reducing prior to injections (low dissolved oxygen and moderately negative oxidation reduction potential) then highly oxidizing immediately after injections (high DO, and strongly positive ORP) to strongly reducing four months after injections. Approximately 24 gallons of LNAPL was removed that significantly reduced measured LNAPL in site groundwater. No product was observed in the adjacent river and the data from the monitoring wells indicated that the plume was stable, shrinking and no longer a threat to the adjacent river. MDE has agreed to no further action for the Site based on the combined success of the in situ treatment train to significantly reduce LNAPL and the dissolved phase plume.

Comparison of In Situ Enhanced Bioremediation/Chemical Reduction and Chemical Oxidation of Mixed Metals and TCE

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Background/Objectives. In an effort to mitigate further vertical migration of a trichloroethylene (TCE) plume deeper into a lower aquifer and address residual source area contamination, a pilot study was conducted to facilitate the development of a full-scale remedy. Based upon a careful review of the remedial alternatives and the site history, this study was designed to evaluate the performance of several remedial alternatives in the field prior to full-scale implementation. The objectives of the pilot study were to provide sufficient data to evaluate the feasibility of chemical oxidation technologies or enhanced bioremediation combined with reductive dechlorination as appropriate remedial alternatives and to support the design of a full-scale remedy at the site.

Approach/Activities. For the purposes of the pilot study, an area was chosen based on the apparent elevated concentration of TCE across the vertical intervals in this sector relative to the other impacted areas of the site. The contaminant mass is believed to be concentrated in this area, therefore the greatest impact on site contaminants will most likely be achieved by focusing on this region of the TCE plume. After a review of the site data, an approach was chosen to focus the initial remedial effort on the TCE plume followed by an aggressive remediation for metals contamination if the groundwater concentrations do not attenuate and/or remediate prior to remediation of the volatile organic compound (VOC) plume. Chemical oxidation options applied included a slow-release, catalyzed peroxide or an activated persulfate technology. The enhanced bioremediation/reductive dechlorination option included microbial inoculant Dehalococcoides spp. (DHC) and a slow-release electron donor coupled with ferrous iron.

Results/Lessons Learned. All technologies demonstrated the ability to reduce the TCE concentrations 82% to 98% by the end of the study; however, the rate at which this was achieved varied with the remedial approach. The response of the chlorinated organic contaminants to treatment followed expected trends for each of the respective remedial strategies. For the slow-release, catalyzed peroxide, a steady decline in both TCE and DCE concentrations was observed over the course of the study. In the case of the sodium persulfate treatment, an immediate reduction in both TCE and DCE occurred followed by subsequent rebound approximately 3 months after the initial injection. The reduction in TCE and increase in DCE concentrations at the location of the substrate and DHC inoculant addition mirrored the increase in the microbial population approximately two months after the injection. These trends are typical of these approaches and demonstrated successful implementation of the remedial technologies for addressing organic contaminants at the site. Continued microbial growth and downward TCE concentration trends are expected to continue resulting in further mass reduction in the area treated with enhanced bioremediation/reductive dechlorination. The combined abiotic/biotic approach at this location was the only one to result in a reduction in the concentration of all three metals of concern (Al, Cr and Mn). Geochemistry and microbial population dynamics are also indicating progress toward remedial goals, but lower pH conditions may be inhibiting microbial activity.

Back to Contents

Screening Nonionic Surfactants for Enhanced Biodegradation of Polycyclic Aromatic Hydrocarbons in Contaminated Soil

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Background/Objectives. The efficacy of bioremediation for soil contaminated with polycyclic aromatic hydrocarbons (PAHs) may be limited by the fractions of PAHs that are less bioavailable to PAH-degrading microorganisms. The concentrations of PAHs remaining after conventional biological treatment might exceed cleanup standards, especially the carcinogenic high-molecular-weight PAHs. We evaluated the effects of adding surfactants on biodegradation of the PAHs remaining after laboratory-scale, aerobic biological treatment of PAH-contaminated soil from a former manufactured-gas plant (MGP) site.

Approach/Activities. Five nonionic surfactants (Brij 30, Span 20, Ecosurf™ EH-3, polyoxyethylene sorbitol hexaoleate [POESH], and a rhamnolipid biosurfactant) were evaluated for their ability to enhance PAH desorption and biodegradation in the bioreactor-treated soil. Two doses less than that required to reach the critical micelle concentration in the aqueous phase were evaluated for each surfactant. Desorption was measured using an infinite-sink desorption method. Biodegradation was measured as further removal of a PAH after a 14-day incubation period, in comparison to controls with no added surfactant. The effect of surfactant-amended treatment on soil cytotoxicity and genotoxicity was also evaluated for Brij 30, Span 20, and POESH using the chicken DT40 B-lymphocyte cell line and two of its isogenic DNA-repair-deficient mutants.

Results/Lessons Learned. Compared to no-surfactant controls, incubation of the bioreactor-treated soil with all surfactants resulted in modest increases in PAH desorption. All surfactants except the rhamnolipid biosurfactant substantially increased PAH biodegradation in the bioreactor-treated soil relative to the no-surfactant control. POESH had the greatest effect, resulting in removal of 52% of total measured PAH. Brij 30, Span 20, and POESH were particularly effective at enhancing biodegradation of four- and five-ring PAH, with removals up to 80%. Significant dose-dependent effects were observed for both Brij 30 and POESH. All treatments except POESH at the optimum dose for PAH removal significantly increased soil cytotoxicity. Only the no-surfactant control and Brij 30 at the optimum dose significantly decreased soil genotoxicity as evaluated with either mutant cell line. Treatment with POESH at the optimum dose resulted in a slight increase in soil genotoxicity as evaluated with one of the two cell lines. Future work will include the setup of a two-stage process to treat effluent from the first bioreactor in a second laboratory-scale bioreactor amended with POESH and to evaluate its performance. We will also evaluate the effect of POESH treatment on soil cytotoxicity and genotoxicity as a function of treatment time.

A Natural Approach to the Remediation of a Recalcitrant BTEX Plume

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Background/Objectives. A recalcitrant soil and groundwater benzene, toluene, ethylbenzene, and xylenes **(**BTEX) plume associated with two leaking historic gasoline underground storage tanks (USTs) was preventing future redevelopment and use of a one acre Site at John F. Kennedy International Airport (JFK). The gasoline USTs were excavated in 1993. In 2009, following the excavation of the gasoline USTs, analytical soil results revealed a saturated gasoline smear zone. The one acre shallow smear zone, located approximately five feet below grade surface (bgs) was apparently preserved by an overlying asphalt cover.

A focused remedial design investigation (RDI) and soil vapor extraction (SVE)/Bioventing pilot test was completed at the Site in 2009. The RDI and pilot test identified a disconnected and irregularly shaped source zone that appeared to be associated with preferential pathways potentially associated with unknown utilities. The RDI also identified anaerobic groundwater conditions with attenuation rates limited by electron acceptor (sulfate) availability.

The objective of the remedial plan for the subject Site was to efficiently remediate and return the Site back to an operational status within a 2 year timeframe. The Port Authority of New York and New Jersey (PANYNJ) requested, application of a sustainable remedial technology, as feasible.

Approach/Activities. Bioventing/Enhanced Anaerobic Biodegradation (EAB) was selected as a sustainable remedial approach that could be designed, implemented, and operated to meet the aggressive, and strict remedial timeframe. Biogas/soil vapor analysis was selected as the most viable tool to delineate the irregularly shaped source zone. Following one year of bioventing, sulfate concentrations in the groundwater increased, which indicated reduced electron acceptor demand. Additionally, soil samples were collected from the smear zone, and analytical results showed a reduction of 90% or greater in BTEX concentrations. Following the dismantling of the bioventing system, the manifolded wells were converted to an injection network, and groundwater was amended with sulfate ($MgSO4$) to accelerate the rate of anaerobic biodegradation of BTEX in the soils and groundwater.

Results/Lessons Learned. Successful design/operation of the Bioventing/EAB system indicated the following:

- Pilot test and soil vapor analysis of biogas concentrations can effectively delineate irregularly shaped, and disconnected source zones;
- Variable electron acceptor demand is a valuable tool to evaluate and identify source zone remedial end points; and
- Bioventing/EAB applications are cost effective and energy efficient remedial technologies which can be readily utilized on accelerated remedial projects.

It is anticipated that the Site will achieve a No Further Action (NFA) status from the New York State Department of Environmental Conservation (NYSDEC) in less than two years from the start of implementation of the remedial action. Accordingly, the site will be available for airport operations in the spring of 2015.

Back to Contents

Substrate Delivery Strategies and Lessons Learned for In Situ Biostimulation/Bioaugmentation Treatment of a Large Chlorinated Ethenes Groundwater Plume

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Background/Objectives. Groundwater at Site 24 of former Naval Station Treasure Island, located in the San Francisco Bay, has been affected by discharges of PCE during operation of a former dry cleaning facility. A large chlorinated ethenes (CE) plume over 1,200 feet in length and 10 acres in areal extent was formed in site groundwater as a result. PCE was detected at a concentration as high as 49,000 µg/L, and the highest total CE concentration was 64,000 µg/L. In Situ Biostimulation and Bioaugmentation (ISB) was studied with various substrates and distribution methods to study the feasibility of ISB on both high and low concentrations of CEs at Site 24. Several phases of a treatability study were completed to address the following study questions: 1) Is ISB effective in reducing CE concentration to below remedial goals and 2) Is ISB effective in reducing persistent low concentrations of CEs in groundwater.

Approach/Activities. Four ISB treatability studies (TS) were conducted at Site 24 over a ten year period. Initially, a pilot study was conducted in 2003 at the presumed source area that successfully demonstrated the ISB process for complete degradation of the CEs in a high concentration area. The second TS demonstrated successful treatment over the extended, lower concentration, dissolved phase plume. Both of these studies were conducted using recirculation systems to distribute the ISB substrates with networks of extraction and injection wells, and using direct injection of substrate to create a biobarrier to limit the migration of the CE plume. PCE concentrations in vicinity of one of the extraction wells were reduced to below detectable concentrations during the second TS but rebounded to greater than 30,000 µg/L afterwards.

Consequently, a targeted investigation using membrane interface probe and FLUTE™ technologies was conducted to evaluate the potential presence of dense non-aqueous phase liquids (DNAPL) in vicinity of the well. DNAPL was not confirmed, however the investigation revealed a separate source area of CEs with very high concentrations. In 2009 and 2012, the TS was expanded to determine if ISB was effective in treating persistent low level concentrations near and down-gradient of the source area. The substrates tested include sodium lactate, hydrogen gas, lactic acid, lactic acid with supplements, and emulsified vegetable oil. The distribution strategies tested include recirculation and direct injection. Additionally, the effectiveness of bioaugmenting with a dechlorinating microbial consortium (SDC-9™) was also evaluated.

Results/Lessons Learned. More than 200 monitoring, treatment (injection and extraction), and small diameter investigation wells have been installed at the site. As of March 2014, only one well has PCE and trichloroethene concentrations above trace concentrations. Vinyl chloride and cis-1,2-dichloroethene concentrations were also reduced, but remain above the remedial goals in a few localized areas. Lessons learned include the value of detailed source area characterization, the value of proactive operation with real-time modifications, the advantages and disadvantages of the various substrates and distribution techniques, and the practicality of achieving low remedial goals across a large dilute plume within a short timeframe.

Enhanced In Situ Bioremediation to Treat Groundwater Impacted with Chlorinated Solvents

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Background/Objectives. A Confidential Site consisting of three buildings and a paved area in Jersey City, NJ is being remediated for chlorinated solvent contamination in the subsurface. Several rounds of subsurface investigations were conducted under the Industrial Site Recovery Act, which was triggered due to a business transaction. Concentrations of tetrachloroethene (PCE) and its degradation products (trichloroethene [TCE], cis-1,2 dichloroethene [DCE], trans-1,2 DCE, and vinyl chloride [VC]) exceeded Groundwater Quality Standards (GWQS). The historic soil sample results and MIP investigation didn't indicate presence of these compounds in unsaturated soils.

The source of the contamination has not been identified, but two hotspot areas have been identified based on groundwater sample results. These areas were around a loading dock and a 1,100 gallon heating oil underground storage tank (UST). The groundwater elevations at the site are very flat and presence of degradation products in groundwater indicate that PCE and TCE are most likely degrading by sequential anaerobic reduction. Enhanced In-Situ Bioremediation (EISBR) is being implemented at the Site as an Interim Remedial Measure (IRM) to address groundwater impacts as approved by the New Jersey Department of Environmental Protection (NJDEP).

Approach/Activities. SRS-SD Emulsified Vegetable Oil® (EVO) and TSI-DC Dehalococcoides Ethenogenes Bioaugmentation Culture® were injected during the first round of pilot study in January 2012 through a network of 60 temporary injection points. Injections targeted an interval between 10 and 30 feet below ground surface. 60% EVO was applied at 10:1 water:EVO ratio and was followed by chase water to provide distribution. A total of 9 liters of bioaugmentation culture was used in the first round. Injection was carried out using a track mount Geoprobe® and five feet top down injection tools. The average injection pressure was 25 pounds per square inches (psi) while sustaining an average flowrate of five gallons per minute (GPM). The performance monitoring events consisted of a baseline sampling event and seven post-injection performance sampling events at 10 monitoring wells.

Results/Lessons Learned. The post injection monitoring indicated that concentrations of CVOCs in the hotspot areas decreased significantly, but there was cis-1,2 DCE stall and slight rebound. It also indicated that the EISBR was very effective to reduce CVOC concentrations in the plume except in one area where PCE and TCE concentrations reduced dramatically, but the degradation product (cis-1,2 DCE and VC) concentrations increased. Elevated CVOC concentrations were not detected in any of the two cross gradient wells as well as one downgradient well. One downgradient well had slight CVOC exceedance during the baseline sampling, but they have not been detected during any of the post-injection sampling events. Second round of EISBR injection was performed in May 2014 to address localized CVOC concentrations exceeding the GWQS in two areas upon conclusion of the first round of pilot study and post-injection evaluation. EVO and bioaugmentation was injected using 36 temporary injection points during this round. Post-injection monitoring is in progress and is anticipated to be significantly complete before the Battelle Conference 2015.

Impacts of Iron (II) Sulfide Precipitation on the Permeability of Porous Media

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Background/Objectives. Anaerobic bioremediation typically relies on electron donor amendment to stimulate dechlorinating bacteria within a contaminated aquifer. However, this biostimulation also provides electron donors to native, non-target microorganisms, including nitrate-, sulfate-, and metal-reducers, as well as methanogens. In addition to potentially outcompeting dechlorinators for available electron donors, non-target microorganisms may have major impacts on the geochemistry and hydrology of the system. For example, iron-reducing bacteria (IRB) reduce abundant, insoluble ferric iron (Fe3+) compounds present in soil to form reactive, soluble ferrous iron (Fe2+); when sulfate-reducing bacteria (SRB) are active in the same system, the resulting hydrogen sulfide (HS-) reacts with Fe2+ to form iron sulfides (FeS). FeS readily precipitates as colloids which bind strongly to soil organic matter. This precipitation and biological growth may be severe enough to reduce aquifer permeability, altering groundwater flow. Though previous studies have presented evidence of such permeability loss, the extent to which precipitation and biological growth impact permeability is unclear.

Approach/Activities. A series of laboratory scale column and aquifer cell experiments was completed to assess the impacts of FeS precipitation on the permeability of porous media with varying total organic carbon (TOC) contents, under abiotic and biotic conditions. Column experiments (15 cm *l* × 4.8 cm ID) were packed with Federal Fine Ottawa sand (< 0.01% TOC), Appling soil (0.66% TOC), Webster soil (1.96% TOC), or Groveland (MA) Wells Superfund site field soil (0.01% TOC). Aquifer cell experiments (63.5 cm *l* × 1.4 cm *w* × 38 cm *h*) were packed with Federal Fine sand, and contained an Appling lens (17.5 cm *l* × 3.7 cm *h*) to evaluate the impacts of FeS precipitation in a heterogeneous system with a zone of low permeability and moderate TOC. In abiotic experiments, a solution containing 2.2 – 4.4 mM (70 – 140 mg/L) sulfide was introduced to each column or aquifer cell to induce iron reduction and precipitation of FeS. Biotic experiments were wet-packed in an anoxic glove box with a culture containing IRB and SRB to ensure even microbial distribution. A solution of 2 mM L-cysteine, 5 mM lactate, 5 mM acetate, and 10 mM sulfate was then flushed through each column or aquifer cell until experiment termination. In column experiments, permeability loss was calculated using data obtained from pressure sensors attached to column influent and effluent, or by monitoring changes in flow rate given a constant head differential. In aquifer cell experiments, permeability losses were determined by monitoring hydraulic head, and dye tracers were used to visualize flow paths. Finally, in all experiments, bromide tracer tests were used to determine system porosity before and after FeS precipitation.

Results/Lessons Learned. All experiments resulted in permeability or porosity reduction, and in most cases resulted in both. In abiotic experiments, permeability and porosity losses ranged from 0 – 73% and 1.2 – 7.2%, respectively, with the greatest losses occurring in columns packed with Appling or Webster soil. FeS precipitation in the abiotic aquifer cell caused local reductions in permeability, which led to alterations in flow paths. Analysis of data from the biotic experiments is ongoing. Results will help to improve understanding of the long-term effects of bioremediation, helping practitioners to avoid potential negative effects, such as hydraulic isolation of contaminated zones due to local permeability losses, or to take advantage of potential positive effects, such as increased contaminant residence time and more complete dechlorination.

Optimizing Bioremediation at Mixed Contaminant Sites: Lessons Learned in the Laboratory and in the Field

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Background/Objectives. Bioremediation is increasingly evaluated and applied at sites where contaminant mixtures present challenges to achieving remediation success. A growing body of knowledge from both laboratory treatability testing and field applications provides insights into opportunities for successful bioremediation at these sites. In many cases, bench-scale treatability testing has proven invaluable in identifying the conditions compatible with bioremediation success or alternatively where bioremediation is unlikely to succeed.

Approach/Activities. Bench-scale testing results from numerous treatability studies and field bioaugmentation applications conducted over the past decade were evaluated to identify the conditions associated with successful outcomes as well those conditions that negatively affected the outcomes. An example of successful application of bioremediation at a mixed contaminant site is provided by an industrial site in Kansas where enhanced bioremediation, including biostimulation and multiple rounds of bioaugmentation, was performed for over a decade to treat a contaminant mixture that included: trichloroethene (TCE), 1,1,1-trichlorethane (1,1,1-TCA) dichloromethane (DCM), 1,1-dichlorethane (1,1-DCA) and 1,1-dichloroethene (1,1-DCE). Total chlorinated VOC concentrations exceeded 200 milligrams per liter (mg/L) in some locations and a key challenge at the site was overcoming the inhibitory aspects of 1,1,1-TCA, DCM and TCE.

Results/Lessons Learned. The treatability study/site survey indicated that 1,1,1-TCA, chloroform, chlorofluorocarbons (CFCs) and hexavalent chromium were significantly inhibitory to reductive dechlorination of chlorinated ethenes and required specialized bioaugmentation cultures and/or remediation approaches. While successful remediation is often possible at mixed contaminant sites they often exhibit reduced biodegradation rates compared to sites with less complex contaminant profiles.

At the Kansas site, pilot-scale bioaugmentation with a TCE degrading culture followed by a 1,1,1-TCA dechlorinating culture was initially performed in 2005 to evaluate the potential for reduction of chlorinated ethenes and 1,1,1-TCA inhibition. Based on the successful pilot test, full scale remediation consisting of organic substrate injections followed by bioaugmentation with a TCE/1,1,1-TCA dechlorinating culture (KB-1® Plus) was performed. Another area at the Kansas site had high concentrations of DCM and demonstrated a complete lack of dechlorination, suggesting toxic inhibition. A treatability study for this site area confirmed that bioremediation of site groundwater containing over 160 mg/L DCM, was not feasible using available bioaugmentation cultures necessitating excavation of 500 tons of DCM contaminated soil. In the meantime, bioaugmentation cultures have been developed capable of DCM biodegradation concentrations exceeding 100 mg/L which may have reduced the extent of excavation required. Progress at the site to-date indicates that a 90% reduction in VOC concentrations in the downgradient plume was possible in as little as 1 year but required up to 7 years in higher concentration source areas.

Biofilm Covered Activated Carbon Particles Enhance Bioremediation of Polychlorinated Biphenyl (PCBs) in Sediment

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Background/Objectives. Removal of polychlorinated biphenyls (PCBs) from contaminated aquatic sediments is a priority because of their ability to enter the food chain and their toxic and carcinogenic properties. The most commonly adopÂted remedies include dredging and capping which are associated with several challenges including disruption of existing habitat and high cost. While *in situ* microbial degradation of PCBs would represent a sigÂnificant improvement in remediation efforts, previous attempts have failed because of PCB stability, low bioavailability, and the low abundance and activity of naturally occurring PCB-degrading microorganisms. The high efficiency of AC and other porous substrates to quickly adsorb and sequester PCBs from sediÂments has been demonstrated. Co-localizing PCB-degrading microbes onto the surfaces of the sorpÂtive particles in the form of biofilms and utilizing them as a microbial inoculum delivery system proÂviÂdes a novel approach to address PCB contamination. In this study, biofilm covered GAC particles were applied for enhancement of PCB dechlorination in sediments.

Approach/Activities. The approach was to employ a novel delivery system utilizing porous materials as attachment and growth surÂfaces for biofilm formation by PCB-degrading bacteria. The system benefits from bacteria being able to be grown to a high density at the surface of sequestering adsorbent. Biofilms of anaerobic *Dehalobium chlorocoercia* DF1, enrichments from wastewater and aerobic *Burkholderia xenovorans* strain LB400 were formed. Mature biofilms were inoculated into PCB contaminated sediment mesocosms. PCB concentrations and individual congener concentrations were determined by GC. Molecular techniques included: DNA extraction, q- PCR with specific 16S rDNA primers, identification by DHPLC and sequencing and microscopic analyses included: DAPI, PNA-FISH, SEM and CLSM.

Results/Lessons Learned. Biofilm formation of DF1, LB400 and enrichments was observed via multiple staining and microscopic techniques. When the biofilms were inoculated into sediment mesocosms, the numbers increased 2-fold and PCB degradation was enhanced (1.5 chlorines/biphenyl for biofilms (31%) vs. 0.3 chlorines/biphenyl for planktonic inoculum (6%) over 200 days. The diversity of the bacterial populations, with up to eight indigenous species of organohalide respiring bacteria in addition to DF-1, was not affected thus not causing the difference in dechlorination. The application of biofilm covered GAC particles enhanced the PCB degradation in the mesocosms. This was likely due to PCB adsorption onto the GAC ensuring direct contact between the PCB degrading biofilms and the adsorbed PCBs. The factors involved in this mechanism are currently being evaluated. This two-phased approach will provide an efficient and cost-effective method for delivering microorganisms for bioaugmentation of PCB contaminated sites thus enabling complete onsite bioremediation.

Biostimulation and Bioaugmentation of 700 Injection Wells to Remediate a 20-acre Chlorinated Solvent Plume

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Background/Objectives. The Grants Chlorinated Solvents Plume (GCSP) Superfund Site in Grants, New Mexico is in a mixed commercial and residential neighborhood, and includes an area of contaminated groundwater containing chlorinated volatile organic compounds (CVOCs) at concentrations four orders of magnitude higher than the remedial goals and average sulfate concentrations of nearly 2,000 milligrams per liter (mg/L). The 2,500-feet long, 100-feet deep CVOC groundwater plume is associated with historical dry cleaning operations. The remedy combines in situ thermal treatment (ISTT) for the source area and enhanced reductive dechlorination (ERD) for the downgradient plume. The ISTT system was installed in the source area, operated, and decommissioned between July 2011 and October 2012. It removed nearly 1,000 pounds of PCE from the low permeability silty and clay layers in the target treatment zone (TTZ).

Approach/Activities. The downgradient ERD system includes nearly 700 nested injection wells with 7- to 20-foot long screens installed in eight transects (biobarriers). Near the source area, the target treatment interval extends from 5 to 95 feet below ground surface (bgs); it is shallower with distance from the source. Up to 300,000 pounds of emulsified vegetable oil (EVO) in 700,000 gallons of water are injected into the biobarriers every 18 to 24 months to sustain the reducing conditions that facilitate the ERD process. Because the injection wells are primarily located in the public right-of-way or on private property, two trailer-mounted injection systems pulled by pickup trucks coupled with appropriate traffic controls are used to deliver the EVO to the subsurface. Potable blending water is obtained from nearby fire hydrants. In addition, as part of the second comprehensive biostimulation in spring 2014, approximately 250 liters (L) of a commercial bioaugmentation culture was injected into 90 percent of the injection wells to accelerate the treatment process. Finally, the ERD system also includes a comprehensive groundwater and biogas monitoring program to assess performance of the remedy. More than 100 monitoring wells and 50 vapor monitoring points are sampled quarterly too annually to assess geochemistry, CVOC concentrations changes, and the timing of subsequent EVO re-injections.

Results/Lessons Learned. Groundwater sampling results about seven years after the initial EVO injections (pilot study) and four years after the start of the full-scale implementation show significant reductions in PCE concentrations (from 20 mg/L to below laboratory detection limits) with the appearance and subsequent reduction of daughter products. Nearly 80 percent of the PCE and TCE mass and 40 percent of the 200 kilograms of the total VOC mass have been removed since ERD system start-up; the footprint of the plume has reduced commensurate with the mass reduction. Finally, the results from the biogas monitoring program indicate that methane is attenuated in the 5-foot thick vadose zone, thereby mitigating vapor intrusion risk. The presentation will review implementation costs, long-term groundwater and biogas data, injection performance, lessons learned from seven years of ERD implementation including a comparison of multiple commercially-available substrates that were concurrently evaluated during full-scale implementation, and provide a summary of the activities planned for 2015 that will further optimize the ERD system and further reduce the time to achieve remedial goals.

Aerobic Bioaugmentation of RDX Contaminated Groundwater

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Background/Objectives. Groundwater at the Umatilla Chemical Depot (UMCD) in Hermiston, OR is contaminated with hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) between 2 and 300 µg L^{-1}. Although anaerobic biostimulation has been successfully demonstrated *in situ* at the site, maintaining the anaerobic conditions across the large aerobic plume at UMCD is costly and technically challenging. We have been investigating the feasibility of bioaugmentation with aerobic explosive-degrading bacteria to remediate the RDX-contaminated aquifer. A mixed culture that was composed of three aerobic RDX-degrading bacterial strains remained viable and able to degrade RDX for at least six months following inoculation into UMCD sediment columns. A field transport test held in 2013, effectively demonstrated the transport of the culture within the UMCD subsurface. The objective of this phase of the project was to evaluate the longevity and *in situ* RDX biodegradation activity of *Gordonia* sp. KTR9 following bioaugmentation of UMCD groundwater. In addition, we compared the bioaugmentation and biostimulation approaches for treatment of RDX-contaminated groundwater.

Approach/Activities. In the Biostimulation Test Plot, wells received low concentration fructose amendments for two months in order to create conditions that favored aerobic biostimulation. At the end of this aerobic phase, higher fructose concentrations were used to create anaerobic conditions in the plot. RDX degradation rates were measured at the end of each phase by performing push-pull tests in the wells. In the Bioaugmentation Test Plot, *Gordonia* sp. KTR9 was injected into three test wells under natural gradient conditions along with periodic low concentration fructose amendments in order to stimulate the growth and activity of KTR9. Rates of RDX degradation in the three wells were measured immediately after inoculation and after two and four months post inoculation. Groundwater samples were periodically monitored for viable KTR9 cell numbers, and quantitative PCR analysis of the 16S rRNA, and *xplA* genes.

Results/Lessons Learned. The KTR9 inoculum colonized the subsurface surrounding the three bioaugmentation wells at significant levels ($> 10^5$ cells ml^{-1} or *xplA* gene copies ml^{-1}) for several weeks. Viable cells and *xplA* copy numbers declined following each fructose amendment, most likely due to dilution from the amendment volumes. Initially, cell inoculation stimulated RDX transformation, but as KTR9 numbers decreased so did the transformation rate. Within the biostimulation plot, RDX transformation was stimulated by fructose amendment in the biostimulation plot with preliminary evidence in favor of the nitro group reduction route. We have demonstrated that bioaugmentation with aerobic RDX-degrading bacteria has the potential to be a feasible option for groundwater remediation of dilute RDX plumes.

Comparison of Enhanced Anaerobic Bioremediation (EAB) to EAB Combined with In Situ Chemical Reduction at Concord NWS

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Background/Objectives. A trichloroethene (TCE) plume at the Concord Naval Weapons Station (Concord NWS) extends over 700 feet down gradient from the source area and up to 100 feet below ground surface. The impacted aquifer consists of unconsolidated silt, sands and clays with highly aerobic groundwater. An Enhanced Anaerobic Bioremediation (EAB) pilot test conducted by CB&I demonstrated complete degradation of the TCE concentrations from approximately 5,000 micrograms per liter (µg/L) to less than 1 µg/L within approximately 400 days.

Approach/Activities. The Navy wanted to evaluate a more aggressive approach for achieving site cleanup. CB&I conducted a second pilot test to evaluate enhancement of the biological approach with In Situ Chemical Reduction (ISCR). This process was selected to expedite treatment of TCE, to reduce the potential for generation of toxic degradation products, and to provide long lasting substrates to lessen the potential for rebound of the contaminants.

The ISCR process applied used zero valent iron (ZVI) to degrade TCE by abiotic processes while minimizing the generation of toxic degradation products. The test incorporated biological degradation processes by augmenting the ZVI with long lasting organic substrates (Emulsified Lecithin Substrate®; ELS [PeroxyChem]). Lactate was added to the amendment water to create reducing conditions prior to injection and to help establish the bioaugmentation culture in the aerobic aquifer. Bioaugmentation was conducted using SDC-9™ (CB&I Federal Services LLC), a dechlorinating microbial culture.

The substrates were distributed using direct push technology implemented by Vironex. At each injection interval, the aquifer was initially fractured by injecting the organic substrate solution (ELS, bioaugmentation culture, and conditioned groundwater). After fracture development, ZVI suspended in guar was injected into the interval followed by the remaining organic substrate solution. The EAB and combined EAB/ISCR pilot test data were compared to evaluate effectiveness of each process.

Results/Lessons Learned. The substrates were observed as far as 15 feet from the injection points. The combined EAB/ISCR process also degraded TCE, dichloroethene (DCE) and vinyl chloride (VC) to below Maximum Contaminant Levels (MCLs) within 220 days; about half the time required for the EAB only approach. TCE degradation appears to be biologically mediated in both approaches. The reduced treatment time in the ISCR approach is attributed to β-elimination of DCE compared to the hydrogenolysis pathway in the EAB approach. Notably, the EAB/ISCR process did not generate arsenic in excess of the MCL as did the EAB process.

Back to Contents

Performance Evaluation of a Source Area Remedial Approach Utilizing Multiple Degradation Pathways to Remediate Commingled 1,1,1-TCA and TCE

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Background/Objectives. An in-situ groundwater remediation program was implemented at a former industrial site in the northeast United States to remediate chlorinated volatile organic compounds (CVOCs) in groundwater, primarily 1,1,1- trichloroethane (1,1,1,-TCA) (41 to 6,310 µg/L), tetrachloroethene (PCE) (9 to 330 µg/L), trichloroethene (TCE) (1 to 50 µg/L), and 1,1-dichloroethene (1,1-DCE) (2 to 420 µg/L). The target treatment area is approximately 4,200 square feet and consists of fine to medium sands with a target treatment thickness of 6 to 31 feet below ground surface. Remediation objectives include the reduction of levels of CVOCs in groundwater by 90% from the pre-remedial high concentrations, limiting the production and off-site migration of vinyl chloride and other daughter products and maintaining concentrations without rebound for a six month period after achieving the project criteria.

Approach/Activities. The proposed groundwater cleanup approach was to use a combination of fast and slow release carbon sources with zero valent iron (ZVI)-enhanced bioremediation via enhanced reductive dechlorination (ERD) with bioaugmentation. This approach was selected to harness multiple CVOC reaction pathways to improve performance and accelerate the overall treatment processes. ZVI and carbon substrate solutions were added to the subsurface through a grid composed of direct-push injection points. Spacing of injection points was approximately 10 feet, based on subsurface stratigraphy. Injections consisted of a combination of amendments including buffered lactate, emulsified vegetable oil, and ZVI into 85 direct-push injection points. Once substrate and ZVI injections were completed and reducing conditions were achieved, bioaugmentation was performed through the use of direct-push injection points. As a secondary measure, an aerobic barrier zone was established near the downgradient property boundary to further reduce vinyl chloride and mobilized metals, if needed.

Results/Lessons Learned. The in-situ groundwater remediation activities occurred in November and December 2012. The volume of all injectates totaled 43,650 gallons. An evaluation of approximately 27 months of performance monitoring and operational data will be presented. Observations include the following: good distribution of amendments and establishment of reducing conditions throughout the injection zone; significant reduction of CVOCs within the treatment volume; no production and no off-site migration of vinyl chloride; and effective establishment of oxidizing, co-metabolic conditions in the vicinity of the down-gradient aeration barrier. CVOC and geochemical temporal trends within and downgradient of the source area will also be discussed. A comparison of the reduction kinetics of chlorinated ethenes versus ethanes will also be presented.

Passive Bioremediation of Co-mingled Perchlorate, RDX, and HMX at an Active Military Range

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Background/Objectives. Perchlorate, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are common and often co-mingled contaminants in soils and groundwater at military ranges worldwide. These contaminants are mobile and persistent in groundwater under aerobic conditions. Although multiple studies have demonstrated *in situ* RDX and perchlorate biodegradation under anaerobic conditions individually, remediation of co-mingled plumes has not been reported. Most groundwater along the east coast of the United States is acidic, which can inhibit biodegradation of many contaminants, including perchlorate and explosives, so aquifer pH must be adjusted to promote robust biodegradation.

Approach/Activities. This project was undertaken to investigate the feasibility of using a passive emulsified oil biobarrier to remediate co-mingled perchlorate, RDX, and HMX at an active military testing range in a low pH aquifer. The approach selected was designed to minimize impacts to routine range activities. Laboratory column experiments constructed using site sediment and groundwater were performed to select the appropriate amendments and derive parameters required for biobarrier design. A pilot scale biobarrier was emplaced in early 2013, and dissolved perchlorate, explosives, and other relevant groundwater parameters have been monitored on a regular basis.

Results/Lessons Learned. Initial laboratory-scale columns packed with subsurface sediment from the contaminated DoD range evidenced reductions of effluent perchlorate and RDX concentrations were reduced by greater than 95%, and reductions in HMX concentrations by 50 to >80%.

The laboratory experiments supported design of a field-scale trial using a passive 100’ biobarrier composed of a buffered emulsified oil. The pH increased and the DO and ORP decreased rapidly after installation, leading to >90% reductions in perchlorate, RDX, and HMX compared to upgradient groundwater. Some nitroso breakdown products were observed immediately downstream of the barrier, but generally decreased to below detection limits farther downgradient. Dissolved metals (including As) were also increased in the wells adjacent to the barrier, but attenuated as the plume re-aerated in the downgradient areas of the test plot.
The project has resulted in no impacts to ongoing range activities. The field trial suggests that an emulsified oil biobarrier with pH buffering can be a viable alternative to remove perchlorate and explosives from shallow groundwater at this and other range sites.

Impact of In Situ Remediation on Groundwater Chemistry at Petroleum Sites in Florida

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Background/Objectives. A variety of in-situ methods are applied in Florida to remediate dissolved hydrocarbons in groundwater. Many of these methods are effective at reducing the concentrations of the original contaminants of concern to below groundwater cleanup target levels (GCTL). However, the application of in-situ remediation tends to increase concentrations of inorganic parameters, especially iron. Elevated iron concentrations can linger for years, requiring the extension of monitoring activities long after the original contaminants of concern have been reduced to below the GCTL. As iron is a common additive for in-situ remediation and also naturally occurring, it is essential to distinguish between elevated concentrations caused by introduced iron and concentrations increased by geochemical reactions or mobilization of precipitated material.

The Florida Department of Environmental Protection (FDEP) provides electronic copies of most documents concerning sites impacted by petroleum hydrocarbons in the OCULUS system. These documents are part of the public record and available to anyone seeking information on a specific site or data on a number of sites.

Approach/Activities. Research on OCULUS identified 43 sites throughout the state of Florida that met the following criteria: 1) impacted by dissolved petroleum compounds at high enough concentrations to require active remediation, 2) a minimum of one in-situ remediation event, and 3) a minimum of one well sampled for total iron a minimum of three times. Data tabulated from these sites included concentrations of iron, manganese, and total dissolved solids (TDS) and field readings of pH and dissolved oxygen (DO).

The author employed statistical analysis to establish median baseline concentrations of naturally-occurring parameters at petroleum-impacted sites in Florida. Statistics were also employed to determine the degree of changes in geochemistry following in-situ remediation events, correlations between different parameters, and length of time inorganic concentrations remained elevated. The results were compared and contrasted based on whether or not iron was introduced during the remediation event.

Results/Lessons Learned. Remediation by injection causes increases in iron concentrations whether iron is included in the injected solution or not. If there is no iron added the concentrations typically return to baseline in approximately one year whereas if iron is added concentrations can remain elevated for more than six years. Some in-situ remediation methods decrease the groundwater pH, which results in increasing the solubility of precipitated iron in the aquifer and increases the iron concentration in groundwater. In addition, increases in manganese and TDS concentrations correlate strongly with iron increases following in-situ remediation events, indicating that a portion of the observed iron exceedance is likely the result of injection fluids flushing clay minerals from pore spaces in unconsolidated material.
As background concentrations of iron at petroleum-impacted sites in Florida commonly exceed the GCTL, it is essential to have a well-established baseline prior to the start of in-situ remediation to provide a firm end point for post-remediation monitoring.

Investigating the Effectiveness of Soil Column versus Soil Slurry Respirometry

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Background/Objectives. Respirometry is one of various methods used to evaluate the treatability of contaminated soils in bioremediation studies. Past EBS studies using soil column and soil slurry respirometric methods have shown very different results. It hasn't been clear if this was due to differences in the methods used, or the soils being tested. A study was conducted to compare both techniques using a single soil sample. Some samples were also spiked with bioaugmentation products to determine if their addition improved treatment. The study was expected to show that both methods would generate identical oxygen consumption values given enough time. Bioaugmentation was not predicted to improve treatment, as it has been reported that it is generally not effective in soil bioremediation.

Approach/Activities. The soil sample was intentionally contaminated with a known amount of petroleum distillate before being separated into two different portions. One portion was set up as a positive control, and the other portion was spiked with a bioaugmentation product. An equal mass of prepared soil portions was used in the column and slurry samples. One half of the soil was placed in a column in which air is circulated to ensure any microbial activity remains aerobic. The second half of the soil was combined with deionized water in an appropriate ratio (in this case 16% w/v), and adequately mixed to maintain aerobic conditions. Oxygen uptake was measured during the study using an RSA PF-8000 respirometer. Samples were analyzed for Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), microbial plate counts, and Total Petroleum Hydrocarbons (TPH), before and after the study. The study was run for a period of approximately two weeks, at 22°C, and a mixing rate of 250 rpm.

Results/Lessons Learned. Initially the soil columns showed higher oxygen uptake rates than the slurry. Though the initial uptake rate was lower in the slurry, it showed more consistent rates over time, whereas the rates measured in the columns showed more variation over the course of the study. The bioaugmented samples showed higher initial oxygen uptake rates than the control samples in both the column and slurry samples. At the conclusion of the two week test period, all samples had reached similar total uptake values, except for the bioaugmented slurry sample, which showed a slightly higher cumulative oxygen uptake than all other samples. The results demonstrate similar cumulative oxygen uptake values can be attained using either of the methods tested. The variability of the oxygen uptake rates observed in the soil columns are believed to be more representative of *in situ* consumption rates that would be expected at the site of treatment, as opposed the more stable rates observed in the slurry samples. Large differences were observed in the final BOD & COD results between the slurry and column samples: slurry control and bioaugmented COD/BOD values were 7720/638 mg/L & 7850/595 mg/L respectively, while column control and bioaugmented COD/BOD values were 1254/23 mg/L & 1246/21 mg/L respectively. Plate counts were very similar in both sample types, with slurry sample values of 2.2×10^8 & 2.6×10^8 cfu, and column values of 1.3×10^8 & 1.6×10^8 cfu (the higher values in each method were in the bioaugmented samples). Respirometric analysis of a loose, porous soil like the one tested in this study can produce similar results in both the column and slurry methods. The column method may not deliver favorable results in soils that are more dense and/or non-porous, due to limited oxygen transfer through the soil. Final physical/chemical results appear to be inherently different between the two methods, and must be interpreted with this in mind.

Success of EHC and ABC Substrates to Treat Chlorinated VOCs, 170-Day Bench Scale Study

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Background/Objectives. A bench scale study was conducted to evaluate two potential treatment substrates for in-situ chemical reduction at a former marine terminal. Significant concentrations of chlorinated solvents, PCE, TCE, vinyl chloride, and cis-1,2-DCE, are detected in site soil and groundwater. The two substrates evaluated were EHC (carbon and zero valent iron combination) and ABC+®, Anaerobic Biochem Plus, a patented mixture of lactates, fatty acids and phosphate buffer. The substrate demonstrating the best degradation results will be used in a permeable reactive barrier and/or direct injection at the Site.

Approach/Activities. Seven sets of reactors (93 total) with contaminated soil and groundwater were prepared for the study and consisted of 1) Baseline, 2) Control, 3) Azide, 4) EHC Low Dose, 5) EHC High Dose, 6) ABC Low Dose, and 7) ABC High Dose reactors. All reactors contained contaminated soil and groundwater in addition to the additives. The reactors were prepared for triplicate sampling at 5 time periods: 4, 8, 12, 18, and 24 weeks after setup. EHC was formulated at concentrations by weight at 12 percent (%) in the Low Dose reactors and at 20% in the High Dose reactors. ABC+® was formulated at concentrations by weight of 3.6% in the Low Dose reactors and 11.1% in the High Dose reactors. ABC+® was supplemented with ZVI. The Control and Azide reactors were used to validate results of the EHC and ABC reactors. Soil and groundwater from each reactor were collected and selectively analyzed for volatile organic compounds (VOCs), total extractable petroleum hydrocarbons, *dehalococcoides*, total bacteria, and metals for evaluation. In addition, vapor from EHC Low and High Dose reactors were analyzed for VOCs to predict the potential for off-gassing and the need for vapor engineering controls.

Results/Lessons Learned. The results of the ABC reactors at 12 weeks differed from the results at 24 weeks and lead to a different remedial recommendation. At 12 weeks, the ABC High Dose reactors contained lower concentrations of VOCs compared to the ABC Low Dose, but at 24 weeks the ABC Low Dose contained lower concentrations of VOCs than the High Dose reactors and even lower concentrations than the EHC Low Dose reactors. The Control and Azide reactors along with triplicate results at each time period validate the ABC and EHC reactor results. Therefore, the duration of the study and the number of reactors are significant factors to consider when developing a bench scale study and have not been evaluated in industry or regulatory literature.

Bench scale studies should be conducted for a minimum of 6 months in order to evaluate long-term degradation capabilities of treatment substrates. The minor increase in the cost of the bench scale study outweigh the benefits of conducting studies that better imitate field conditions and result in better selection of treatment alternatives. Both increased study duration and increased number of reactors for triplicate sampling improve study validity and improve appropriate selection of remedial technology and alternatives. Many pilot and full-scale implementation of remedial technologies fail to meet the cleanup objective goals. Therefore, the benefit of long-term bench scale testing is to identify and prevent use of remedial technologies that will not be effective. If a technology fails in a controlled testing environment, it is highly unlikely that the treatment technology will be successful in the field.

There's more than One Way to Bioaugment that Aquifer!

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Background/Objectives. Successful bioaugmentation of groundwater can reduce the acclimation period for complete reductive dechlorination of chlorinated solvents to occur. This can accelerate remedial timeframes and minimize accumulation of undesirable intermediate compounds (e.g., vinyl chloride). Four general criteria need to be met to implement a successful bioaugmentation approach: proper geochemical conditions/redox poise of the aquifer, successful delivery of the culture to the targeted zone, co-located delivery of an electron donor, and application of macro- or micro-nutrients as needed. The objective is to present several bioaugmentation approaches, compare advantages and challenges of each, and provide insight as to where each is most applicable based on site-specific conditions. The case studies presented vary in the bioaugmentation culture used, carbon substrate employed, mixing method, delivery approach, and performance monitoring mechanism. A comparison of these high-level criteria against project-specific criteria will illustrate that there is more than one way to bioaugment an aquifer successfully.

Approach/Activities. The bioaugmentation approaches taken at several different case studies make a useful comparison regarding the effectiveness of the different methods employed. For example, multiple commercially-available bioaugmentation cultures were used and include consortia developed to address chlorinated ethenes and those capable of degrading chlorinated ethanes. Carbon substrates were either soluble (e.g., dilute molasses) or longer-lasting (e.g., emulsified vegetable oil). In some cases pH adjustment was necessary or a chemical reductant was added to consume dissolved oxygen present in the water source. Mixing methods varied from aboveground batch mixing to use of chase water after in-situ injection. Bioaugmentation culture was delivered via permanent injection wells or temporary direct push points. In one case study, a conservative tracer was used to track the delivery of the bioaugmentation culture, while in others more conventional parameters were employed.

Results/Lessons Learned. While each of the approaches was successful based on performance monitoring data, other measures of success differed. For example, in-well delivery of the bioaugmentation culture was easier to implement than aboveground mixing. Likewise, injection of the bioaugmentation culture into existing injection wells was more cost effective than application via direct push locations. When pH adjustment was needed due to the lack of natural buffering capacity of the aquifer, some noteworthy complications in bioaugmentation application arose. Conversely, use of a chemical reductant as part of a carbon substrate mixing program was more effective and easier to implement than originally anticipated. Lessons learned from comparing these case studies do not provide a preferred approach to be applied at every site. However, they do provide insight and an overall thought process to determine what implementation techniques may or may not be effective under a given set of site-specific conditions.

Multiple Carbon Source Types and Distribution Methods for the Reduction of Chlorinated Ethenes

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Background/Objectives. There are many in situ enhanced bioremediation (ISEB) carbon amendments available to promote anaerobic dechlorination and methods of distribution. At the former Kelly Air Force Base (AFB) in San Antonio Texas, the different types of carbon sources and ongoing remediation systems were considered in the design to reach site goals. Two types of carbons sources, two distribution methods (DPT and active recovery systems), and a bioaugmentation culture were used. The decision making process used to choose the correct strategy at each of the sites/injection areas will be presented along with the changes that were made during the remedial phase to accelerate the degradation of the chlorinated ethenes.

Approach/Activities. Many of the ISEB carbon sources available have different molecular and microscopic structures which effect movement through the aquifer and longevity. Although the carbon sources have specific attributes, it is often the site conditions that aid in determining which type of carbon that will ultimately be selected during the remedial approach.

At the former Kelly AFB, in San Antonio Texas, a soluble carbon source, two different droplet size emulsified vegetable oils [EVO], and a bioaugmentation culture, were used to treat chlorinated solvent plumes at the former Kelly AFB. These carbon sources and amendments were chosen based on site conditions including plume size, contaminant concentrations, proximity to a creek, and previously installed active groundwater extraction systems.

Results/Lessons Learned. At the former Kelly AFB, decreases were observed in trichloroethene (TCE) from over 200 micrograms per liter (mg/L) to below the detection limit along with production of each of the daughter products. However in some areas, the expected degradation was not observed and site goals were not being met in the timeframe expected. Based on chlorinated ethene concentrations, geochemistry, and additional hydrology information, additional injections were performed using different distribution methods, carbon types, and amendments, including the addition of ferrous iron to aid in maintaining reducing conditions. The degradation of chlorinated ethenes at each sites will be compared between the different carbon source types and distribution methods, and the results of first and second injections will be presented.

Coupled Reduction/Oxidation Approach to Treat Chlorinated Solvents in an Aquifer Influenced by Regional Irrigation

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Background/Objectives. Reductive dechlorination of chlorinated ethenes, such as tetrachloroethene (PCE), is a widely accepted practice. When taken to completion in a highly reductive environment, the generally benign biological end product is ethene. However, conditions at the former Frank Wear Dry Cleaners site in Yakima, Washington, present a set of challenges to the traditional complete reductive dechlorination approach. The city is serviced by an aging regional irrigation system, and one of the major trunk lines abuts the upgradient property boundary for the length of the PCE plume. While the irrigation system is operating during the spring and summer, groundwater elevations can increase by as much as 15 feet and carry high concentrations of dissolved oxygen and nitrate. Even though the soil matrix is comprised of gravel and cobbles with sand, groundwater gradients still shift by approximately 45 degrees during irrigation system operation. Further complicating the remedy, suspected releases from a former heating oil tank at the site appear to have entrained PCE-laden oil near the top of the smear zone. Before the remedy began, contamination in a single groundwater well could vary between 12 µg/L and 17,000 µg/L of PCE, depending on the groundwater elevation.

Approach/Activities. The overall approach is to simply support mobilization and conversion of PCE to either dichloroethene (DCE) or vinyl chloride (VC), not necessarily to ethene. Continuous groundwater recirculation was selected to control delivery and distribution of amendments through the reactive zone. When system operation discontinues, DCE and VC will exit the reductive zone and migrate into highly oxidized geochemistry to undergo oxidation using molecular oxygen or nitrate. Reducing conditions were initially established using ReducED® AQ, a soluble blend of both simple and complex organics with nutrients. During periods of irrigation operation, ethyl lactate has been intermittently introduced as a co-solvent and electron donor, along with ReleaSE-Dx™ surfactant, to mobilize both residual petroleum organics and PCE. Near the end of seasonal irrigation operation, 4,200 pounds of Newman Zone® non-ionic emulsified vegetable oil was recirculated through the source area treatment cell to support continued dechlorination activity in the smear zone during non-irrigation periods.

Results/Lessons Learned. The groundwater recirculation system has operated for nearly one year. We have only been able to shift the geochemistry to slightly reductive, supporting denitrification and conversion of PCE to DCE and VC but not ethene. The mobilization effort has been extremely successful, increasing PCE concentrations upwards of 68,000 µg/L at the extraction points as organic carbon concentrations remain below 10 mg/L. Higher concentrations of DCE and VC have been unexpectedly detected down-/cross-gradient of the recirculation cell, prompting rebalancing of the injection/extraction rates to accommodate for strong irrigation cross-gradient influence. Additional data will be presented, along with assessing the fate of dechlorination products.

Demonstration of Aerobic Cometabolism to Support Selection of Monitored Natural Attenuation as a Remedy

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Background/Objectives. An evaluation of microbial aerobic cometabolism was completed to support the occurrence of natural attenuation of trichloroethene (TCE) in groundwater at Travis Air Force Base (AFB), California. This evaluation was completed as part of a multiple lines of evidence approach used to select monitored natural attenuation (MNA) as a groundwater remedy in a recently approved Groundwater Record of Decision (ROD) for Travis AFB. Additionally, to expedite treatment and reduce life-cycle costs for the Air Force, and to complement the MNA remedy, technology demonstrations are planned for several Travis AFB groundwater sites. These demonstrations are expected to support microbial aerobic cometabolism.

Approach/Activities. Several different types of bacteria can cometabolize or co-oxidize chlorinated ethenes under aerobic conditions. An investigation was conducted at Travis AFB to 1) determine if cometabolic enzymes are present and active, 2) identify the presence or absence of microbial genes linked to TCE cometabolic enzymes, and 3) identify the presence or absence of bacteria that produce cometabolic enzymes. Quantitative polymerase chain reaction (qPCR) and enzyme activity probe (EAP) sampling were conducted to support this evaluation.

Technology demonstrations are planned for several Travis AFB groundwater sites beginning in late 2014. These demonstrations will involve different methods of dispersing total organic carbon (TOC) substrate through groundwater plume core areas, to support enhanced reductive dechlorination (ERD). Dissolved methane generated during the ERD technology demonstrations, and dissolved propane and butane that could potentially be generated abiotically, are expected to support aerobic cometabolism in the aerobic/anaerobic groundwater transition area.

Results/Lessons Learned. The qPCR data demonstrated the presence of bacteria that produce TCE cometabolic enzymes at Travis AFB groundwater sites, and EAP data demonstrated that the enzymes responsible for aerobic cometabolism are active. The qPCR and EAP results provided evidence of intrinsic aerobic cometabolic degradation of TCE. These data contributed to a multiple lines of evidence approach that supported selection of the MNA remedy. Lessons learned from the sampling and data evaluation will be presented.

ERD technology demonstrations are expected to complement the aerobic cometabolism degradation pathway where MNA has been selected as the remedy. Dissolved methane in particular is expected to be generated in sufficient quantities to support and enhance aerobic cometabolism at the fringes of the TOC treatment areas, and potentially in the technology demonstration plume core areas once the TOC is consumed and aerobic conditions return over time. Results and lessons learned from the initial implementation of the technology demonstrations will be presented.

Engineering Principles of Implementing Aerobic Cometabolic 1,4-Dioxane Biodegradation with Groundwater Recirculation for Dilute Plume Treatment

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Background/Objectives. Treatment of groundwater contaminated with 1,4-dioxane (1,4-D) and chlorinated solvent compounds is required at many cleanup sites. The presence of 1,4-D in a chlorinated solvent plume often forces the selection of a more costly pump-and-treat remedy during the Feasibility Study process. Due to the high costs of ex-situ treatment, viable in-situ treatment technologies for 1,4-D are desired. Although numerous studies on aerobic biodegradation of 1,4-D have been published, most of them have been laboratory studies at high 1,4-D concentrations, not the low 1,4-D levels comingled with other contaminants typically found. Based on extensive research on aerobic cometabolic biodegradation (ACB) of chlorinated ethenes, factors that may affect the performance of ACB include, but are not limited to, the following: substrate competition, product toxicity, and population dynamics of microbial community. To increase the certainty of performing a successful in-situ ACB treatment of 1,4-D and some co-contaminants, the conditions that would result in unstable system performance needs to be recognized.

Approach. To better understand how to achieve stable performance of an in-situ ACB reactor created through groundwater recirculation, chemical fate and transport modeling was used to evaluate the interactions of intrinsic factors, such as growth and reaction kinetic parameters and composition of native microbial consortia (which cannot be changed readily through engineering control) and extrinsic factors, such as substrate loading rate and frequency or bioaugmentation (which can be manipulated through engineering control). A one-dimensional reactive transport model has been developed using relevant growth and microbial reaction kinetic parameters published in the literature. To assess the effects of potential microbial population dynamics on system performance, two or more sets of reaction and microbial growth-decay parameters were used to represent different types of microorganisms in the system. The one-dimensional fate and transport model can be used to evaluate the effectiveness of ACB along one of the streamlines originated from a substrate injection well. The key system operation variables in this modeling study include (1) concentrations of propane (an energy and carbon source to stimulate ACB) and oxygen (electron acceptor) at the injection well, (2) duration and frequency of propane addition, and (3) effects of microbial population dynamics.

Results/Lessons Learn. The simulation results indicate that ACB can degrade 1,4-D and trichloroethene to levels below 1 µg/L. The balance between the propane and oxygen loading rates are important to maintain adequate 1,4-D degradation activity. The presence of bacterial predators, such as protozoa, can result in a sudden termination of 1,4-D degradation in the system. The simulation results were used to develop several engineering principles that are important to design and implement an in-situ ACB treatment process. These engineering principles are expected to help (1) plan initial data collection, (2) conduct a more cost-effective laboratory study, (3) perform a thoughtful pilot test to demonstrate the certainty of ACB to meet site-specific cleanup objectives, (4) facilitate a full-scale ACB system design.

Cometabolic Bioremediation of TCE and 1,4-Dioxane with Methane and Oxygen at Air Force Plant 44

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Background/Objectives. This presentation summarizes the laboratory bench test results and lessons learned from field implementation of a treatability study to evaluate cometabolic bioremediation of TCE and 1,4-dioxane in groundwater at Site DP003 (Site 3), located at Air Force Plant 44 in Tucson, Arizona. Unlined excavated pits at the site were used for disposal of TCE and 1,1,1-trichloroethane (1,1,1-TCA) from 1966 through 1977, resulting in the parts per million (ppm) concentrations of TCE and 1,4-dioxane currently detected in site groundwater.

Approach/Activities. Prior to field implementation, a laboratory bench-scale treatability test performed by SiREM and Tersus Environmental indicated intermittent infusion of methane gas and air into site soil and groundwater microcosms could promote an effective decrease in TCE and 1,4-dioxane concentrations, provided dissolved oxygen levels were kept relatively low and adequate concentrations of micronutrients were added to support the growth of methane oxidizing bacteria and production of monooxygenase enzymes known to destroy TCE and 1,4-dioxane via the cometabolic pathway. Lessons learned from the microcosm studies were used to design the field implementation.

Thirteen boreholes, placed at 50-feet on-center spacing, were installed in a 400 feet by 150 feet area with high 1,4-dioxane (~2 ppm) and TCE (~0.7 ppm) concentrations. The boreholes were drilled to a depth of approximately 145 feet below ground surface (bgs), and fitted with blank casings in the targeted depth interval, from approximately 110 feet bgs to 140 feet bgs. Due to the presence of fine-grained (silty-clayey) aquifer material in the target depth interval, hydraulic fracturing (FRx Inc.) was used to fracture the borehole casings, in order to generate permeable pathways for the distribution of the added gases and nutrients. The fractures were filled with proppant sand to keep the apertures open. Passive gas infusion (iSOC®) units (Tersus Environmental) were installed in each borehole, with conveyance piping to the oxygen and methane cylinders, which were kept in an aboveground enclosure. Prior to routine methane and oxygen gas infusion, methane-infused water and micronutrients were mixed and injected into the fractures.

Results/Lessons Learned. Field implementation activities were completed in early 2015. This presentation will provide the results of bench testing, as well as lessons learned and baseline and post-implementation groundwater monitoring results following field implementation of the technology. A “first-impression” evaluation of the effectiveness of cometabolic bioremediation - using methane and oxygen gas infusion – on 1,4-dioxane and TCE concentrations also will be presented.

Cometabolism of Vinyl Chloride in an Aquifer Co-contaminated with Benzene

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Background/Objectives. The Voda Petroleum Inc. State Superfund Site operated as a waste oil recycling facility from October 1981 to November 1991, receiving, storing, and reprocessing waste gasoline, oily wastes, used oil, and wastes from crude oil and tank bottom reclamation activities. In the reprocessing and material storage activities areas of the site, impacted soil was observed from the ground surface to the top of the unconfined groundwater-bearing unit (GWBU). Soil and groundwater were impacted by non-chlorinated and chlorinated volatile organic compounds (VOCs) and total petroleum hydrocarbons (TPH). The uppermost GWBU at the site occurs within the Queen City Sand, a minor but important drinking water resource in northeast Texas. This unit is subdivided into a shallow groundwater transmissive zone, a semi-confining layer (leaky aquitard), and a deeper transmissive unit. All three zones contain concentrations of benzene and vinyl chloride that exceed federal and state drinking water standards.

Approach/Activities. Response action for soil and groundwater were performed in 2010, consisting of excavating the impacted source area soil and installing an enhanced in-situ bioremediation (EISB) groundwater treatment system. The EISB system consists of 18 treatment wells that incorporate iSOC® gas diffusion units, which alternates delivering oxygen and ethylene to groundwater to promote biodegradation of benzene and vinyl chloride.

Results/Lessons Learned. Groundwater monitoring wells have been sampled semi-annually since November 2010. In April 2014, groundwater samples were collected from one treatment well and one nearby monitoring well for analysis using the QuantArray® molecular biological tool. Groundwater in both wells had less than 1 milligram per litter of dissolved oxygen, indicating nearly complete consumption of the oxygen being supplied by the iSOC® units.
The QuantArray® quantifies key organisms and functional genes responsible for biodegradation of petroleum and chlorinated compounds. The analysis indicated that *Dehalococcoides* sp., *Dehalobacter* sp. and *Dehalogenimonas* sp. were present at low concentrations in each well. These bacteria are capable of reductive dechlorination of chlorinated ethenes and ethanes; however, genes responsible for anaerobic degradation of vinyl chloride were not detected. The QuantArray® results did show that genes responsible for aerobic metabolism or cometabolism of vinyl chloride were present in both wells. Genes encoding soluble methane monooxygenase, particulate methane monooxygenase, and toluene monooxygenase 2 were detected at levels from 9.40E+01 cells per milliliter (cells/mL) to 2.42E+05 cells/mL. These enzymes, which are produced by methanotrophs, are capable of cometabolically degrading vinyl chloride under aerobic conditions. In addition, genes encoding ethene monooxygenase and epoxyalkane transferase were detected. These enzymes are also capable of metabolically degrading vinyl chloride under aerobic conditions. Lastly, genes encoding phenol hydroxylase were detected. This enzyme is involved in the aerobic degradation of benzene.
The QuantArray® findings indicate that genes responsible for the degradation of both vinyl chloride and benzene are present, indicating that the EISB system is maintaining conditions needed to attain the objectives for the groundwater response action.

Kinetics of Aerobic Cometabolism of 1,4-Dioxane by Propane Oxidizing Bacteria

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Background/Objectives. Under aerobic conditions, biodegradation of 1,4-dioxane has been demonstrated by metabolic and cometabolic processes. Biodegradation via metabolic processes is often preferable since it does not require the addition of a primary substrate, the oxygen demand is lower, and the potential for well-fouling due to excessive biomass growth is lower. Nevertheless, several considerations weigh in favor of a cometabolic process, including the potential for higher rates of biodegradation and achieving lower ultimate concentrations. A thorough comparison between metabolic and cometabolic processes requires use of kinetic models that fully describe both processes. For aerobic cometabolism of 1,4-dioxane, the most detailed kinetic information available is for tetrahydrofuran as the primary substrate. This may be relevant for industrial wastewater applications, but not for *in situ* bioremediation. Propane is a more viable primary substrate; it is relatively inexpensive, widely available, and non-toxic. However, the kinetics of 1,4-dioxane cometabolism by propanotrophs is not well characterized. The main objective of this study was to obtain these kinetic coefficients and compare them to Monod parameters for cultures that use 1,4-dioxane as a sole source of carbon and energy.

Approach/Activities. Two propane oxidizing cultures were evaluated: *Rhodococcus ruber* ENV425 and a mixed culture designated ENV487. A systematic approach was employed to evaluate the Monod kinetic coefficients for growth on propane and the cometabolic parameters following growth on propane. The cultures were grown in BSM medium and 20% headspace volume of propane. Kinetic parameters were determined from batch studies.

Results/Lessons Learned. For growth of the ENV425 and ENV487 cultures on propane, the biomass yields are 1.43 and 1.55 mg protein/mg of propane, respectively. The maximum specific growth rates are 0.88 and 0.89 d^{-1}, the half saturation coefficients are 4.8 and 3.4 mg/L, the maximum substrate utilization rates are 0.61 and 0.58 d^{-1}, the endogenous decay coefficients are 0.11 and 0.21 d^{-1}, and the oxygen half saturation coefficients are approximately 2.4 and 1.6 mg/L. For resting cells of ENV425 and ENV487, the transformation capacities are 0.54 and 0.38 mg 1,4-dioxane/mg protein and the transformation yields are 0.77 and 0.59 mg 1,4-dioxane/mg propane, respectively. The maximum specific rates of 1,4-dioxane cometabolic biodegradation are 0.34 and 0.31 d^{-1} and the half saturation coefficients are 2.4 and 2.7 mg/L. Experiments are in progress to measure self-inhibition and the co-inhibition coefficients for 1,4-dioxane. A preliminary comparison between metabolic and cometabolic processes was made based on first order rate coefficients, calculated from the maximum specific utilization rates and half saturation coefficients. For resting cells of ENV425 and ENV487, the first order coefficients are 0.14 and 0.11 L/mg protein·d. For CB 1190, one of the best characterized microbes that grows on 1,4-dioxane, the first order rate coefficient is 0.16 L/mg protein·d. A more extensive comparison will be possible once all of the cometabolic parameters have been measured.

Successful Field Demonstrations of In Situ Remediation of Three Key Emerging Contaminants Using Co-metabolism

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Background/Objectives. The addition of alkanes, including propane, methane, and butane has been used in the past to treat contaminants, including chlorinated solvents and fuel oxygenates. The main challenges with these earlier applications were competitive inhibition between the alkane and target substrates, the inability of specialized organisms to compete with native organisms, and the production of toxic metabolites (e.g., TCE epoxide) that can poison the process. Recent laboratory and field studies have shown that *in situ* bioremediation of key emerging contaminants such as 1,4-Dioxane, N-nitrosodimethylamine (NDMA), and 1,2-Dibromoethane (EDB) can be successfully applied, and many of the issues encountered with previous co-metabolic approaches for treatment of chlorinated solvents are not apparent.

Approach/Activities. Initial studies conducted in our laboratory revealed that a number of bacteria, including *Rhodococcus ruber* ENV425, were capable of co-metabolizing 1,4-Dioxane, NDMA, and EDB after growth on alkane gases. Based on promising laboratory results, a pilot-scale *in situ* biosparging system was designed and installed at the Aerojet site in Rancho Cordova, CA to deliver propane gas and oxygen to the subsurface in order to stimulate native propanotrophs to biodegrade NDMA. The same biosparging system was later transported to Vandenberg Air Force Base, CA, and used for a demonstration of *in situ* bioremediation of 1,4-Dioxane that included bioaugmentation with our ENV425 culture. The promising results of this field-scale demonstration lead to a successful full-scale application of biosparging and bioaugmentation for 1,4-Dioxane bioremediation at Vandenberg. A third successful *in situ* demonstration at Joint Base Cape Cod involved the recirculation of groundwater that was amended with oxygen and ethane gases for the treatment of EDB.

Results/Lessons Learned. One key question addressed by these field demonstrations is whether treatment levels of 1,4-Dioxane, NDMA and EDB in the low µg/L(1,-Dioxane) to ng/L (NDMA, EDB) range can be achieved using a co-metabolic bioremediation approach. The *in situ* treatment during these demonstrations showed reductions in groundwater exceeding 2 to 3 orders of magnitude. The key results from these three pilot-scale demonstrations and single full-scale application will be discussed. The key findings of these projects were as follows: (1) a variety of co-metabolically stimulated bacteria are capable of degrading these contaminants to innocuous products; (2) no toxic intermediates are produced during contaminant metabolism by these bacteria; (3) biodegradation of these contaminants from typical groundwater concentrations (e.g., 1-1,000 µg/L, depending on the contaminant) to low µg/L or ng/L levels by these bacteria is achievable; (4) bacteria capable of degrading these contaminants are indigenous to many different environments, and these organisms can be stimulated to degrade these contaminants through the addition of alkane gas and oxygen; and (5) the addition of alkane gases do not appear to be a significant inhibitor of biodegradation by many bacteria even though the reaction is co-metabolic. The key findings of these field demonstration projects suggest that an *in situ* approach for 1,4-Dioxane, NDMA and EDB treatment based on co-metabolism can be successful and widely applicable.

Propanotrophic Cometabolism of 1,4-Dioxane at High Concentrations

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Background. Aerobic biodegradation of 1,4-dioxane by propanotrophs is emerging as an option for in situ bioremediation. Most previous studies have focused on sites with relatively low concentrations of 1,4-dioxane (i.e., <1 mg/L), where it occurs as a co-contaminant along with chlorinated solvents. However, at some locations, 1,4-dioxane is present at notably higher levels. The primary objective of this study was to evaluate the potential for aerobic biodegradation of 1,4-dioxane at concentrations in the range of tens, hundreds, and thousands of milligrams per liter.

Approach. Soil and groundwater samples were obtained from three sites. For each site, microcosms were prepared (160 mL bottles with 20 g of soil and 50 mL of groundwater and air in the headspace) with an initial 1,4-dioxane level of 10 mg/L. Headspaces were periodically sparged with air to restore oxygen. For one of the sites, additional microcosms were prepared at initial concentrations of 470 and 1,250 mg/L, representing locations closer to the source area. Three treatments (in triplicate) were prepared for each location: unamended; with propane added; and with propane and a propanotrophic bioaugmentation culture added (ENV487, courtesy of CBI, Inc.). Propane and oxygen were monitored by headspace analysis; 1,4-dioxane was quantified by direct injection of aqueous samples onto a gas chromatograph equipped with a ZB-624 capillary column and flame ionization detector.

Results. For microcosms with an initial 1,4-dioxane concentration of ~10 mg/L, complete biodegradation proceeded at an average rate of 0.36-0.58 mg/L/d. Transformation yields (T_y) varied from 0.15 to 0.68 mg 1,4-dioxane per mg of propane. The upper end of this range is similar to the T_y observed with ENV487 grown on propane in mineral medium. The low end was a consequence of providing an excess of propane. For two of the locations, addition of propane alone stimulated propane consumption (indicating the presence of native propanotrophs) and biodegradation of 1,4-dioxane, at a rate of approximately 0.14 mg/L/d and T_y values of 0.018-0.40 mg 1,4-dioxane per mg of propane. No propane or 1,4-dioxane consumption occurred with microcosms from one of the three sites. In microcosms without propane or culture added, a slow rate of 1,4-dioxane biodegradation (0.092 mg/L/d) occurred in microcosms from one site and none at the other two.

Complete biodegradation of 470 mg/L 1,4-dioxane occurred within 124 days in microcosms amended with propane and culture, at an average rate of 3.0 mg/L/d and a T_y level of 0.43 mg 1,4-dioxane per mg of propane. In microcosms amended with propane but no culture, 59% of the 1,4-dioxane was consumed over the same interval, at an average rate of 2.4 mg/L/d and a T_y level of 0.56 mg 1,4-dioxane per mg of propane, and a 96% of 1,4-dioxane consumption occurred within 302 days, at an average rate of 1.49 mg/L/d and a T_y level of .52 mg 1,4-dioxane per mg of propane. At an initial 1,4-dioxane concentration of 1,250 mg/L, approximately 50% was removed over 302 days in the treatment with propane and culture added; no significant activity occurred in the other treatments. Overall, these results demonstrate that high rates of 1,4-dioxane biodegradation are achievable by propanotrophic cometabolism at concentrations at least as high as 470 mg/L. Addition of a bioaugmentation culture noticeably increased 1,4-dioxane degradation rates over indigenous propanotrophic activity.

Back to Contents

Optimizing Gas Delivery System for Co-Metabolic Bioremediation of 1, 4 Dioxane

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Background/Objectives. Aerobic cometabolic treatment of groundwater contaminants entails biostimulation of indigenous soil bacteria by adding oxygen and a growth substrate to trigger the production of enzymes that can oxidize the target pollutant. The method is most useful for bioremediation of pollutants that are not themselves good growth substrates for bacteria. A pilot scale treatment system was designed using oxygen (electron acceptor) to maintain aerobic conditions and periodic additions of propane (electron donor) to stimulate bacterial growth and the production of monoxygenase enzymes. The objective was to maximize enzyme competition for substrate and target contaminants.

Approach/Activities. DoD recommended using a Gas Infusion technology to dissolve treatment gases to stimulate cometabolic degradation of 1,4-Dioxane by placing iSOCs in fifteen 185-ft injection wells. The gas delivery system operated solely on cylinder gas pressure, while O&M operations consisted of manual switching of treatment gases as well as replacing depleted gas cylinders. To prevent mixing of oxygen and fuel-gas cylinders, a manual gas switching device was designed using SS components with check valves and color coded tubing with gas switching valves.

Results/Lessons Learned. The presentation will describe the gas delivery setup design with manual nitrogen, oxygen and methane switching. The presentation will finish by suggesting system optimization features attendees can understand and how different site conditions can be adapted for a Cometabolic approach.

Evaluation of Co-metabolic Biodegradation Potential for 1,4-Dioxane

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Background/Objectives. Few in situ treatment methods have proven successful and economically feasible for remediation of 1,4-dioxane in groundwater. Co-metabolic treatment approaches are particularly attractive when a target chemical is not a good growth substrate for bacteria or when it must be degraded to very low concentrations to meet regulatory requirements, as is the case for 1,4-dioxane. During co-metabolic treatment, robust growth of the degradative microorganism is supported by a primary substrate (e.g., propane) while the enzymes produced to grow on that substrate (e.g., propane monooxygenase) also degrade the target, often to very low concentrations (e.g., parts-per-trillion). In addition, the natural occurrence of some co-metabolic substrates in the environment (e.g., methane and ethane) may support the natural attenuation of contaminants, including 1,4-dioxane.

Approach/Activities. A laboratory study was conducted with samples from several 1,4-dioxane contaminated sites. Aquifer microcosms were amended with several potential co-metabolic substrates, including methane, ethane, and propane. Various other treatments, including the addition of copper chelators (to encourage production of soluble methane monooxygenase; sMMO), inorganic nutrients, and/or bioaugmentation cultures were evaluated. In microcosms where degradative activity was observed, enrichment cultures and/or pure cultures were isolated and evaluated for their potential to biodegrade 1,4-dioxane as well as chlorinated solvents that commonly co-occur with this compound in groundwater. Studies with several different pure cultures of propane, ethane, and methane oxidizers were also conducted to assess the kinetics and extent of 1,4-dioxane degradation by these different strains.

Results/Lessons Learned. The degradation of 1,4-dioxane was observed in microcosms from a site in South Carolina after addition of propane or ethane gas. Although methane was degraded in site microcosms, addition of methane did not appear to support 1,4-dioxane degradation. Enrichment cultures were isolated from the same site on each of the three co-metabolic substrates. As observed in the microcosms, cultures isolated on ethane and propane readily degraded 1,4-dioxane as well as other common chlorinated VOCs, including trichloroethene (TCE), *cis*-dichloroethene (*cis*-DCE), and vinyl chloride (VC). Interestingly, the methane enrichment culture readily degraded the same VOCs, but not 1,4-dioxane. Kinetic studies are currently ongoing with the ethane enrichment culture to quantify degradation kinetics of ethane and 1,4-dioxane. At two other sites, propane, ethane and methane were all ineffective at stimulating 1,4-dioxane biodegradation, but bioaugmentation with a propanotroph (*Rhodococcus ruber* ENV425) resulted in complete 1,4-dioxane degradation in site samples. Pure culture studies were also conducted with propane, ethane and methane degrading organisms to assess relative rates and extents of 1,4-dioxane degradation. The data suggest that co-metabolism may be a viable technology for in situ 1,4-dioxane treatment, but that the specific co-metabolic substrate applied and the requirement for bioaugmentation may be site specific.

Indoor Radon as an Option for Sustainable On-going Screening/Monitoring of Short-Term Risks from Low/Episodic Chemical Vapor Intrusion

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Background/Objectives. This proposes and evaluates three evidence-based options for on-going-screening/monitoring of a specific scenario of chlorinated-Chemical Vapor Intrusion (CVI); i.e., uncontrolled (naturally-varying) CVI with relatively-low baseline levels (e.g., source concentrations <100x generic regulatory screening levels), but potential for episodic/unpredictable peaks of chemicals associated with risks from short-term-exposures.

Approach/Activities. The strengths and weaknesses of ‘Ideal’, ‘Conventional’, and ‘Hybrid’ options are compared for a number of characteristics based on a comprehensive review of existing radon and CVI evidence, including the most recent from the most-studied CVI houses in the world.

Results/Lessons Learned. A Hybrid option would involve trade-offs to approach ‘Ideal’ characteristics, while remaining at-least-as sensitive, specific, and more cost-effective, than the ‘Conventional’ option. A Hybrid option would be an innovative approach for evaluating CVI risks using indoor-radon levels as a tracer/surrogate/indicator of soil-gas migration and building-specific susceptibility to the intrusion of nearby soil-gas. When combined with confirmed chemical contamination in near-building soil gas, elevated indoor radon levels indicate a probability for some chemical intrusion/short-term risks.

Finding these (‘probable CVI exposure) conditions, further higher-quality on-going-screening/monitoring could involve indoor air samples analyzed for CVI-chemicals and collected either: 1) at an on-going-frequency not greater than the shortest exposure-period of concern, or; 2) less frequently, when combined with intrusion-reducing controls and ‘continuous’ indoor-radon monitoring validating its effectiveness. This innovative option integrates/blends and blurs the distinctions between monitoring and mitigating, by taking the best components of screening/monitoring and mitigation to provide a reliable, but still cost-effective, approach for managing CVI with relatively-low baseline levels but episodic peaks of chemicals associated with risks from short-term-exposures.

Note, on-going research will help quantify how much “less frequently” CVI indoor air sampling would be needed, with mitigation, to achieve specific levels of confidence in protection.

Are Industrial Buildings Different? Implication of a Quantitative Vapor Intrusion Analysis of DoD Industrial Buildings Nationwide

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Background/Objectives. Most vapor intrusion (VI) policy in the US is informed primarily by studies conducted in residential structures of volatile organic compounds (VOCs) in groundwater, located away from the primary contaminant release. For example the default attenuation factors used routinely are derived from the EPA database analysis of residential structures. It has been frequently suggested that nonresidential buildings vary significantly in their resistance to VI due to foundation and ventilation characteristics, but few datasets are available to support that hypothesis. In addition, when faced with large populations of buildings within screening distances of volatile subsurface contaminants, innovative methods are needed to:1) prioritize those buildings in an area most likely to be effected by VI, and 2) make decisions concerning investigation and mitigation strategies based on subslab and groundwater data sets.

Approach/Activities. We assembled a relational database containing information on 150 sampling zones in 49 military structures at 12 different installations where measurements of chlorinated VOCs were available in indoor air, subslab soil gas and/or groundwater. The relational database contains chemical measurements, multiple observations characterizing the buildings, and descriptions of specific locations within a building where the chemical measurements were made. Building characteristics analyzed include dimensions, use, and construction date, HVAC type, flooring types, subgrade structures and atypical preferential pathways. Subsurface characteristics analyzed include soil type, depth to groundwater and distance to location of primary release. Exploratory data analysis was conducted using graphical presentations and descriptive statistics. Frequency of detection and issues regarding data censoring were assessed. Screening to minimize the impacts of indoor sources on the analysis was performed. Buildings influenced by atypical preferential pathways were analyzed separately.

Results/Lessons Learned. Graphs of subslab versus indoor air concentrations from this dataset display a “hockey stick” shape with an inflection point. These plots suggest that subslab concentrations in the lower range (below the inflection point) have no apparent effect on indoor air concentrations, suggesting that in this range the measured indoor air concentrations are background-related. The inflection point for industrial buildings points to an attenuation factor that is generally considerably higher than would be implied by current regulatory approaches. Similar relationships were observed between groundwater and indoor air concentrations.

A preliminary finding is that indoor air concentrations are higher for buildings with fine soils than coarse soils, while previous analyses have suggested that fine soils minimize migration of VOCs from groundwater. One possible explanation is that this database contains many buildings located above or near a primary vadose zone release, where fine grained soils may minimize the vertical movement and/or volatilization of VOCs. Preliminary correlations were also observed between indoor air concentrations and previously little studied factors as flooring type. As expected, source strength and distance appear to correlate with the potential for significant indoor air impacts. Multivariate analyses of these factors will be presented to inform building prioritization. We are developing a quantitative decision framework to prioritize buildings, reduce the number of sampling events and reduce decision uncertainty.

In Situ Bioremediation of Chlorinated Solvent Compounds and Implications for Vapor Intrusion Risk

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Background/Objectives. Chlorinated ethenes, most notably tetrachloroethene (PCE) and trichloroethene (TCE), are commonly detected groundwater contaminants at National Priority List sites. PCE and TCE are not easily degraded in groundwater under most conditions, and effective remediation of these compounds is challenging. In situ bioremediation (ISB) by reductive dechlorination has been demonstrated to be an effective remedial option for degrading of chlorinated ethenes in groundwater. Reductive dechlorination can achieve a substantial decrease in PCE and TCE relatively quickly with low cost and long-lasting amendments. It is well known that vinyl chloride (VC) is formed during the microbial reduction of PCE and TCE. In most cases, VC generation is transient and VC is readily degraded among a number of different anoxic and aerobic pathways. Yet the perceived risk of VC impacts to indoor air via the vapor intrusion pathway has resulted in the selection of other technologies instead of ISB, even though ISB would likely be most effective for groundwater cleanup. The objective of this presentation is to compare potential vapor intrusion risks associated with concentrations of TCE and VC in groundwater before and after ISB.

Approach/Activities. Case studies at sites where ISB has reduced concentrations of TCE in groundwater are presented to illustrate typical concentration trends. TCE concentrations can be reduced rapidly, while increased concentrations of VC are observed for several months following TCE reduction. A comparison of the toxicity criteria and fate and transport properties of TCE and VC demonstrate that TCE presents a more significant vapor intrusion risk than VC. Due to recent updates to the toxicity criteria for TCE, the long-term indoor air screening levels for TCE and VC are comparable. Inhalation exposures to TCE are also evaluated with new short-term indoor air action levels; these short-term levels are driving vapor intrusion evaluations at off-site study areas in residential neighborhoods in Northern California. There are no equivalent short-term action levels for VC. The natural degradation of VC in the vadose zone and indoor air limits the potential for indoor air exposures. VC is rapidly degraded in air due to attack by photochemically produced hydroxyl radical (half-life of 18 hours) and is susceptible to aerobic degradation in the subsurface. The natural degradation of VC is supported by a review of EPA’s vapor intrusion database, which indicates that VC is rarely detected in indoor air. In contrast, TCE is detected in indoor at a concentrations several orders of magnitude greater than its indoor air screening levels.

Results/Lessons Learned. The production of VC from ISB was not shown to be a substantial risk driver based on actual field data at several case studies. TCE concentrations rapidly decrease with ISB, often translating to a substantial decrease with risks associated with the vapor intrusion pathway.

Remediation of Chlorinated Solvents in Groundwater & Soil Gases using "Green" Pressure-Based Pseudo-Convective Transport Processes

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Background/Objectives. The study Site is a former dry cleaner with elevated levels of chlorinated solvents in its groundwater. During 1986 demolition activities, almost all original vadose zone soils were removed along with VOC source areas within them. Prior to October 2013, Groundwater contamination levels (up to 20 ppm) were only slowly decreasing and VOCs in the soil gases were predominantly at low levels (>5 ppbv), except within a cluster of phytoremedial TreeWells® located at the center of groundwater contamination. Due to the slow progress of the existing phytoremedial system, assessments were undertaken to identify which passive treatment methods could be used to increase the impact of the existing site-wide treatment system.

Approach/Activities. After the installation of 40 small diameter BVE™ Treatment System probes and conversion of the cased phytoremedial TreeWells® into large diameter GVE™ vents, the temporal and spatial soil gas pressures/distribution patterns radically changed with time across the entire Site. These changes were unexpected but were measured with pressure data loggers in several sealed soil gas wells and with other loggers used to monitoring concurrent changes in the barometric pressure. VOC and applicable pressure monitoring activities were also conducted multiple times a day in each probe with daily changes in groundwater VOC being analyzed by 8260 methods.

Results/Lessons Learned. Via daily monitoring activities and the collection of over 1,200 measurements, soil gas VOC levels periodically increased by orders of magnitude (up to 3,100 ppmv) and were very mobile, with velocities exceeding 80 feet/day as they passively migrated across the property. Due to the elevated Henry's constants for the chlorinated solvents, the contaminants that degassed into the vadose zone appeared to periodically dissolve back into groundwater elsewhere as they migrated toward the GVE™ vents. This Henry's Constant flux appears to be similar to large-scale landfill processes previously identified by Morris (1994). A combination of soil gas/barometric pressures and the developed preferential pathways of the BVE™/GVE™ Treatment Systems were the driving factors for the enhanced groundwater remediation via the pseudo-convective transport mechanism that was created. The large data set generated during this study "strongly indicates" 1) single event SOV surveys may have a negligible value in correctly identifying contaminated source area(s) or vapor intrusion issues; 2) very small but important contaminated groundwater areas are not likely to be detected during conventional field studies, but they should be detected as their continual contaminant input will significantly extend remediation timeframes/cost; and 3) contaminants-degassing from groundwater may occur when routes of transport are inadvertently created during assessments, construction activities or other events. Unless a vent is provided, these gases are likely to migrate into adjacent buildings. Due to the uncertainty associated with most data collection activities, high density proactive mitigation measures should be universally considered to break pathway(s) between known/unknown contaminant sources and nearby receptors.

Back to Contents

Modified Active Gas Sampling: A Multifaceted Approach to Environmental Site Assessment and Remedial Design of Chlorinated Solvent Contamination

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Background/Objectives. Modified Active Gas Sampling (MAGS) is an environmental assessment method which promptly detects volatile organic compounds in vadose zone soils to identify potential source area chemical contamination. The method was originally developed by HSA Engineers & Scientists in 2002 and is currently a required site assessment method utilized by the state of Florida Drycleaning Solvent Cleanup Program. MAGS increases the ability to identify chemical source areas which may be missed by traditional discrete soil sampling methods by providing an overlapping radius of influence (ROI) based on vapor well placement throughout the area of interest. As part of initial site assessment activities, MAGS can also provide projected flow rate, radius of influence, and mass recovery rate information essential to evaluate the feasibility of soil vapor extraction (SVE) for site specific remediation. For the purposes of this study, three sites part of the Florida Drycleaning Solvent Cleanup Program were selected, Classic Touch Cleaners, Sunland Cleaners, and Jimmy’s Discount Cleaners.

Approach/Activities. MAGS involves the extraction and analysis of soil gas from a temporary vapor extraction well(s) screened through the unsaturated soil column. At each of the three drycleaning facilities MAGS vapor extraction well installation locations were chosen based on their orientation with respect to site features that would suggest potential source areas (drycleaning machine, chemical/waste storage areas, drains) and considerations of MAGS airflow direction in the subsurface. Utilizing a regenerative blower system, a large volume of soil can be assessed from a single well point with a limited number of samples collected. The vacuum extraction system was connected to each VEW point individually and soil gas extracted from each point for approximately 30 minutes. Soil vapor constituents were field screened using a photoionization detector (PID) after each 5-minute interval. A soil gas sample from each VEW was collected and submitted laboratory for analysis, in all cases this was from the beginning of the sampling interval. In addition, vacuum measurements were collected from surrounding VEW locations to estimate the effective radius of influence of each sampling point. As part of the initial site assessment activities discrete soil samples were also collected at each site located within the boundaries of the MAGS study area and submitted for laboratory analysis.

Results/Lessons Learned. Soil gas analytical results identified the presence of Tetrachloroethylene (PCE) at all three of the drycleaning facilities. However, only one of the three facilities yielded an analytical result of PCE in the discrete soil samples collected. Based on the results, initial site assessment outcome and future remedial application of a MAGS study dataset is greatly dependent on both surface and subsurface materials and conditions. Vapor well depth, amount of well locations, and distance between well locations may exist as a limiting factor in subsurface soils with low permeability or sites with shallow groundwater elevations. In addition, areas that lack a sufficient surface seal (cracks, joints, grass, and gravel area), the resulting short-circuiting can limit ROI and introduce ambient vapors that may be detrimental to the study. The PID readings appear to correlate well with the analytical result, that is, the higher PID reading corresponded to the higher analytical result.

Bleach—A Smoking Gun?
A Multiple Lines of Evidence Evaluation of Vapor Intrusion Data at a Commercial Cleaning Product Facility

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Background/Objectives. When conducting a vapor intrusion investigation, evaluation of potential indoor air background sources of contaminants is standard practice to help discern whether or not vapor intrusion is occurring in a particular building. This case study presents the results of a vapor intrusion investigation conducted at a large commercial cleaning product blending and packaging facility where unexpectedly high levels of trichloroethylene (TCE) in indoor air were observed and the subsequent lines of evidence evaluation that was conducted. Elevated concentrations of TCE and other volatile organic compounds (VOCs) were detected in both the shallow groundwater and sub-slab soil gas beneath the Site building. However, no spatial relationship was identified between the groundwater/soil gas and indoor air sample locations with elevated TCE concentrations. Additionally, no HVAC or other pathway within the building was identified that would encourage the vapor intrusion pathway. Furthermore, the facility personnel indicated that TCE was not present in any materials used or stored at the Site.

Approach/Activities. Ratio analyses of TCE and other VOCs in various environmental media were conducted to evaluate attenuation. Relative proportions of TCE and other VOCs in groundwater were similar to those in the overlying soil gas samples as would be expected. However, the ratios of these same VOCs in indoor air indicated a greater relative abundance of TCE in indoor air as compared to soil gas and groundwater. Thus, to the extent that soil gas from the VOC groundwater plume was entering the building, one or more other sources caused the proportions of TCE to increase in indoor air relative to other VOCs. The Site building is used for blending and packaging of commercial cleaning products such as detergents, soaps, and bleach. The literature indicates that head space TCE concentrations from pure bleach products can be as high as 5.4 μg/m^3 TCE (Odabasi, 2008).

Results/Lessons Learned. In the evaluation of multiple lines of evidence, the most compelling line of evidence is the substantial difference in the relative proportions of VOCs in the sub-slab soil gas and indoor air. Based on the evaluation of multiple lines of evidence, vapor intrusion of groundwater constituents is most likely not the cause of the observed elevated TCE concentrations in indoor air. The presence of open tanks containing large quantities of bleach is a possible source of TCE within the building. Additionally, the practitioner should carefully consider information provided by facility personnel, conduct independent research into potential background contribution from facility operations, and consider screening of potential background sources prior to the collection in indoor air samples.

Back to Contents

Evaluation of Vapor Intrusion Risks of Benzene-Contaminated Sites Using Various Guidance: KMOE, USEPA, ASTM, and Dutch RIVM

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Background/Objectives. Vapor intrusion of petroleum-based soil contaminants into residential buildings around army installations is an emerging environmental issue in Korea. Korea Ministry of Environment (KMOE) suggested evaluation methodology of vapor intrusion risk. KMOE guidance suggests that, unless indoor air samples were taken, indoor vapor concentration should be determined by multiplying default attenuation factor (i.e., 0.1 or 0.01) by soil gas concentration, which is estimated from soil concentration using three-phase partitioning equation. KMOE guidance adapted the default attenuation factor from United States Environmental Protection Agency (USEPA) guidance while the partitioning equation was adapted from American Society for Testing and Materials (ASTM) guidance or National Institute for Public Health and the Environment of the Netherlands (Dutch RIVM) guidance. However, KMOE guidance adapted only numbers or equations shown in the other guidance without comprehensive understanding on these guidance (for example, USEPA guidance notes that site-specific attenuation factor, not default attenuation factor, should be used for the vapor risk evaluation, but KMOE guidance requires to use the default attenuation factor); therefore, the validity of KMOE guidance in evaluating the vapor intrusion risk is questionable. In this study, we evaluated vapor intrusion risks for many residential areas around army installations using these guidance, then compared the evaluated risks to each other. Further, we also discussed corrective suggestions for KMOE guidance using the comparison data.

Approach/Activities. The vapor intrusion risk evaluation was conducted at various locations, where will be redeveloped as residential area, around army installations, and benzene was selected as a model compound due to its high inhalation toxicity and volatility. Soil and soil gas samples were taken, and soil and soil gas benzene concentrations were analyzed. Then, benzene concentrations in indoor air were estimated using KMOE, USEPA, ASTM and Dutch RIVM guidance, then the vapor intrusion risk was evaluated using the estimated indoor air concentrations.

Results/Lessons Learned. At first, we observed serious inconsistency between measured soil gas concentration and estimated soil gas concentration (using partitioning equation) of benzene. In some areas, benzene was not detected in soil, and thus, estimated benzene concentration in soil gas is also expressed as “non-detect”. However, certain level of benzene (e.g., 30 $\mu g/m^3$) was detected in soil gas, meaning that the soil gas concentration estimation using partitioning equation caused underestimation error. On contrast, in other areas where soil benzene was detected, estimated soil gas concentration of benzene (e.g., 120,000 $\mu g/m^3$) was about four orders of magnitude greater than the measured soil gas concentration (e.g., 20 $\mu g/m^3$) even the soil benzene concentration was fairly low (approximately 0.6 mg/kg), indicating that soil gas concentration estimation using partitioning equation caused overestimation error. Thus, the soil gas estimation caused both underestimation and overestimation errors.

Beyond the Guidance—A Summary of ITRC's PVI Guidance Document and How it was Developed

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Background/Objectives. The Interstate Technology and Regulatory Council (ITRC) has been working for the past three years to develop a consensus-based document providing guidance on the assessment of petroleum vapor intrusion. The targeted users of this document are state/federal regulators and consultants as well as site owners and public and tribal stakeholders. As such, representatives from each of these groups have been active during document development.

Approach/Activities. An update on the status of the PVI guidance document (estimated to be finalized prior to the AEHS conference) will be provided as well as a summary of the main topics. This will include a summary of the PVI assessment strategy, site screening, investigation tools, mitigation options and community engagement detailed in the document. This presentation will also go beyond the guidance to provide insight into the development of the document. How was the guidance documents created? How do you build consensus between multiple stakeholders with varying opinions and perspectives?

Results/Lessons Learned. The development of the PVI guidance document was challenging and required the dedication of a core group of regulators, practitioners and subject matter experts as well as input from the regulatory and environmental community at large. The development process, including the give and take, the debates and the "hot topics", will be discussed.

Vertical Screening Distances for Petroleum Vapor Intrusion Risk Assessment

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Background/Objectives. Current methods used in petroleum vapor intrusion screening are not generally effective in identifying low-risk sites that require no further characterization. As a result, petroleum underground storage tank (UST) sites are routinely investigated for potential inhalation exposure and risk to human health unnecessarily. The issue can largely be attributed to conservative screening levels derived for petroleum hydrocarbons using models that do not account for biodegradation and with little consideration of empirical (soil-gas) data.

Previous studies have shown that concentrations of petroleum hydrocarbons can biodegrade over several orders of magnitude within short vertical distances (e.g. 1 – 2 m) in the unsaturated zone. Biodegradation is most prolific at the aerobic-anaerobic interface where hydrocarbon and oxygen concentrations become optimal for biodegradation. The aerobic-anaerobic interface occurs in close proximity (e.g., capillary zone) to dissolved-phase sources and farther above light non-aqueous phase liquid (LNAPL) sources. The observed reactive behavior of hydrocarbon transport in the unsaturated zone supports a screening methodology for petroleum vapor intrusion based on vertical source-building separation distance. This study was undertaken to derive vertical “screening” distances for dissolved-phase and LNAPL sources.

Approach/Activities. A large database containing soil-gas measurements taken at hundreds of petroleum UST sites was evaluated. The database spans a range of environmental conditions, geographic regions, and 16-years (1995 – 2011) of data collection. The database was extensively reviewed to ensure data quality for interpretation and analysis. The soil-gas data were evaluated using Kaplan Meier statistics to calculate vertical screening distances for specific petroleum VOCs (benzene, xylenes, hexane, C_5-C_8 aliphatics, C_9-C_{12} aliphatics, and C_9-C_{18} aromatics) and for dissolved-phase and LNAPL sources.

Results/Lessons Learned. Results of the analysis indicate that benzene is the primary constituent of potential concern for screening evaluations. In addition, greater than 95% of benzene concentrations in soil gas are attenuated below a specified soil-gas screening 30 mg/m^3 at any measured distance above dissolved-phase hydrocarbon sources and at distances greater than 13 ft (4 m) above LNAPL sources. The results are consistent with those reported in other empirical soil-gas database assessments. Consideration of vertical screening distances in petroleum vapor intrusion guidance is likely to eliminate unnecessary site characterization at numerous petroleum UST sites.

Modeling of Vertical Exclusion Distance Criteria for Assessing the Vapor Intrusion Pathway at Petroleum Hydrocarbon Sites

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Background/Objectives. The research conducted in the last decades has provided increasing insights about the key role of biodegradation in attenuating petroleum hydrocarbon vapors migrating into the indoor environments. Despite this, due to the too conservative screening models generally used in the risk analysis framework, vapor intrusion is still considered a critical pathway in most of petroleum contaminated sites. To overcome this limitation, in the last decades more detailed models including biodegradation were developed. More recently, a big effort was also made to identify separation screening distances from the source, beyond which the potential for vapor intrusion can be considered negligible. This was mainly made by carrying out statistical analysis of large soil vapor datasets collected from the field. However, these empirical screening distances are associated to a certain probability percentage (e.g. 95% of cases) that for a given type and source concentration (e.g. dissolved-phase or LNAPL source) the contaminant of concern will be attenuated below a target soil-gas screening level. To support and further justify these empirical analyses, mathematical modeling can be certainly of help.

Approach/Activities. In this work, we present a very simple and fast approach that allows, using an explicit analytical solution, to directly estimate, on a site-specific basis, the risk-based vertical screening distance for petroleum hydrocarbons. The proposed solution relies on a 1-D vapor intrusion model that incorporates a steady-state subsurface vapor source, diffusion-dominated vapor transport in a homogeneous soil, aerobic biodegradation limited by oxygen availability, diffusive and convective mass transfer across the building foundation and mixing within the indoor environment. In addition, the model accounts for the transport of oxygen due to diffusion and its consumption resulting from the different sources of oxygen demand (aerobic biodegradation of the compound(s) of concern and natural soil oxygen demand). In order to test the capability of the developed model, some comparison with a 3-D numerical model were first carried out. Next, the vertical exclusion distances predicted by the developed model were compared with the empirical screening criteria reported in the literature.

Results/Lessons Learned. The comparisons carried out showed that the model predictions are consistent with the results obtained using a 3-D numerical model and with the empirical screening criteria reported by U.S.EPA (2013) and Australia (CRC care, 2013). However, the different simulations carried out showed that in some specific cases (e.g. large buildings, high methane concentrations, low attenuation in the capillary fringe) these empirical screening criteria could be not sufficient to guarantee soil-gas concentrations below acceptable risk-based levels. Hence, the developed model could support the site-generic screening empirical distance criteria, thus allowing to obtain a site-specific evaluation of the relevance of the volatilization pathway in the conceptual model of the site.

Back to Contents

Five-Year Vapor Monitoring For Risk Management at a Hydrocarbon Polluted Site

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Background/Objectives. For risk assessment purposes at contaminated sites, petroleum mixtures are divided into "fractions" including sets of compounds with fraction-specific fate and transport behavior and toxicity. They also differ in biodegradability, resulting in the enrichment of the heaviest fractions in soil and attenuation in vapor migration of light compounds towards ground surface.

This work reports about the risk management strategy performed at a site in Milan (Italy) where soil remediation (excavation and off site disposal) was partially carried out in 2005, leaving a residual volume of soil polluted with petroleum-derived hydrocarbons.

Approach/Activities. Indoor air, outdoor air, crawl-space air and soil gas samplings were carried out since January 2009. In March 2011 the monitoring network was upgraded to its final configuration (18 indoor, 7 outdoor and 4 crawl-space sampling locations, 60 soil gas probes at four different depths from ground surface); after that, one monitoring campaign a season was performed till November 2013, fractionating hydrocarbons according to a modified version of the Massachusetts Department of Environmental Protection approach.
In order to permanently keep risk below acceptable levels, a mitigation system of the contaminated source was installed in December 2013 and it is still working. Three monitoring campaigns of ambient air have been performed since then.

Results/Lessons Learned. Data collected in soil gas at 1 m b.g.s. resulted in calculated risks lower than those based on data from soil gas probes deeper in soil; the estimates differed by up to about two orders of magnitude for indoor exposure. This result was ascribed to the variation with depth of soil lithology, but also to biodegradation, which is actually going on as suggested by the low O_2 and the high CO_2 concentrations measured at 10 and 15 m b.g.s. in many monitoring probes.

Comparison between the different monitoring campaigns at a specific soil gas depth highlighted that the estimated risks differed by up to one order of magnitude without a systematic seasonal effect.

A few ambient air and crawl-space measurements resulted in episodic high values. However, as a general trend, the average outdoor and indoor concentrations did not differ significantly from the background values. The worst air quality was found in autumns and winters, when the atmospheric conditions promote stagnation and sources other than pollution in soil (vehicular traffic, heating systems) are active. Compared with background values, indoor and outdoor air concentrations at the site suggested that hydrocarbons were widely spread and sources other than pollution in soil were affecting the quality of the inhaled air.

Although not strictly necessary in terms of time-averaged health risk, the mitigation system allowed to extract significant amounts of mono- and light poly-cyclic aromatic hydrocarbons. This has helped manage worries about future uncontrolled exposure of people working at the site.

Back to Contents

State-of-the-Practice: Innovative Tools for Evaluating Vapor Intrusion Risk

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Background/Objectives. Over the last 20 years, the vapor intrusion pathway has progressed from being largely ignored to becoming a major driver of site investigation and remediation, particularly at sites with chlorinated solvents in groundwater. During that time, the conceptual model for vapor intrusion and the tools available to characterize the pathway have evolved significantly. Intensive multi-year studies of individual structures funded by the USEPA and the Department of Defense SERDP/ESTCP program have provided new insights into the mechanisms for vapor intrusion. Additionally, a number of tools and investigation approaches recently considered innovative or experimental have, by now, been well validated. Additional tools continue to be developed that have the potential to further improve our understanding of the vapor intrusion pathway.

Approach/Activities. The greatest current challenges for characterizing vapor intrusion are i) characterization of spatial and temporal variability in VOC concentrations, ii) identification and characterization of alternative migration pathways (such as sewer lines), and iii) distinguishing between indoor and subsurface sources of VOCs. On-site analysis of samples using a portable GC/MS can be used to characterize spatial variability, identify VOC sources, and test alternative migration pathways. Building pressure monitoring and manipulation can be used in conjunction with on-site or off-site analysis of samples to evaluate the contribution from indoor sources (positive building pressure) or to evaluate the upper end of temporal variability in vapor intrusion (negative building pressure). Passive sorbent samplers are a cost effective tool for addressing temporal variability through the collection of time-integrated samples. Perfluoronated tracers and other tracers can be used to identify the significance of alternative migration pathways.

Results/Lessons Learned. Accurate and efficient evaluation of the vapor intrusion pathway requires flexibility and innovation from investigators, project managers, and regulators. Continued development and validation of innovative tools will be required in order to properly address vapor intrusion at sites with chlorinated solvents or other volatile contamination. A significant remaining challenge is the development of consistent methods to evaluate investigation results to support definitive decisions concerning the presence or absence of vapor intrusion at a site.

Passive Samplers for Vapor Intrusion Monitoring: Update on EPA's Technical Support Document and Research Results

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Background/Objectives. Recent studies of indoor air quality in buildings where vapor intrusion occurs show that temporal variability can be greater than an order of magnitude. Because they can capture this variability as time-weighted average concentrations over a sampling durations of weeks to months, passive samplers provide data that are more representative than conventional 24-hour methods of the long-term average concentrations that are of most interest for indoor air exposure assessment. However, the acceptance of passive sampling by U.S. regulators has been hampered by a lack of familiarity with the performance data and standard international and European methods that are available for measuring volatile organic compounds (VOCs) at low concentrations in indoor air. To meet this need EPA conducted research and recently developed an Engineering Issue Paper (EIP) to help users obtain high quality passive sampler data for vapor intrusion applications.

Approach/Activities. The EIP *Passive Samplers for Investigations of Air Quality* reviews the current literature and summarizes available standard methods and performance data for passive samplers. In addition, field research studies have examined passive sampler performance for a variety of VOCs over different field conditions and exposure durations. One study was designed to compare the performance, under realistic indoor conditions, of passive samplers exposed for long durations to sequentially exposed passive samplers at durations (1- to 2-weeks) for which sampler performance characteristics are already known. Another study investigated the performance of different passive sampler sorbents and starvation effects related to flow conditions and uptake rates.

Results/Lessons Learned.
The new EIP covers the basics of passive sampler design, compares passive samplers to conventional methods of air sampling, and discusses practical considerations when implementing a passive sampling program. The EIP also discusses field sampling and sample analysis considerations to ensure data quality is adequate and data interpretations are supportable. In this presentation we will provide an overview of the content of the EIP including:

- Sampler types – sorbents, sorbent combinations, sampler geometry, and uptake rate control
- Recommendations for planning passive sampling campaigns – how to select the right sampler for the target compounds, necessary reporting limits, and desired duration(s).
- Suggestions for sampler locations, deployment, handling, storage, and transport
- Commercially available sampler types

Research results show that for radial charcoal samplers percent bias varied by chemical and there was a general increase in negative bias with increasing VOC volatility and sample duration. Toluene and PCE met the performance criteria (±30%) for all durations tested, with negative biases well below 7% except for 21% for PCE for a 1-year sample duration. Chloroform did not perform well past 1-month sample durations. A second study showed that solvent extracted sorbents retain VOCs better than thermally desorbed sorbents, that starvation can cause a negative bias when a high uptake rate sampler is used in a low-flow environment, and that passive samplers can provide quality data comparable to conventional samplers over longer sampler durations.

The Use of the Waterloo Membrane Sampler for Long-Term Monitoring of VOCs

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Background/Objectives. Temporal variability in indoor air concentrations poses a significant challenge when assessing health risks attributable to subsurface vapor intrusion of volatile organic compounds (VOCs). Decades of research on radon show similar temporal variability. Indoor air radon sampling is typically conducted over long intervals (a 90-day sample is referred to as a “short-term” sample by the USEPA) in order to provide a time-weighted average radon concentration that is considered to be a reliable estimate of the long-term average. Conventional VOC indoor air sampling methods (EPA Methods TO-15 and TO-17) are not well suited for sample durations longer than about 24 hours. Alternative sampling technologies are required in order to collect indoor air VOC samples over time intervals that minimize the impact of temporal variability.

The Waterloo Membrane Sampler™ (WMS™) is a passive permeation-diffusion sampler which is ideally suited for long-term VOC measurements. The sampler is small, discrete and inexpensive. VOCs diffuse through a polydimethylsiloxane (PDMS) membrane into the sampler, where they are sequestered and retained by a sorbent. The PDMS membrane serves to predictably regulate the uptake rate of VOCs, thereby allowing a quantitative measurement of concentration. The membrane also provides a barrier to water, which can interfere with the sorption and retention of VOCs, and a barrier to wind, which can cause a positive bias by advective uptake in high air velocity settings.

Approach/Activities. Controlled laboratory experiments were conducted over a duration of up to 90 days to test the performance of the WMS sampler. A low-uptake rate variety of the WMS sampler was developed to minimize the chance of saturating the sorbent. Several different sorbents were tested, including Anasorb 747, Carboxen 1016, Carbopack B, Dowex Optipore, XAD-2 and Tenax TA. 52 different VOCs were included in the tests, based on the EPA Method 8260 analyte list. Samplers were deployed in triplicate for 1 month, 2 month, and 3 month intervals. Periodic analysis of the chamber concentrations was performed by Method TO-15 as an active sampling control.

Results/Lessons Learned. Of the six sorbents assessed, Anasorb 747, Tenax TA and Carbopack B provided the most consistent results over the three-month sampling period. This was attributed to the appropriate sorbent strength, i.e., not so weak that analytes are not retained quantitatively during the sampling period, and not so strong that analytes are not released quantitatively during desorption. Proper selection of sorbents is critical for long-term VOC sampling. Results of six-month exposure tests currently under way will also be discussed. The implications of this research are important because they allow the long-term average vapor intrusion risks to be assessed with a simple, low-cost method with less variability and lower costs compared to multiple rounds of sampling with conventional methods.

Laboratory Simulation of Subsurface Airflow Beneath a Building

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Background/Objectives. Vapor intrusion is the vapor-phase migration of volatile organic compounds (VOCs) into buildings resulting from subsurface soil and/or groundwater contamination. The physical transport of soil gas through the vadose zone and into basements has been studied in both the field and laboratory, but is still not fully understood. It is commonly assumed that under natural conditions, soil vapor diffusion dominates the migration of VOCs through unsaturated soils. However, soil vapor entry into basements is often thought to be dominated by advection caused by the depressurization of buildings (Swartjes et al. 2011). In addition to the physical transport of soil vapor in the vadose zone, the subsurface oxygen (O_2) replenishment rate is an important factor in characterizing and controlling biodegradation rates of petroleum hydrocarbons (PHCs) during their migration from the source to the building. This study examines subsurface flow of air beneath a model building through two laboratory experiments. The Wind Experiment is the first of its kind in a laboratory-controlled setting and quantifies the O_2 replenishment rate beneath a building as a result of variations in above ground wind speed. The Depressurization Experiment uses an innovative approach to model the flow of air flow into a building as a result of negative building pressure.

Approach/Activities. For the Wind Experiment, various wind speeds created by a fan and building configurations (i.e., basement, slab-on-grade, presence of a simulated sidewalk) were factors studied to quantify O_2 replenishment rates through porous media beneath a model building. The model building consisted of a one cubic foot box constructed of plywood. The shape of the building simulates a two-story building with approximate footprint of 625 square feet (1:25 scale). For the Depressurization Experiment, the same model building was depressurized to various levels of vacuum using a system of peristaltic pumps. A data logger recorded real-time differential pressure beneath the building within a tank filled with porous media at each level of vacuum to test the effects building configuration (i.e., basement and slab-on-grade) and foundation “crack” percentage have on subsurface air flow into the building. The resulting pressures were used to calculate flow nets modeling the flow of air in the subsurface beneath the building. Flow rates of air through the porous media, as well as O_2 replenishment rates, were then obtained from the flow nets.

Results/Lessons Learned. The primary findings of the Wind Experiment show that the presence of an upwind sidewalk reduced the O_2 replenishment rate beneath the building by approximately 50%, while basement vs. slab-on-grade construction did not have a significant impact on this rate. The results also provide guidance for determining relative risk among existing buildings affected by a VOC plume, such as in a residential neighborhood, based on prevailing wind direction, foundation integrity, and configuration of the house and its surroundings. The Depressurization Experiment displayed how even minor building vacuums (5 Pa) can result in significant infiltration (14 cm^3/s) of soil vapors. This work demonstrated that the experimental approach used is effective and provides a solid basis for expanded laboratory exploration of factors that control vapor intrusion.

Evaluating Vapor Intrusion Potential via Groundwater Interface Sampling

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Background/Objectives. The need to investigate off-site vapor intrusion (VI) is governed in many regulatory jurisdictions by the concentrations of dissolved volatile organic compounds (VOCs) in groundwater and their potential to off gas from the groundwater interface. However, conventional groundwater sampling methods are designed to collect samples representative of the primary saturated zone to evaluate direct contact via the ingestion exposure route rather than the groundwater interface where off-gassing occurs. A new sampling method was developed to evaluate VOC concentrations at the groundwater interface within a chlorinated VOC groundwater plume as it migrates towards occupied structures in order to assess the necessity for, and to appropriately design, vapor intrusion investigations.

Approach/Activities. A unique sampling method using customized polyethylene diffusion bags (PDBs) was developed and tested in six monitoring wells at increasing downgradient distances from the source area at an industrial facility in Indianapolis, Indiana where groundwater is impacted by chlorinated VOCs. PDBs are typically deployed at fixed positions within well screens for a minimum two-week equilibration period, during which time water-level fluctuations make the depth to groundwater unpredictable. To ensure the PDBs remained submerged when groundwater levels were low and still reliably sample groundwater near the groundwater interface to evaluate the VI potential, Wilcox engineered the PDBs to be “buoyed”, i.e., to rise and fall with the groundwater level and maintain their positions immediately below the groundwater interface during the deployment period. The analytical results from the buoyed PDB sampling method were compared to data from conventional low-flow sampling at the six test locations for two quarterly groundwater monitoring events in 2013.

Results/Lessons Learned. The analytical data from the low-flow and buoyed PDB groundwater samples from monitoring wells near the source area showed good agreement, while the data from the low-flow and buoyed PDB samples from the downgradient test locations were more disparate. The VOC concentrations in the buoyed PDB samples from the distal end of the plume were up to five times lower than in the low-flow samples, indicating that low-flow groundwater sampling may not accurately represent the potential for groundwater VOC off gassing and subsequent vapor intrusion. By refining methods to sample groundwater only at the groundwater interface where off-gassing occurs, unnecessary VI investigations and their associated costs and liability can be avoided. Further evaluation of the groundwater interface sampling method is planned for 2015.

Vapour Intrusion Risk Assessment: Combined Approach using Modelling and Direct Measurement with Case Studies from Contaminated Sites in South Africa

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Background/Objectives. The vapour intrusion (VI) exposure pathway is recognized to drive human health risk at numerous sites that have been contaminated by petroleum products and other volatile contaminants. The risks related to VI are typically evaluated using direct measurement (vapour sampling and laboratory analysis) or modelling methods. The authors have developed a toolbox approach using a combination of exclusion distance criteria, direct measurement and modelling methods to assess risks and achieve closure. For direct measurement, samples of vapour are taken beneath the floor slab of buildings (sub-slab sampling) or from the air inside the buildings (indoor air sampling). Indoor air sampling can be compromised by interferences from unrelated sources or from background air quality and can be further confounded by the potential temporal variability in ambient air quality within the structures which are being assessed. Modelling methods are therefore often used to estimate the partitioning of volatile contaminants from soil or groundwater sources into the vapour phase and the subsequent transport of vapours from the subsurface environment into habitable buildings. A limitation of modelling approaches is that they are designed to be conservative to avoid the potential for under-predicting risk. Furthermore, the models do not typically take into account the degradation of hydrocarbon vapours in the presence of oxygen, which has been found to be a significant process for petroleum hydrocarbons.

Approach/Activities. The authors have compiled a dataset of petroleum vapour and groundwater results from over 50 petroleum release sites in southern Africa. These data were used to develop exclusion distance criteria (i.e. distance from the source at which sufficient attenuation by reaction with oxygen has occurred for the risk to be negligible) for vapours emitted from contaminated groundwater sources. The data are broadly consistent with similar criteria developed globally. A standard “lines of evidence” approach has been applied to the assessment of VI risk by firstly applying the exclusion distance criteria to sites with groundwater contaminant plumes beneath buildings. Sites which meet these criteria are considered to have no unacceptable VI risk. Where exclusion screening criteria cannot be applied or are exceeded, risk is estimated using modelling, and if a potential risk is predicted, then direct sub-slab measurements are taken to more accurately assess the risk. Lastly, where sub-slab assessment predicts a potential VI risk, indoor vapour measurement are taken to evaluate actual risk, taking into account interferences from other sources and background levels of contaminants. Mitigating measures are then applied as appropriate.

Results/Lessons Learned. The authors will present various case studies demonstrating different approaches to the assessment of VI risk, including direct measurements at an industrial office complex overlying a plume of light non-aqueous phase liquid (LNAPL), direct measurements at a residential hotel overlying a dissolved phase hydrocarbon plume, and modelling methods at a residential property adjacent to a service station with hydrocarbon impact.

A risk-based approach to the assessment of contaminated land provides a sustainable and cost effective methodology to assess contaminated sites and avoid unnecessary remediation. Risks are often found to be driven by VI and the examples presented in this paper illustrate that these risks can be adequately addressed with a toolbox approach using multiple lines of evidence to assess sites and achieve closure.

Back to Contents

Interpretation and Utilization of Soil-Gas Survey in Petrochemical Plants

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Background/Objectives. The management of contaminated sites in operation often relies on the implementation of safety measures aimed at avoiding the propagation of the contamination and the exposure of the workers. The first goal is usually achieved by the installation of hydraulic barriers or other engineered approaches, that allow to stop the flow of contaminated groundwater from the site. In more flexible legislative framework, this result can be achieved also relying on Monitored Natural Attenuation approach, i.e. by controlling the plume migration. As to the safety measure related to the protection of workers, apart from direct contact through soil ingestion and dermal contact, which are highly unlikely for workers wearing suitable PPEs, the main exposure route of concern is represented by the inhalation of volatile and semi-volatile compounds in outdoor and indoor environments. The preliminary assessment of the risks for workers related to this exposure route is usually performed using models based on the well known Johnson-Ettinger approach. Due to the too conservative character of this model, generally used in the risk analysis framework, the risk for inhalation of volatile and semi-volatile compounds often results not acceptable. To overcome this limitation, it is commonly accepted to conduct soil gas survey, using either soil gas probes installed at least 1-2 meter belowground or flux chambers, in the case of contaminated superficial soil or very shallow contaminated groundwater. Despite there is already evidence of this approach, especially in the United States, the interpretation of the collected data and their use in the management of the contaminated site are still somehow open issues, especially as far as its acceptance by environmental agencies is concerned.

Approach/Activities. Recently, versalis (eni) has started one of the largest soil gas survey performed so far in Italy, in the framework of the management of different important petrochemical sites located in Italy. These sites are typically characterized by the presence of BTEXS and other volatile and semivolatile petroleum hydrocarbons and by the localized presence of chlorinated solvents. Namely, four large petrochemical sites are being investigated, with an average of 60 soil gas monitoring points per site, with the program of performing four seasonal surveys in one year. The monitoring plans are mainly based on single-level soil gas probes, but also include a few multi-level soil gas probes per site and, where needed, flux chamber to characterize the effect of shallow contamination. The soil gas data are first used to evaluate the risk for inhalation and secondly to estimate the site-specific target level of the contaminated soil or groundwater, relying on the site-specific attenuation measured between soil gas and soil /groundwater concentration.

Results/Lessons Learned. The preliminary data collected in some of the investigated sites show that the risk for inhalation calculated from soil gas data is generally not an issue. This preliminary result was obtained (not surprisingly) in a small area of a site contaminated by BTEXS, showing clearly an attenuation of 2-3 orders of magnitude between the deep soil gas survey (4.5 m b.g.) and the more superficial one (2 m b.g.). A similar result (more surprisingly) was obtained for a shallow groundwater contaminated by volatile chlorinated compounds: in this case, despite the risk assessment based on screening models suggested risk for outdoor inhalation, the preliminary data obtained by flux chamber did not show evidence of risk. These results will be integrated with those obtained at larger scale during winter and spring in four petrochemical sites, allowing to perform a comprehensive assessment of risks resulting from vapor inhalation and to define the cleanup goals for the corresponding contaminated matrix.

Application of a Probabilistic Risk Assessment Approach for Quantifying Risk and Uncertainty Associated with Vapor Intrusion

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Background/Objectives. Inhalation of indoor air resulting from vapor intrusion is frequently a primary human health risk driver. Defining the extent and impact of vapor intrusion on human health risk is of critical importance to provide the most technically appropriate and cost-effective remediation strategy for sites with potential vapor intrusion concerns. However, studies have shown that the impact of vapor intrusion on concentrations of chemicals of concern in indoor air is difficult to accurately quantify. Furthermore, confounding factors are numerous and vary from site to site (e.g., heterogeneous vadose zone) and building to building (e.g., preferential pathways and slab/foundational integrity). These include uncertainties in the location of subsurface sources (e.g., dissolved chlorinated solvents or dense non-aqueous phased liquids in shallow aquifers); temporal variability in the extent of VOCs in soil vapor due to seasonal and meteorological effects, such as the vertical position of the groundwater table, building stack effects during the heating season, and barometric pressure fluctuations; and the presence of background sources of VOCs in indoor air from consumer products. Recent studies have shown that industry-standard site characterization and risk assessment practices do not adequately address the uncertainty and variability in estimating indoor air concentrations. Despite these known technical shortcomings, point-in-time sampling and traditional, deterministic applications of the Johnson and Ettinger (J&E) model using unrealistic and conservative input parameters is the status quo within the environmental industry. While alternatives to the J&E model have been evaluated at specific study sites, deterministic modeling approaches for vapor intrusion are not optimal to evaluate this exposure pathway due to the complex, variable, and uncertain nature of environmental systems and building structures. Therefore, a probabilistic risk assessment (PRA) application of the J&E model has been developed to more effectively quantify risk and uncertainty at sites with potential vapor intrusion issues.

Approach/Activities. The Probabilistic Risk Informed Analysis for Vapor Intrusion (PRIA-VI) tool represents variable and uncertain parameters as distributions that can be used in Monte Carlo simulations to provide the best possible estimates of vapor intrusion based on complex inputs, such as heterogeneous subsurface conditions, changing weather patterns, and uncertain building foundation characteristics. The benefit of using a probabilistic application of the J&E model is that this approach: (1) is not a significant deviation from risk assessment practices currently approved by federal and state regulatory agencies; (2) provides a mechanism for quantifying the uncertainty and variability related to key input parameters for vapor intrusion investigations; (3) supports vapor intrusion investigations that use site characterization techniques familiar to environmental consultants, approved analytical laboratories, regulators, and responsible parties; and (4) supports dual tracking of probabilistic and deterministic risk assessments in the short term to foster an eventual transition from the traditional approach.

Results/Lessons Learned. The fundamental benefit associated with using the PRIA-VI tool is the potential for significant cost avoidance resulting from informed remedial decision-making at sites with potential vapor intrusion concerns, including lower remediation costs and decreased long-term costs associated with environmental monitoring and managing institutional/engineering controls.

Around the School in 40 Days—Assessment and Mitigation of Vapor Intrusion Potential on an Accelerated Schedule

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Background/Objectives. An expedited vapor intrusion investigation and mitigation program was conducted over a forty-day period to assess and address the vapor intrusion (VI) potential at a high school in New York that had been built on land previously used for a wide range of industrial activities. The sampling program began a few days after classes recessed for summer break and an optimized mitigation system was up and running prior to the start of classes in early September.

Approach/Activities. The VI assessment program was focused on twenty-three potential areas of concern (PAOCs) below the school that had been identified by the New York Department of Environmental Conservation (NYSDEC). The program included collection and analysis of more than three hundred twenty five (325) samples using field screening (PID & Landfill Gas meters), traditional summa sampling and high volume sampling (HVS) techniques. Initially, traditional indoor air and sub-slab summa samples were collected to conform to New York State's vapor intrusion assessment policies. Those samples were supplemented with HVS tests that included periodic field screening and summa sampling of a large volume (7,600 to 58,000 L) of extracted sub-slab vapor to more broadly characterize the distribution of volatile organic compounds (VOCs) below the slab at each PAOC. Rapid turn-around of the TO-15 analysis of the summa samples was used to expedite risk management decisions. Static vacuum and transient vacuum response data were also collected during the HVS tests to provide insights into the transmissive properties of the sub-slab fill material, and to support the design of a mitigation system, if needed, at any of the test locations.

Results/Lessons Learned. The results of the traditional sub-slab summa, PID screening and HVS summa samples were reassuringly consistent and were used to identify the presence of elevated concentrations (up to 39,000 mg/m^3) of TCE in the sub-slab vapor beneath one wing of the school. Based on the test results, a sub-slab depressurization system (SSDS) that included four suction points connected via a header system to a single riser and an Obar GBR 76 SOE fan was installed as an interim remedial measure (IRM) to reduce the vapor intrusion potential. Post-mitigation pressure field and indoor air testing were used to demonstrate the efficacy of the SSDS. Follow up testing will be conducted during the heating season to confirm those findings. These data support the use of HVS tests as an alternative to traditional sampling approaches. The HVS tests provide a more comprehensive depiction of sub-slab VOC distribution than traditional summa sampling and also fill facilitate design of an effective mitigation system where needed by providing insights into the transmissive properties of the sub-slab fill.

Back to Contents

Use of a Passive Vapor Intrusion Mitigation System for Beneficial Redevelopment of a State Superfund Site

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Background/Objectives. A site undergoing remediation under a state Superfund Registry Consent Agreement was purchased by a major retailer for beneficial redevelopment as a warehouse store. Groundwater and soils beneath the site are contaminated with BTEX and chlorinated volatile organic compounds. The new store is positioned directly over a large zone of impact.

Given the lack of vapor intrusion (VI) Applicable or Relevant and Appropriate Requirements (ARARs) for the site, the retailer proposed use of passive sub-slab depressurization. The governing agency made the following stipulations for any VI mitigation system at the Site: use of a liner that is chemically resistant to site constituents of concern (COCs); the passive system must be designed so that conversion to an active system could be readily accomplished; and development of criteria that would clearly establish when the system must be converted to an active system prior to system installation.

Approach/Activities. In order to meet the agency criteria and an agressive store opening schedule, the Geo-Seal vapor barrier system (manufactured by Land Science Technologies) was selected. The installed system consists of a multi-layer membrane, trenchless venting grid, and vent pipes equipped with wind turbines for sub-slab venting. The monitoring system includes nylon sample tubing affixed to soil vapor implants to facilitate sub-slab monitoring. Electrical conduits installed near rooftop vent locations allow for addition of blowers should conversion to an active system be necessary.

The system monitoring plan includes collection of sub-slab soil gas, vent riser gas, and indoor air samples using Summa canisters. Screening and action levels were developed for comparison to sub-slab soil vapor and indoor air concentrations, and decision rules for triggering conversion to an active mitigation system are based on these levels. Decrease in monitoring frequency will be decided based on results from a vapor intrusion evaluation

Results. Results from a sample event prior to store opening showed exceedance of the TCE indoor air action level at one location, however, sub-slab results showed the highest concentrations were four orders of magnitude below the screening levels. It is speculated that interference from building finishing materials caused the TCE exceedance in the store. Results from the subsequent first regular monitoring event did not show any screening or action level exceedances, but did indicate buildup of Site COCs underneath the vapor barrier. Results from the second semi-annual monitoring event will be available prior to the conference date.

Lessons Learned. Data obtained thus far show that passive vapor barrier systems can be effective in mitigating VI for chlorinated and non-chlorinated VOCs. Many state agency VI programs are new, which can lead to frustration and extra costs. Decision rules for monitoring of passive vapor barrier systems must clearly outline the basis for all actions to be taken and the steps that are to be followed should VI occur.

Taking the Pressure Off Sub-Slab Mitigation Design: New Methods for Design and Performance Monitoring

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Background/Objectives. Sub-slab depressurization (SSD) is the most common method of mitigation for radon and subsurface vapor intrusion to indoor air. The standards of practice for design and performance monitoring have changed little over the past few decades, which presents an opportunity for improvement using recently developed technologies. Performance monitoring has traditionally been focused on generating a sustained vacuum of several pascals everywhere below the building floor; however, this metric is challenged by baseline fluctuations in the cross-slab pressure differential. The objectives of this study were to demonstrate and validate an alternative design and performance monitoring approach that uses mathematical analysis of transient vacuum response data to calculate the transmissivity of the materials below the floor and the leakance of air across the floor, and independently verify the approach with independent lines of evidence including sub-floor helium tracer testing and mass flux monitoring.

Approach/Activities Optimization of an existing SSD system was performed at Building 205 at the former Raritan arsenal in Edison New Jersey. The system consists of 9 high vacuum radon fans, each connected via a header to three suction points. Testing included measuring individual vent-pipe flows and vacuums with a thermal anemometer and manometer, measuring a month-long time-weighted average concentration of VOCs in the discharge of each vent pipe, measuring transient vacuum response to turning the fans off and on in several locations, injecting helium below the floor in several discrete locations and measuring the breakthrough in nearby vent-pipes to measure the sub-floor flow velocities, running the system overnight with only a single fan (in the area of highest VOC flux) to characterize the vacuum distribution, and reversing the flow direction for one of the fans and blowing air amended with helium below the floor to track the rate of migration beneath the building. Radon was monitored in the exhaust of each fan, in indoor air and outdoor air. Attempts were also made to monitor CO_2 and formaldehyde, although these two parameters did not yield useful data.

Results/Lessons Learned. The total trichloroethene (TCE) mass flux withdrawn by all 9 vent fans is approximately 0.4 grams per day (g/d). Assuming an air exchange rate of at least 1 per hour, the mass flux of TCE that would be required to maintain an indoor air concentration of 2 mg/m^3 (approximate indoor air screening level) would be 2.6 g/d. The vent-pipe VOC vapor concentrations at the north end of the building were on average lower than the indoor air screening levels, indicating the concentrations of potential concern are limited to the southern end of the building. With only one fan operating in the southern portion of the building, vacuum of several pascals or more was achieved throughout the area of elevated vent-pipe VOC concentrations. The pneumatic testing showed the subfloor materials had a moderate to low permeability and the floor slab leakance was also low. The helium tracer testing demonstrated that a single fan can flush vapors from most of the area of interest within a few hours. These data support a reduction in operating costs (about $4,500/yr savings for electricity to power the fans and about $5,000/yr in the cost of building heating, ventilating and air conditioning). By redirecting the discharge of the one remaining vent-fan, the re-entrainment of radon was reduced so the health risks were actually reduced in the optimization process.

Model Applications for Soil Vapor Mitigation Design: Three Case Studies

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Background/Objectives. Vapor intrusion into buildings from soil or groundwater impacted by volatile organic compounds (VOCs) is often of concern at sites where limited remediation options exist, or where residual contamination following remediation poses a potential risk to human health through vapor exposure. Soil vapor fate and transport models such as the Johnson and Ettinger (J&E) model can be used to estimate attenuation factors for existing site conditions using simplifying assumptions about the building and soil properties. In cases where the subsurface soil is heterogeneous, or an active or passive ventilation component is considered as part of a soil vapor management system, a more customized model that accounts for site specific factors is required to estimate attenuation factors and optimize design parameters. The objectives are to present the use of two semi-analytical models and a numerical model that have been used in the design of vapor management systems.

Approach/Activities. We present three case studies for projects in France, Canada, and Australia, where a modified J&E model, a subslab depressurization (SSD) civil engineering design tool, and a reactive transport numerical model (MIN3P-DUSTY) were used, respectively, to support the design of soil vapor management systems. The case study in France involved a building development with a proposed ventilated parking garage at a site with PCE and TCE contamination in soil and groundwater. For this site, a modified version of the J&E model was used to accommodate a second sub-building compartment in addition to the building enclosure. The sub-building compartment can consist of a parking garage, crawlspace, aerated floor or gravel layer. The model was used to calculate the chemical mass fluxes in different compartments, including mass removed through garage ventilation. The second case study involved the use of a SSD design tool to predict pressures and flows in a pipe network and venting layer. Both an active (fan) or passive (wind turbine or stack effect) system may be considered, and pressure losses due to friction in a gravel layer or aerated floor and piping laterals/headers are calculated. Standard civil engineering formulas for pressure loss using the Colebrook equation and D'Arcy-Weisbach friction coefficient were used for the calculations. The tool enables the evaluation of various configurations of alternating air inlet and outlet pipes and the selection of appropriate fans or wind turbines. The third case study involved the use of the MIN3P-DUSTY model to evaluate the effectiveness of methane interception system configurations on the perimeter of a former landfill. The model was used in three dimensions to estimate the capture of methane by an interception system consisting of various configurations of shallow continuous trench and deeper gravel columns. Soil gas advection and diffusion of methane, carbon dioxide, and other atmospheric gases were considered in the model.

Results/Lessons Learned. In the first case study, the modified J&E model allowed for more realistic and less conservative estimates of vapor attenuation factors that could be applied to the risk assessment of the proposed building development for various types and dimensions of the building and the sub-building compartments. In the second case study, the results of the SSD design tool enabled the comparison of active and passive venting and the design of pipe network and fans. Data obtained during commissioning of the SSD indicated good comparison to model predictions for this site. Finally, for the third case study, the results of the 3D numerical model were used in recommending a configuration for the methane interception trench, where the modeling approach at this site was approved by the regulators.

Best Practices for Design and Operation of the Most Effective and Sustainable Active Soil Depressurization Systems

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Background/Objectives. Active soil depressurization (ASD) is a common technology utilized for mitigation of radon and chemical vapor intrusion (VI) into buildings. The technology involves the utilization of a fan or blower to induce vacuum or pressure gradient beneath the building foundation in order to maintain negative sub-slab pressure differential with reference to the indoor environment. When properly designed and operated, this type of mitigation system is capable of reducing soil vapors by 99% or greater in the indoor air environment while utilizing minor energy consumption (typically less than 100 watts per fan), thus making this technology one of the most effective and sustainable methods for the mitigation of chemical vapor intrusion. However, ASD technology is often incorrectly applied and maintained. The purpose of this presentation is to identify the best practices involved in and the factors that influence the design, installation, and operation of an effective and sustainable ASD vapor mitigation system. Such factors include, but are not limited to, client and property owner requirements, meteorological conditions, environmental and mechanical influences, sub-slab permeability, soil properties, preferential pathways, foundation walls, conveyance pipe routing options, and HVAC systems.

Approach/Activities. To install an effective ASD system, information about the building construction, building mechanics and all of the factors that influence VI must be evaluated and understood. Specifically, a pilot test/diagnostic evaluation is necessary to gather information on the ability to extend the pressure field throughout the area of impact, as well as characteristics of the building, such as mechanical influences and potential preferential pathways, that may impact the mitigation system design. These data are used to determine the type, design and location of the system(s) to be installed. However, pilot test diagnostics may not provide information on all of the factors that influence the success of an ASD system. A review of the installation of hundreds of ASD systems indicates that many factors including, complex foundation types and environmental influences, such as karst geology, need to be considered when designing and installing a mitigation system. To quantify the effect of these various factors, a scoring matrix was developed using data from multiple radon and chemical vapor intrusion mitigation projects. The scoring matrix considered the effectiveness of reducing the chemical of concern and the overall sustainability of the ongoing operation, maintenance and monitoring of the system. Based on this analysis, top-scoring mitigation systems were identified and further analyzed in order to characterize the common design and operation elements. Using these elements, best practices for the design and operation of the most effective and sustainable ASD mitigation systems were developed.

Results/Lessons Learned. The science behind VI and effective mitigation is still being studied and with each project, new lessons are learned and applied to future decisions. This presentation will discuss the results and lessons learned through the careful evaluation of the VI pathway and installation of hundreds of mitigation systems. Through a scoring matrix, the various factors that influence design, installation, and operation of an ASD system were identified and evaluated for optimizing system performance and sustainability. Moreover, the analysis demonstrated that some variables were more sensitive than others and that these factors should be considered more important when making decisions about designing and installing ASD systems.

Telemetric Management—The New Standard in Vapor Intrusion Mitigation Operations, Maintenance and Monitoring (OM&M)

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For the past 25 years technical advancements in soil depressurization systems and the application of allied technologies to better manage Vapor Intrusion sites have been at a virtual standstill. Post mitigation Operations and Maintenance Programs are typically proposed as part of commissioning reports but only occasionally do they advance to the next stage of field application. Schedules for site visits, manual monitoring of gauges and vacuum indicator lights are all listed in the O&M section of the commissioning report with the best of intentions but the reality is that an overwhelming number of systems are not attended to after start up or the conclusion of the first year warranty period. These practices have led to orphaned systems with tremendous shortfalls in the areas of stewardship and extended care for the health of the building occupants.

Advancements in telemetry and an increased awareness of the importance of delivering an extended standard of care have ushered in a new era of Vapor Intrusion Operations Maintenance, Monitoring and Management. Telemetric measuring equipment and active remote management equipment have been integrated into the installation process to facilitate real time monitoring and active offsite management. With a greater understanding of the need for continued care, consultants have been able to work with the responsible parties to include telemetric monitoring and active management into the sites long term stewardship agreement.

The presenter will discuss the framework of a comprehensive OM&M plan and explain how the application of telematics can achieve regulatory compliance, provide a greater level of care through real time performance monitoring, fault notification and active management with preemptive maintenance indicators. Through the implementation of energy saving dynamic controls and managed monitoring, consultants have gained a greater understanding of how vapor mitigation systems react to weather induced variables such as temperature change, wind loading and barometric shifts. This new information can now be applied to the design and start-up phase for improved efficiency and greater levels of occupant protection. Telemetrically managed systems can deliver automated regulatory and client reports all within the umbrella of energy savings, reducing operational costs and limiting liability.

Back to Contents

Assessment of Vapor Migration Pathways and Remedy Implementation to Achieve Screening Levels

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Background/Objectives. Past operations at a former dry cleaner resulted in soil and shallow groundwater impacts beneath and adjacent to the building. Prior to site redevelopment for a future restaurant, vapor intrusion risk was evaluated and a flexible remedial approach was developed. A series of mitigation measures and remediation technologies were implemented over a five year period before, during, and after re-development. The remediation efforts were conducted individually and in combination, which allowed for evaluation of their individual and collective impact on vapor intrusion.

Approach/Activities. The migration pathways of impacted soil vapor were evaluated through implementation of a helium tracer test, use of an infrared camera, and collection of vapor samples from an exterior concrete block wall. Soil and groundwater were characterized and 13 indoor air sampling events were conducted.

Source remediation of impacted soil was accomplished through selective excavation followed by application of a spray-applied vapor barrier. Additional changes included operation of a HVAC system designed to positively pressurize the building. An active sub-membrane vent system was powered by a low vacuum fan initially and subsequently upgraded to a regenerative blower. Influent samples were periodically collected from the vapor collection system. Source remediation of shallow groundwater beneath the building (at a depth of 2 meters below land surface) was conducted during the third year.

Results/Lessons Learned. Excavation of soils beneath the floor slab and vapor barrier installation resulted in PCE concentrations in indoor air decreasing by over 97.9 percent. Impacted soils located along the building footer were not excavated and likely contributed to continuing vapor intrusion. Results of a helium tracer test confirmed that vapor migration through the wall had the potential to circumvent the vapor barrier. Helium concentrations decreased one order of magnitude between the vadose zone and block wall and were another order of magnitude lower in indoor air. The attenuation of PCE concentrations displayed a similar relationship to that of helium. Operation of the HVAC system, which relies on outside make-up air, had a negligible effect on indoor air impacts likely due to its intermittent operation. Operation of an active vent system powered by a low vacuum fan only resulted in a modest decline in PCE indoor air concentrations. During operation of the regenerative blower, PCE influent concentrations from the sub-membrane extraction system declined over three orders of magnitude. Ethene, which was likely generated as a result of groundwater remediation, was detected in influent vapor samples and provided confirmation of the system's ability to capture at least a portion of vapors originating from shallow groundwater. This was further highlighted by a significant increase in PCE concentrations in the wall and indoor air after a temporary shutdown of the vent system. The active vent system's effectiveness was likely limited by placement of the extraction piping, which did not provide complete coverage beneath the entire building footprint. While significant reductions of PCE concentrations in groundwater were observed within two months after injection, corresponding maximum reductions to PCE concentrations in indoor air lagged and were not observed for another 12 months. The collective impact of the remedies resulted in PCE concentrations in indoor air declining over 99.8 percent compared to baseline conditions.

Vapor Intrusion Mitigation Under Surface Obstructions Using Horizontal Environmental Wells Applications and Results

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Background/Objectives. Dry cleaners, gasoline stations, factories and many other facilities have contaminated soils and groundwater beneath them. Remediation companies have tried a variety of methods to access contaminated soil and groundwater beneath these structures with varying degrees of success. Unless there is easy access to the facilities for vertical drilling machines or other heavy equipment to penetrate the floors and enough space to install conveyance lines and/or treatment systems, there have been few options for remediation.

Approach/Activities. Horizontal wells allow relatively easy access to contamination under buildings. Hundreds of air sparge, soil vapor extraction and amendment systems have been installed across the US with outstanding success. The lessons learned from the installation and operation of these remediation systems will provide information to the scientists and engineers considering their remediation options.

Results/Lessons Learned. The author(s) will provide a statistical analysis of the performance of dozens of horizontal remedial well installations. The analysis will include a discussion of the contaminants of concern, soil types, depth of installation and, where available, the results from the remediation efforts.

Vapor Intrusion Mitigation Issues Associated with Mercury-Impacted Soil and Groundwater

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Background/Objectives. Addressing vapor intrusion issues for mercury-impacted soil and groundwater is challenging due to the complexity of mercury in the environment. Due to the level of toxicity associated with mercury and its various potential forms in the environment a complete evaluation of mercury pathways is required. Mercury in soil and groundwater is found in multiple forms with varying levels of toxicity and mobility. In order to assess the pathways and mobility of mercury, speciation analysis must be conducted to establish mercury's form and its associated risks.

Approach/Activities. A site in New Jersey is currently being assessed to determine the appropriate remedy to address mercury in soils and groundwater. A conceptual site model was developed to allow a better understanding of mercury in soils and groundwater including its form and associated risks. The site is complicated by additional contamination associated with benzene in soils and groundwater at elevated concentrations. The conceptual site model had to account for various co-mingled levels of benzene and mercury and the potential synergistic effects of the two compounds interacting in the environment. Mercury speciation testing was conducted on representative soil and groundwater samples to establish the overall form and mobility of mercury. The mercury speciation results and conceptual site model identified the vapor intrusion pathway to be the major risk associated with the mercury-impacted soils.

Results/Lessons Learned. A vapor intrusion assessment was conducted to assess the potential for benzene and mercury vapors to impact nearby structures. The vapor intrusion assessment identified significant mercury vapors located in sub-slab soil gas and indoor air resulting in an Immediate Environmental Concern (IEC). A sub-slab depressurization system was installed to address benzene and mercury vapor intrusion. The depressurization system was effective at reducing the benzene vapors but not fully effective for mercury vapors in specific areas of the structure. Additional testing was conducted to evaluate the effectiveness of the mitigation system and the cause for continued mercury vapor detections in indoor air. Conclusions were presented for the continued levels of mercury in indoor air at the facility.

Control of Methane Intrusion in a Large Shopping Mall in São Paulo City, Brazil

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Background/Objectives. The Tietê River suffered a process of rectification in its stretch that crosses the north area of São Paulo City, Brazil, initiated in the 50s of the 20th century, which resulted in changes to the river course and in the urban utilization of areas that in the past harbored its floodplain. A wide area of this floodplain in the north bank of the river, which in the past harbored the Tietê River's flooding plain not yet rectified, received throughout the 1960s and 1970s soil resulting from excavations of several works in São Paulo's capital, in addition to solid waste from civil construction and municipal solid waste. In mid-1980s, the area received the implementation of its first big commercial center, which has been in operation since then. It was the first Shopping Mall in the north of São Paulo City, occupying an area of approximately 300,000 m^2 and nowadays is still one of the biggest commercial centers of Latin America, where about 150,000 people circulate on a daily basis. Environmental studies performed in the area in 2010 and 2011 identified the presence of methane gas in the surface immediately below the floor (sub-slab) per deep wells (1.5m) monitoring. In some occasional events in 2011, the presence of methane gas in interferences inside mall's floor, such as columns, junction boxes, electrical ducts and fractures on the floor, was also identified. Such situation characterized potential risk of flammability, creating the corresponding urgent demand for its control.

Approach/Activities. A series of investigation activities were done, as geophysics (ground penetration radar), soil gas survey, soil borings, installation of groundwater monitoring wells and installation of gas monitoring wells (sub-slab and depth). In the sequence, monitoring actions were developed and implemented inside the mall, also in the sub-slab region and in depth, in addition to a wide gas extraction systems acting in the solid waste mass on which the commercial center was built. It was used landfill gas drains, tubular-vertical gas drains and sub-slab gas drains depending on the soil lithology. Such systems, in operation since October 2011, promotes vacuum in the sub-slab area where methane was already measured, controlling the scenario of potential risk for methane migration. The general monitoring activities includes a daily-basis environmental monitoring to flammability risk in every place inside and outside the mall, and a monthly-basis monitoring of all the gas wells. Two pilot studies of air sparging tests were done in some specific areas, as a groundwater stripping pilot test aiming to decrease the methane gas concentration dissolved in the groundwater.

Results/Lessons Learned. This presentation will be about the initial scenario mapped, the establishment of investigation, monitoring and intervention criteria, as well as the engineering solutions adopted and the results of the air sparging and groundwater stripping pilot tests. We did a comparison between the theoretical mass of methane gas generated by the solid waste disposal (using USEPA methodology) and the current data of methane gas extracted by the drains and blowers in operation. We will discuss also the particularities regarding working in a very famous public commercial center with all polity pressure in the way.

Performance of an Active Aerated Floor Vapor Intrusion Mitigation System in a Large Building

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Background/Objectives. Vapor intrusion mitigation typically requires the removal of air from below the building slab to create negative pressures and/or dilute sub-slab vapor concentrations. The effort required to remove air from below the slab is directly related to the resistance of the sub-slab venting media to air flow. Therefore, traditional mitigation systems use clean gravel as the venting layer, with perforated pipe and/or geogrid venting strips to help convey the air to riser pipes. Nevertheless, considerable head loss can occur within the gravel and piping system, often requiring the use of several suction points and large fans to create the necessary air flow rate and vacuum levels for mitigation. Aerated floors provide an alternative vapor intrusion mitigation system that provides a continuous void space below the floor slabs, allowing more efficient venting of vapors. The objective of this project was to install an active aerated floor (Cupolex) in an approximately 23,000 square foot new building as a vapor intrusion mitigation system to mitigate the intrusion of benzene, utilizing a single riser and small 20 watt fan for air removal.

Approach/Activities. Design and implementation of a Cupolex active mitigation system was completed for an approximately 23,000 square foot building in Texas. Cupolex is a patented concrete forming system, which interlocks to create a continuous cover of the building's footprint and is made from 100% recycled plastic. The Cupolex forms were installed as slab-on-grade and concrete was poured directly over the forms. One 4-inch cast iron riser pipe was located in the northeast part of the building. After the building's foundation was poured and the riser pipe construction completed, a series of tests were conducted to evaluate the vacuum distribution in the building's sub-slab void space. The tests consisted of using two Radon Away fans, an RP-140 (~135 scfm at 0-inches water column (WC)) and an RP-265 (~334 scfm at 0-inches WC), on the building's riser pipe to pull air from the sub-slab void space. Differential pressure readings were collected at the riser pipe itself, as well as at two different locations on the building's foundation. The first location was located approximately 47 feet to the northeast of the riser pipe, and the second was located approximately 311 feet to the south of the riser pipe. Leak testing was also conducted along major joints in the building's foundation to evaluate if there were any preferential pathways for air to enter the sub slab void through the building itself during venting.

Results/Lessons Learned. The smaller of the two fans, the 20W RP-140, created a uniform 0.5 inch WC vacuum under the entire slab at an air flow rate of 30 scfm. The uniform vacuum indicates negligible friction losses at this air flow rate. Calculations show that a gravel venting layer would have required multiple and/or much larger fans to achieve the same vacuum levels. These results suggest that the Cupolex system is an effective means to control vapor intrusion, even using very low air flow in a very large building. In addition, the vacuum readings were well above the required levels for vapor intrusion mitigation and are easily monitored. The Cupolex system was also easily installed by an inexperienced crew and was conformable to a complex building geometry.

Back to Contents

State-Of-The-Practice: Military Munitions Response Program

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Background/Objectives. The purpose for this presentation is to provide an update on the state-of-the-practice for military munitions response from the perspectives of the contracting community, the Government agencies (who are doing the contracting and contractor oversight), and the Regulatory agencies. As a case study, the US Navy has been implementing a Non Time Critical Removal Action (NTCRA) at Operable Unit B-2 of the former Adak Naval Complex since 2013. The objective of the work is to clear former training ranges, impact areas, and disposal areas of munitions and explosives of concern (MEC). The work must be performed in a manner that ensures the site is safe for future re-use. This requires a well documented process that demonstrates that pre-determined performance requirements have been met to achieve regulatory concurrence. To achieve this objective the Navy's production contractor is required to have an internal QC program to monitor and document performance. A second QA contractor is the Navy's representative on the island and performs independent quality inspections. Over many years the Project Team (Navy, ADEC, EPA, contractors, etc.) has developed processes and procedures to manage the various aspects of the work and ensure a high quality end product.

Approach/Activities. The state-of-the-practice will be presented in the context of technical approach, safety, contracting and oversight, and regulation. “Technical Approach” will detail the requirements for the QC and QA programs, application of the geophysical program, and discuss how QC and QA interact. “Safety” will focus on current DDESB and NOSSA requirements for safety and how this impacts work on Adak. “Contracting and Oversight” will focus on considerations while developing contracts and recommendations for setting up the project to achieve success, particular focus will be on resolving QA/QC disagreement and the constraints associated with the current emphasis on fixed price contracting. Finally the regulatory agency perspective will detail the regulators role in the process, identify opportunities for involvement, and methods for evaluating/monitoring project quality.

Results/Lessons Learned. The presentation will provide a benchmark for each of the respective topic areas, discuss the path forward and describe any significant changes that are anticipated for the future and present a sampling of lessons learned. As a result of the robust quality process developed over the years on Adak we regularly have “lessons learned” incorporated into subsequent field seasons. This ensures efficiencies identified in one field season are passed onto the next and problems that occur are resolved prior to experiencing them again the following year. Some aspects of changes that have been implemented include: Increased QC of surface clearance, detailed requirements for clearing excavations, prompt response to QA/QC deficiency, changing IVS testing requirements, and the construction of contract terms and conditions.

Munitions Response Site Management: An Auditor's Perspective

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Background/Objectives. Since fiscal year (FY) 04 when the Department of the Navy (DON) established their Munitions Response Program, they have spent $480M to clean up former ranges, depots, and manufacturing facilities contaminated with Munitions and Explosives of Concern (MEC). By FY19 the MRP budget is projected to grow to $225M per year. Back in FY04, in an effort to ensure there was sufficient oversight of the new MRP, the Chief of Naval Operations tasked the Naval Ordnance Safety and Security Activity (NOSSA) to establish a verification program to ensure MEC contractor performance met DON requirements. Auditing MEC contractors while they executed work at Munitions Response Sites (MRSs) was considered an essential part of this oversight program.

Approach/Activities. Between FY05 and FY14 the author audited MEC contractors at 82 MRSs on current and former Navy installations scattered throughout the Continental United States, Alaska, Hawaii, and Guam. The purpose of the audits was to ensure the MEC contractors were complying with applicable explosives safety, environmental and occupational health and safety requirements, and that in the cleaner property was suitable for reuse or for transfer back to the private sector.

Results/Lessons Learned. This presentation summarizes the auditor's analysis of ten years' worth of NOSSA audits, identifies trends, and offers suggestions to improve MEC contractor performance.

Upgrading the Munitions Classification Polarizabilities Library

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Background/Objectives. Munitions response site management strategies are constantly evolving to include and make the most of what advanced electromagnetic induction (EMI) sensor systems have to offer. What started as government-funded project developments, these systems and supporting processing software are now commercially available and have largely been accepted as essential tools in any munitions response project arsenal. Their foremost strength is in the ability to classify buried metal items as either munitions, or scrap that can be left in the ground. This is performed by using the system response model to extract polarizability curves characteristic of the item being measured and comparing them to a library of munitions curves. The currently available library, however, is limited in both its applicability and scope. We are, therefore, in the process of upgrading the library to address the two deficiencies by: 1) expanding the classification capability to survey data; and, 2) adding library entries for less common munitions.

Approach/Activities. The approach to meet our objectives is to gather data using three different advanced EMI systems – the MetalMapper, TEMTADS2x2 and a modified PEDEMIS – over items from the Blossom Point inert munitions repository, followed by visits to a number of munitions museums with one of these sensors. The first phase has already started and involves collecting controlled table-top measurements for each unique item of the repository using three different sensor acquisition parameter settings – the common survey mode setting and two standard static mode settings. These settings result in munitions polarizability curves over three distinct decay windows – i.e. 2.78 ms, 8.33 ms and 25 ms – that may be perceptibly different for a given item in agreement with the underlying physics.

Results/Lessons Learned. A couple of results are expected to emerge from the data collection effort. The first is that the three libraries will be applicable to a number of advanced EMI systems, with the relevant library depending on the acquisition parameters being used. The second result will be a larger library including a wider range of munitions. The lessons learned during the project will be documented in a standard operating procedure that will allow members of the community to easily and confidently make their own additions to any of the three libraries. A thorough discussion of the data collection effort and the library generation process, along with lessons learned along the way, will be presented.

Adaptations to Digital Geophysical Mapping (DGM) Instrument Verification Strip (IVS) Metrics to Account for Rough Terrain: A Case Study

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Background/Objectives. The Instrument Verification Strip (IVS) was developed to replace the expansive Geophysical Prove Out (GPO) in Munitions Response Sites (MRS) as a reliable and efficient way to verify the geophysical equipment used for Digital Geophysical Mapping (DGM) is working properly. Generally speaking, an average IVS consists of 5 Industry Standard Objects (ISOs) buried at various depths and orientations and sized to imitate potential munitions in the field. The advantage of ISOs is that they are consistent in design and construction; therefore the DGM response (amplitude) at various depths can be reliably computed and then compared to IVS surveys collected prior to and after DGM activities occur. The typical metrics to which the collected data are held to are generally positional +/- 9.8 in., and amplitude no greater than 20-25% the running average. As such, these metrics were also applied to the MRS in Adak, Alaska, a site characterized by rough terrain and steep slopes. In this project, three separate IVSs were utilized due to logistical reasons. These IVSs served six production DGM teams, one QC DGM team and one QA DGM team.

Approach/Activities. After three weeks of data collection, it became apparent that the typical amplitude metrics were not appropriate for the Adak project. The terrain on Adak is comprised of very uneven tundra overlying the soil, where distance from the tundra (or walking surface) to the soil can vary significantly over a few feet. In a couple of cases, surface water turned the tundra/soil into mud with only a couple of passes by a DGM team. A stretcher transport mode was used for the DGM system primarily to accommodate the lumpy and often steep terrain. The combination of the variable terrain and sensor bounce introduced by the transport mode resulted in varying coil distances from the ground and thus the ISOs. In contrast, in typical IVS installations in flat terrain using a cart mode transport, the coil height is much better controlled. In the second week of IVS measurements on Adak the six DGM teams had a total of 17 amplitude failures, and in the third week had another 16 amplitude failures. However, no positional failures were reported. Exceedances were recorded as both positive and negative, ranging from an average of about +40% to -35%. Note that despite the individual team's variance, the all team's average was consistent from week to week.

Results/Lessons Learned. As per the work plan, a non-conformance report was issued. A detailed analysis was conducted concluding that, because of the terrain features and EM61 MK2 transport mode, new amplitude metrics should be adapted. In addition to the positional metric, which was now based on a run forward and backward, the amplitude metric was now no more than 3 ISOs exceeding +40% to -35% of the previous week's average of all teams. To supplement the IVS test, a static spike test was also implemented where an ISO was set at fixed position and the amplitude of each time gate channel was recorded, with passing metrics set at measured values of each channel within +/- 10% of the initial measurement and all teams within +/- 25% of the average of all team's initial measurement. After the implementation of the new IVS metrics, there were no significant failures spanning the 2013 and 2014 field seasons. As a contrast, IVS data collected at an MRS in Concord, California in 2012, characterized by flat, dry terrain where all of the surveys were collected with an EM61 MK2 in cart configuration, showed that amplitude variations were always less than 20% and typically about 10% of the average. These results are more consistent with what we were expecting for Adak until the issues of terrain and transport mode were identified.

Back to Contents

Geophysical and UXO Operations In Support of Soil Remediation, South East Kuwait

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Background. The Kuwait Oil Company (KOC) has developed a strategy of "Sustainable Environmental and Economic Development" (SEED). Under SEED, KOC is carrying out remediation and rehabilitation of a number of contaminated features within the South and East oilfield assets associated with oil and gas exploration and production. These features include gatch (borrow), effluent, and sludge pits that resulted from oilfield operations. As a consequence of the 1991 Gulf War, there is a potential for explosive remnants of war (ERW) or unexploded ordnance (UXO). This potential safety hazard must be investigated and removed prior to conducting intrusive remediation activities. AMEC was contracted as the project management consultancy (PMC) to oversee the works during the UXO investigations as well as all aspects of the remediation effort under SEED.

Objectives. As part of this project, an AMEC geophysicist and UXO technical expert have been engaged as consultants in oversight of assuring that the prime contractor hired qualified UXO and geophysical sub-contractors to perform UXO detection and intrusive investigation of target anomalies found during the digital geophysical mapping and target anomaly selection. The AMEC tasks also included review, comment and support to the subcontractors to assure quality plans, methods statements and quality assurance procedures for accurate detection, thorough intrusive investigations, and sound site clearance certificates were produced prior to remediation activities.

Approach. Kuwait Oil Company initiated a process prior to contracting that screened a pool of qualified remediation contractors. In addition, screening was performed for UXO Contractors and UXO Detection Contractors. Subsequently, three remediation contractors were hired and required to select the UXO and detection contractors from the approved list. AMEC's UXO and Geophysical Specialists reviewed the qualifications of personnel from these selected subcontractors and provided recommendations where improvements were needed. Contractors were required to employ International Mine Actions Standards (IMAS) qualified UXO personnel for project oversight, Battle Area Clearance and UXO investigation and identification. Also required of each contractor was a qualified UXO geophysical lead and data processing personnel. All UXO and detection personnel were required to have experience with the geophysical detection systems, and the processor was to have thorough knowledge and experience with UXO geophysical data processing software and interpretation.

Results/Lessons Learned. The prime contractor was a remediation specialty company or engineering firm with credentials for this work. Though a qualified UXO and detection team was hired, the prime contractor had no experience or knowledge of UXO operations, the detail required for this work nor the time required undertaking these operations safely. In addition, the logistics of working in the Kuwait oil fields with climate extremes as well as difficult remediation sites posed extreme challenges. This included munitions response strategies for investigation requirements in extreme heat, limited working hours in summer months, working in gatch pits, effluent pits and sludge pits to detect and remove anomalies that could be UXO.

Back to Contents

Novel Microorganisms Linked to RDX Degradation Across Soil Communities

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Background/Objectives. The explosive RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) has contaminated many military sites. This chemical is particularly problematic because it is highly soluble and toxic and has the potential to move off-site. The objective of this study is to identity the microorganisms able to degrade RDX across a number of soils. The final aim is to create a short list of microorganisms linked to RDX degradation in soil samples, so that removal through natural attenuation can be better predicted.

Approach/Activities. The work investigated RDX degradation in four agricultural soils and one soil from a Navy Base (from a denotation area). To determine which microorganisms were responsible for RDX removal, stable isotope probing (SIP) was combined with high throughput sequencing. SIP experiments involved the exposure of microcosms to labeled ($^{13}C_3$, 99%; $^{15}N_3$) or unlabeled RDX (present as the only nitrogen source). Following complete RDX degradation, DNA was extracted, ultracentrifuged and then fractioned. The fractions generated were amplified using a set of multiplex indexed primers targeting the V4 region. In addition, total DNA extracts from the initial soils, from the RDX degrading microcosms and from no RDX controls were submitted for sequencing. The samples were sequenced with the Illumina MiSeq platform using a standard MiSeq paired end (2x250 bp) flow cell. The high throughput data generated were analyzed using Mothur.

Results/Lessons Learned. RDX degraded faster in the agricultural soils compared to the soil from the Navy Base. The SIP results indicated different phylotypes were linked to label uptake. The sequencing results from the total DNA extracts also generated interesting data. In the agricultural soils, several common phylotypes were more abundant in the RDX amended microcosms compared to the no RDX controls. Specifically, either unclassified *Bacillaceae* 1 and *Brevundimonas* or both illustrated an increase in abundance following RDX degradation. These data indicate, that, at least agricultural soils, these phylotypes are important for RDX removal. In the soil from the Navy Base, five different phylotypes illustrated an increase in relative abundance in the RDX amended microcosms compared to the no RDX controls suggesting these were key microorganisms involved in RDX degradation. From these five phylotypes, only *Pseudomonas* has previously been linked to RDX degradation in pure cultures. To our knowledge, this work represents the first attempt to combine both SIP and high throughput sequencing to investigate RDX degraders and provides a short list of phylotypes linked to RDX degradation in mixed communities.

Evaluation of RDX Biodegradation using C and N Stable Isotope Analysis

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Background/Objectives. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is a common groundwater contaminant at current and former military facilities, including many training and testing ranges. One potential remedial alternative for military ranges and other facilities is monitored natural attenuation (MNA), in which contaminant losses by natural chemical and biological processes are evaluated. However, one limitation of this approach for RDX is the inability to accurately evaluate whether the nitramine is biodegrading under field conditions, particularly in groundwater, where rates may be relatively slow. The objective of this study was to quantify the microbial fractionation of C and N stable isotopes in RDX under both aerobic and anaerobic conditions and to assess whether such isotopic fractionation could be used to document RDX biodegradation in the field.

Approach/Activities. Gas-chromatography isotope-ratio mass spectrometry (GC-IRMS) methods were developed to quantify stable isotope ratios of both nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) in RDX. These methods were subsequently used to assess stable isotope enrichment during aerobic and anaerobic degradation of RDX by eleven different pure cultures that degrade the nitramine through known aerobic and anaerobic pathways. Stable isotope ratios of C and N also were analyzed in RDX extracted from groundwater samples from an active DoD range where a biobarrier was installed to enhance anaerobic degradation of RDX in groundwater.

Results/Lessons Learned. There were clear distinctions in the stable isotope fractionation which occurred via aerobic and anaerobic RDX degradation pathways. Among four aerobic RDX degrading strains that were tested, fractionation of N but not C was observed. The mean $\varepsilon^{15}N$ for the four strains was -2.4 ± 0.5 ‰, and the $\varepsilon^{13}C$ was -0.3 ± 1.0 ‰ (not different from zero). A larger N fractionation ($\varepsilon^{15}N$ between -6.8‰ and -13.2 ‰ for different strains) was observed for seven different pure cultures degrading RDX through various anaerobic pathways. This large N fractionation is consistent with various proposed mechanisms of initial enzymatic attack on the RDX molecule, most of which involve a N-N bond. Interestingly, fractionation of C in RDX under anaerobic conditions also was observed ($\varepsilon^{13}C$ between -2.1‰ and -7.1‰ for different strains). In groundwater samples from an active range, the $\varepsilon^{15}N$ in RDX was -7.8 ‰, and $\varepsilon^{13}C$ was -2.7 ‰ downgradient of a biobarrier, which confirms RDX biodegradation, and is consistent with data from pure cultures under anaerobic conditions. Overall, the results suggest that stable isotope analysis can be a viable approach to document aerobic or anaerobic RDX biodegradation.

A Pilot to Full-Scale Success Story: Combined Anaerobic Biostimulation and Aerobic Bioaugmentation for Explosives-Contaminated Groundwater Cleanup

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Background/Objectives. Explosives-containing wastewater disposal to unlined lagoons contaminated groundwater at the Umatilla Chemical Depot (UMCD) near Hermiston, OR. Less soluble explosives (e.g. TNT) generated a small plume whereas highly soluble RDX formed a larger plume currently over 200 acres in size. In situ bioremediation is being considered for optimizing the increasingly inefficient pump & treat groundwater remedy. Anaerobic biostimulation was previously demonstrated to effectively reduce groundwater explosives concentrations in single well push-pull tests (PPTs) at UMCD (Michalsen et al. 2013). In addition, *aerobic* bioaugmentation is an innovative RDX remediation approach that has potential to preserve groundwater quality and significantly reduce growth substrate quantities required compared to anaerobic biostimulation. Three field-scale tests were performed to transfer pilot results into full-scale design; test objectives included verifying 1) anaerobic biostimulation could achieve and sustain explosives concentration reduction to cleanup levels; 2) injection/extraction wells could achieve desired growth substrate distribution at field scale; and 3) *aerobic* bioaugmentation is cost effective compared to anaerobic biostimulation.

Approach/Activities. First, corn syrup (substrate)-amended site groundwater was injected through an infiltration gallery underlying the original source area 3 times over the course of 2 years. Second, substrate-amended groundwater was injected into 3 wells over a one month period while using extraction wells to facilitate distribution. Third, a series of replicate PPTs were conducted to quantify rate and extent of RDX transformation in wells that received aerobic bioaugmentation treatment (see Crocker et al. abstract) compared with wells that received aerobic and anaerobic biostimulation treatments.

Results/Lessons Learned. Infiltration gallery injections successfully achieved targeted 24 mM substrate concentration over 1.5 acres within the source area, reduced explosives concentrations to cleanup levels, and sustained reduced concentrations over 2 years via anaerobic biostimulation. Substrate-amended groundwater injections in three wells under forced gradient conditions followed by ambient gradient transport achieved substrate distribution over 2 additional acres. Preliminary PPT results showed that aerobic bioaugmentation supported rapid, more complete RDX removal compared to aerobic biostimulation. However, RDX degradation rate and extent decreased with time in the aerobic bioaugmentation treatment, possibly due to substrate concentration and injection frequency. Anaerobic biostimulation PPT results are currently pending. Cell transport tests confirmed ability to transport the RDX-degrading strain *Gordonia* sp. KTR9 over 10s of feet in situ; a larger-scale test is planned for October 2014 to confirm cell transport over 100s of feet. Field-scale testing results support use of anaerobic biostimulation in the comingled source area explosives plume and aerobic bioaugmentation in the distal RDX plume. Strategically phased pilot and field-scale testing supported efficient remedy optimization decision making and accelerated progress towards full-scale design. Full-scale remedial action construction is tentatively scheduled to begin in 2015.

Biodegradation of the Insensitive Explosive, 2,4-Dinitroanisole

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Background/Objectives. 2,4-Dinitroanisole (DNAN) is an insensitive munitions ingredient used in explosive formulations as a replacement for 2,4,6-trinitrotoluene (TNT). TNT has been a major component of military munitions for nearly a century. Over the past 30 years there have been numerous attempts to develop biocatalysts for destruction/degradation of TNT with very limited success. The enzymes that are known to attack TNT all require substantial amounts of energy input in the form of external cofactors and electron donors. Such enzymes are very fragile outside the cells that produce them. As a result there are no bacteria that grow using TNT as a carbon source and no enzymes that can attack TNT in the absence of highly specialized conditions. In contrast, there are recent reports of microbial transformation of DNAN to dead-end products although no bacteria with complete biodegradation capability have been reported.

Approach/Activities. *Nocardioides* sp. strain JS1661 was isolated from activated sludge based on its ability to grow on DNAN as the sole source of carbon and energy under aerobic conditions. The genome was sequenced and the genes encoding the catabolic pathway were identified.

Results/Lessons Learned. Enzyme assays indicated that the first reaction involves hydrolysis of DNAN to produce stoichiometric amounts of methanol and 2,4-dinitrophenol (2,4-DNP), both of which are biodegradable by a variety of soil bacteria. The hydrolase is stable and robust in preliminary experiments and the genes that encode its synthesis have been identified and sequenced. The enzyme requires no cofactors and is highly active and robust outside the bacterial cells that produce it, thus there are no obvious constraints to its application in a variety of aqueous systems. Growth yield and enzyme assays indicated that 2,4-DNP undergoes subsequent degradation in the isolate by a previously established pathway involving formation of a hydride-Meisenheimer complex and release of nitrite. The catabolic pathway seems to have been assembled recently by recruitment of the genes encoding the hydrolase to extend the well-established 2,4-DNP catabolic pathway. The discovery of the enzymes involved in DNAN degradation will potentially provide the basis for the development of DNAN detection and destruction technologies that will be much simpler than current technologies for dealing with TNT.

Environmental Fate and Transport of a New Military Explosive, IMX-101

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Background/Objectives. As the US military begins replacing TNT with the newly approved IMX-101 munition formulation, research should be directed to understanding the environmental transport and fate of IMX-101. This new insensitive munition, IMX-101is composed of 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-trizole-5-one (NTO), and 1-nitroguanidine (NQ). The manufacture and use of IMX may result in contamination of soils and surface waters and result in industrial wastewater needing treatment. There is little known about the fate and transport of the IMX-101 constituents DNAN and NTO on testing and training range soils.

Approach/Activities. Laboratory studies were undertaken to 1) identify microorganisms capable of degrading DNAN and NTO, and measure the rate of growth and degradation of these organisms, 2) evaluate the potential dissolution rate of IMX-101 particles under simulated rainfall conditions, 3) evaluate soil sorption coefficients for IMX-101 constituents, and 4) evaluate contaminant removal from soil and/or uptake by grasses from IMX-101 contaminated soils.

Results/Lessons Learned. Simultaneous aerobic biodegradation of the IMX-101 formulation constituents 2,4-dinitroanisole (DNAN), 3-nitro-1,2,4-triazol-5-one (NTO), and nitroguanidine (NQ) was observed producing: nitrourea, 1,2-dihydro-3H-1,2,4-triazol-3-one, and 2,4-dinitrophenol. The enrichment culture maximum specific growth rate of 0.12 per hour and half saturation constant of 288 mg per L during degradation of IMX-101 as a sole nitrogen source suggest that enrichment culture growth kinetics may closely relate to those of other explosive and nitroaromatic compounds. IMX-101 particles were found to dissolve slowly under simulated rainfall conditions with NQ and NTO dissolving first, leaving DNAN crystals. DNAN and NTO sorption to soils fit Freundlich isotherms. DNAN and NQ were shown to be taken up into the roots and shoots of a mixture of grasses during phytoremediation of soils contaminated with up to 50 mg per kg of IMX-101. Complete degradation of IMX-101 to below detection limits occurred over 225 days. These studies will aid in understanding the fate and transport of these compounds in the environment and in the development of treatment strategies.

Back to Contents

Production, Fate and Transport of Microscale Energetic Residues

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Background/Objectives. Military training activities at operational ranges result in the production and dispersal of munition constituents (MCs). These compounds are persistent in the environment, and can serve as a source of contamination of groundwater and surface water. While the larger residues (>1 mm) produced from high- and low-order detonations are being studied with regards to their dispersal and dissolution, the production, transport, and fate of microscale MC residues (, especially the <50 µm sized material) has not been extensively examined. These microscale MC residues have the potential to be transported by percolation and surface runoff during precipitation events, and serve as a mobile and fast dissolving sources of explosive compounds (i.e., HMX, RDX, TNT) that can facilitate migration to groundwater and surface water receptors.

This research used Composition B (Comp B) as the model MC for this research, given its widespread use and that it contains the widely detected explosive compounds TNT and RDX, and examined the main fate and transport processes believed to control the production, movement, and dissolution of microscale energetic compounds on testing and training ranges.

Approach/Activities. Laboratory experiments have simulated the likely processes that allow distribution of Comp B detonation residues on testing and training ranges. Macroscale residues (>0.5 cm) were shown to breakdown under realistic simulated precipitation, producing a flush of microscale particles (mean particle diameter ~10 µm), followed by a sustained release of particulates. The particulate mass released from Comp B residues averaged around 20% of the total explosives mass released during precipitation-driven weathering.

Microscale particles (20-45 µm diameter) of Comp B applied to the surface of sand columns were shown to migrate into the sand farther than mm-sized Comp B particles upon application of artificial rainwater. The migration of the microscale Comp B resulted in a larger effective contact time with the infiltrating rainwater, and increased dissolved concentrations of explosives in the column effluent when compared to the mm-sized particles.

When examined in flow-through dissolution chambers that did not allow for particle movement, the inherent mass transfer coefficients for microscale and mm-sized Comp B particles were similar on a surface area normalized basis, indicating that previous determination of mass transfer coefficients for a range of energetic compounds should be scalable. However, an inverse relationship was observed between the Comp B particle diameter and the RDX:TNT mass transfer rate coefficient ratio for dry-attritted particles, which suggests that RDX may be more readily dissolved (relative to TNT) in microscale particles compared to macroscale particles. Additionally, microscale Comp B particles that were produced by aqueous weathering exhibited mass transfer coefficients that were up to 20-fold higher than dry-attritted particles, indicating that once the inherent low-wettability (e.g., hydrophobicity) of Comp B particles is overcome, more rapid dissolution is possible. This may be of special concern in wet areas of ranges (e.g., marshes, swales, ditches).

Results/Lessons Learned. This research has demonstrated that microscale particulates can be generated from larger Comp B detonation residues. These microscale particles can migrate into the soil profile, thereby increasing their contact with infiltrating rainwater, and giving rise to elevated dissolved explosives concentrations. While the surface area normalized mass transfer coefficients are comparable between microscale and mm-sized Comp B residues, there are indications that the mass transfer coefficient ratios for the components of Comp B vary with particle size. The environment and manner in which particles form (e.g., dry vs. wet attrition) also needs to be taken into consideration. This information should lead to better modeling of energetic compound fate and transport on testing and training ranges.

Engineering Arabidopsis to Detoxify the Environmental Pollutant and Explosive 2,4,6-trinitrotoluene (TNT)

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Background /Objectives. The explosive 2,4,6-trinitrotoluene (TNT) is a major, worldwide military pollutant. The presence of this toxic, and highly persistent, pollutant at military sites and former manufacturing facilities presents various health and environmental concerns. The Environmental Protection Agency has classified TNT as a class 1 carcinogen and, along with the military, they are addressing methods by which TNT can be contained and detoxified on military ranges. The bioremediation of TNT has proven to be particularly challenging because the chemically resistant structure of TNT means that it is highly recalcitrant to biodegradation by microorganisms. In line with this, plants have only a limited innate ability to detoxify the levels of TNT found at contaminated sites. The main objective of this study is to understand the biochemistry behind the detoxification of TNT in plants and use this knowledge to engineer enhanced resistance and detoxification capabilities *in planta*.

Approach/Activities. Microarray analysis, and subsequent quantitative PCR analysis, on TNT-treated Arabidopsis plants revealed eight upregulated tau class glutathione transferases (GSTs), with GST-U24 and GST-U25 being significantly up-regulated in response to TNT. Following affinity chromatography purification and characterization of recombinant forms of both enzymes, we identified three distinct TNT-glutathionyl conjugates. GST-U25 produced pH-dependent ratios of these three conjugates and HPLC-based assays, with subsequent mass spectrometry and NMR spectroscopy, identified conjugate 3 as 2-glutathionyl-4,6-dinitrotoluene. The production of conjugate 3 is concurrent with the release of nitrite. As it is the electron withdrawing nitro groups on the TNT molecule that provide stability to the aromatic ring through resonance, 2-glutathionyl-4,6-dinitrotoluene has the potential to be more amendable to subsequent biodegradation than the TNT-GSH conjugates. In order to further investigate the detoxification abilities of these GSTs *in planta*, both GST-U24 and GST-U25 were constitutively expressed in Arabidopsis. Soil studies and hydroponic cultures using a range of TNT concentrations were used to evaluate the detoxification abilities of the GST over-expression lines.

Results/Lessons Learned. In Arabidopsis, GST-U24 and GST-U25 contribute to the TNT detoxification pathway and the over-expression of these GSTs confers enhanced resistance to TNT. In TNT-contaminated soil, GST over-expressing plants produced larger shoot and root biomasses, and removed more TNT from the soil than unmodified plants. In hydroponic-based experiments, conjugate 3, 2-glutathionyl-4,6-dinitrotoluene, was detected in the medium from GST-U25 over-expressing plants dosed with TNT whereas conjugates 1 and 2 were not, suggesting that the cytosolic pH environment favours the production of conjugate 3. The removal of TNT from the soil by the GST over-expression lines correlated with a reduction in glutathione levels, indicating that glutathione could be limiting detoxification of TNT at the higher concentrations found on military ranges. These results will aid the selection of more robust plant species for the phytoremediation of TNT.

Simulating Biodegradation Kinetics of TNT to TAT via Isomeric DANTs/ADNTs for Bioremediation at TNT-Contaminated Sites

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Background/Objectives. 2,4,6-Trinitrotoluene (TNT) reductive biodegradation progresses through the sequential reduction of each nitro group to an amino group and leads to the formation of much less toxic 2,4,6-triaminotoluene (TAT) via isomeric aminodinitrotoluene (2-ADNT and 4-ADNT) and diaminonitrotoluene (2,4-DANT and 2,6-DANT) intermediates. Thus, bioremediation via enhanced in-situ biodegradation (EISB) is potentially a viable in-situ remedial alternative at sites with TNT contaminated groundwater. However, prior attempts at simulating the kinetics of TNT reductive biodegradation have been unsuccessful at addressing the fate of its degradation products due to the complex branching of pathways involved. This is in contrast to the similar but linear process of reductive dechlorination whose kinetics are well understood and incorporated in a number of multi-species reactive solute transport codes. A review of the literature points to gaps in the ability to describe and mathematically simulate the complex branched kinetics involved in the reductive biodegradation of TNT during EISB. This talk will present a mathematical model developed for simulating complex kinetics of TNT reductive biodegradation and validated using data from controlled laboratory experiments. The aim of our work is to provide a non-prescriptive framework that provides sufficient flexibility for application to reductive biodegradation pathways of other similar recalcitrant contaminants.

Approach/Activities. Two previously published laboratory studies of TNT biodegradation, in both presence and absence of sorption were chosen to validate the model. The proposed kinetic differential equations based on modifications to the Michaelis-Menten kinetic model describing the rate of biodegradation were converted to finite-difference formulations and solved by employing an explicit solution. To address branched pathways where a parent compound degrades to multiple daughter compounds, a novel branching coefficient was introduced. Sorption was incorporated using a linear equilibrium isotherm. The mathematical model does provide flexibility to substitute other sorption models (non-linear equilibrium and kinetic). Microbial growth lag time as well as inhibition by indigenous and competing electron acceptors was also incorporated The goodness of fit of the model equations to the experimental data was evaluated by calculating the coefficient of determination R^2. A sensitivity analysis was performed for each compound to minimize the number of calibration parameters by identifying the correlated and excluding the insensitive calibration parameters. The values of the calibration parameters in the model were determined by systematically adjusting inputs in order to achieve the smallest value of the residual sum of squares and evaluating the best visual fit to the data.

Results/Lessons Learned. Excellent correlation was observed between the model calculated and experimentally observed concentrations of TNT and its biodegradation products and the total mole balance for the two prior published laboratory studies, both in the presence and absence of sorption to clay. The model calibration determined maximum specific rates of biodegradation decreased with increasing substitution of nitro groups with amino groups from TNT to TAT and correlate well with the progressively increasing reducing conditions required for reduction of each subsequent nitro group to an amino group. The biodegradation of DANTs was found to be strongly inhibited by the presence of ADNTs which corresponds well with the reduction of DANTs determined to be the overall rate-limiting step in the reduction of TNT to TAT in the experimental studies. The total molar balance calculated decreases with the formation of TAT thus providing evidence of TAT's biodegradation to unidentified compounds.

Optimization of Remedial Approach for Treatment of Contaminated Groundwater at a Former Munitions Constituent Manufacturing Facility

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Background/Objectives. The former West Virginia Ordnance Works, now the McClintic Wildlife Management Area (MWMA) near Point Pleasant, WV was used by the US Army to manufacture 2,4,6-trinitrotoluene (TNT) during the early 1940s. Residual nitroaromatic contamination is still present in some areas of the site which is listed on the National Priorities List (NPL). A wastewater handling system (consisting of a pumping station, two small tanks, and two large earthen constructed wet wells) was used to handle red and yellow wastewaters during TNT manufacture. A record of decision was approved in 1988 to address contamination in these areas. The remedy included groundwater extraction and treatment until cleanup criteria were met. A groundwater treatment system was constructed and operation began in 1997. After six months of operation, the system was shut down due to discharge violations. The system was restarted in late 2000 and continues to operate nearly continuously. Excavation and treatment of approximately 1,000 cubic yards of contaminated soil was completed in 2004 and new extraction wells were installed in a more highly contaminated area in 2005. New extraction wells are achieving capture; however, contamination levels have remained essentially constant. A treatability study using in situ enhanced bioremediation was conducted 2008-2010 which was very effective in reducing concentrations of nitroaromatics; however, concentrations rebounded once the carbon source was exhausted, indicating a contaminant source may still be present. A study began in January 2014 to further characterize soil and groundwater to better identify the contaminant source, and fate and transport. Recommendations will be made to optimize the remediation approach.

Approach/Activities. Field activities include approximately 20 soil borings drilled using direct-push techniques to collect soil samples and 15 temporary piezometers installed to collect groundwater samples. Following review of soil and groundwater data, four permanent groundwater wells will be installed. Groundwater samples will be collected from the four new wells and 14 existing wells. Groundwater level measurements and contaminant concentrations (both historic and current) will be used to develop a fate and transport model. Recommendations will be developed to optimize remedial action at this site that will provide an exit strategy for the existing operating extraction and treatment system.

Results/Lessons Learned. This paper will present the methods and techniques used to complete the field sampling activities. Results of these sampling activities, modeling results and findings will also be presented. All laboratory analytical results are expected to be available at the time of the conference. Any lessons learned associated with this expanded characterization of the site will be discussed along with recommendations for future remedial actions for optimization of remedial approach to achieve site closure.

Natural Attenuation of RDX on an Active Hand Grenade Range

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Background/Objectives. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is an important component of many explosives and is commonly found in military training ranges. Due to its low sorption and biodegradation properties under typical field condition, it expected to be mobile and eventually leach into groundwater. RDX leaching is an important concern since it has been classified as a potential human carcinogen by U.S. EPA. In this project, a series of laboratory and field experiments are being conducted to improve our understanding of the key factors controlling Monitored Natural Attenuation (MNA) of RDX and other munitions constituents (MCs) in two throwing bays (A and B) at Range RG40, an active hand grenade range at Fort Bragg, NC.

Approach/Activities. Range RG40 has been in almost daily use for over 20 years. Soils at the site consist of sandy loam and sandy clay loam. In March 2013, instrumentation was installed to monitor changes in soil moisture and its impact on redox condition. Suction and bucket lysimeters were installed and sampled quarterly to evaluate RDX leaching and the potential impacts of changing redox conditions on natural attenuation process. In parallel with the field monitoring, batch laboratory studies are underway to measure sorption of the different MCs to soil at RG40 and measure biodegradation rates under aerobic and anaerobic conditions. In addition, laboratory column studies are being conducted to evaluate MNA of MCs under controlled condition.

Results/Lessons Learned. Ft. Bragg experienced a wet period in the Spring and Summer of 2013. In throwing bay A with slightly finer grained soils, the high rainfall resulted in saturated soil conditions. Reduced oxygen transport in the saturated soils combined with natural organic carbon resulted in anoxic/anaerobic conditions with average Eh values ranged from - 360 to - 210 mV at 4 ft bgs and from - 350 to - 80 mV at 5 ft bgs. Following the onset of anaerobic conditions, RDX concentrations declined rapidly from 113 to 3 µg/L at 4 ft bgs and from 67 to 2 µg/L at 5 ft bgs. In Fall 2013, rainfall was lower and the Eh rebounded to +480 mV. However, there has not been a corresponding rebound in MCs and RDX concentrations in soil pore water remain below 5 µg/L.

However, in the adjoining throwing bay (B), the soils have slightly less fine grained material and a higher hydraulic conductivity. As a result, soils in throwing bay B remained unsaturated, Eh declined much more slowly, and RDX biodegradation was limited.

Relatively minor changes in soil properties can result in major changes in soil moisture and redox status. If range soils occasionally go anaerobic, this can greatly accelerate RDX biodegradation and reduce leaching to groundwater.

A Study of Microbial and Geochemical Responses to Substrate Injections for RDX Biotreatment of Groundwater

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Background/Objectives. The Iowa Army Ammunitions Plant (IAAAP) is located near Middletown, Iowa. RDX is the prime contaminant of concern in groundwater and was present in several plumes associated with assembly and testing (mortars, shells, projectiles, mines, and fuses), demolition areas (DA), and dismantling and washing activities. RDX has also migrated offsite. Over the past few years, anaerobic biotreatment via the injection of carbon substrates has been shown to be the most effective groundwater remedy. Pilot studies using two types of carbon substrates, namely, high fructose corn syrup (HFCS) and sodium acetate have been examined, followed by successful full-scale treatment that has attained site cleanup goals in one of the large offsite locations. Microbial analyses including biomass measurements, community structure (PLFA), and physiological analyses were performed on groundwater. In addition, a suite of geochemical parameters was also analyzed during the pilot and field scale efforts.

Approach/Activities. Baseline RDX concentrations offsite were greater than 5000 ppb at several locations prior to pilot and full-scale biotreatment. Based on an examination of HFCS and sodium acetate, the latter was selected as the carbon injectate of choice and four separate designed injections were performed into injection wells located along a groundwater transect perpendicular to groundwater flow. Several groundwater monitoring wells (historical and new remediation monitoring wells) were installed downgradient of the transects to periodically monitor chemical, geochemical, and microbial parameters in groundwater. Data was evaluated to track and examine the effectiveness of RDX bioreduction in order to ensure the attainment of the active cleanup goal of 50 ppb within the RDX plume. In addition, trend analyses and correlations were performed on the relationship between geochemical data and the microbial data with the changes in RDX concentrations that changed during treatment.

Onsite pilot studies to demonstrate anaerobic biological treatment began in 2008/2009. Results indicated that while RDX is amenable to anaerobic biological treatment, areas that contained significant concentrations of native iron appeared to respond much more rapidly to the injection of organic carbon and attainment of reducing conditions. A comparative analyses of the role of iron and other significant geochemical parameters was performed. Data and conclusions which indicate a strong relationship between Fe (II) and RDX concentrations will be presented. A similar pilot study was performed on offsite groundwater, in which two different substrates were employed. Anaerobic biological treatment followed by MNA was the selected remedy for full-scale remediation, and was performed via the installation of a full-scale transect-type biobarrier system. Active treatment has now been completed and RDX concentrations well below the 50 parts per billion (ppb) goal have been attained. Results and findings of this effort will be presented.

Results/Lessons Learned. The effect of specific geochemical parameters as they relate to progress of RDX bioreduction will be presented. The parameters which are strong indicators of RDX anaerobic biodegradation will be highlighted. The parameters that correlate the strongest with RDX reduction, namely, dissolved oxygen, iron, and nitrate will be examined and detailed further. In addition, specific microbial markers and the response of the microbial community in response to carbon substrate injections and RDX destruction will be presented.

Microbially Mediated 2,4-Dinitroanisole (DNAN) Degradation by Reduced Electron Shuttles

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Background/Objectives. The insensitive munition 2,4-dinitroanisole (DNAN) has been used in newly developed explosives as a replacement for the more sensitive munition, trinitrotoluene (TNT). These new formulations are more insensitive to external shocks, for example heat or strikes, in storage, transport, and battle conditions and are safer to handle. It is important to understand the fate of DNAN in the environment and to establish effective remediation methods due to its high toxicity and potential environmental hazards.

Approach/Activities. This study is an investigation of DNAN degradation by reduced Fe(II) or hydroquinones (AH2QDS) using a model Fe(III)-reducing microorganism: *Geobacter metallireducens*. Fe(III) is common in subsurface environments; therefore, it can be employed for in-situ remediation when Fe(III)-reducing microorganisms are active and generating Fe(II). Electron shuttles are present in aquifers as humic material or other organic molecules, hence quinone/hydroquinone couples were used in this study to represent this group. Additionally, DNAN degradation by photosysthetic purple bacteria *Rhodobacter sphaeroides* was tested. Experimental bottles were buffered at pH 6.0-9.0, with initial DNAN concentration of 100µM. Liquid samples, taken over the duration of the experiments, were analyzed for DNAN presence by high performance liquid chromatography (HPLC).

Results/Lessons Learned. DNAN was completely reduced by soluble Fe(II) at pH between 7.0 and 9.0, and pH had a significant effect on DNAN reduction. Rates of DNAN reduction increased with increasing pH. Fe(II) alone did not reduce DNAN at pH 6.0; however, Fe(II) complexed by organic ligands such as tiron, 2,3,4-THBA, and 2,3-DMSA could overcome the pH limitation and promote DNAN reduction. Hydroquinone (AH2QDS) reduced DNAN at all pH values tested. Fe(II) pre-adsorbed to Fe(III) increased the rate of DNAN transformation. DNAN was also reduced by *Geobacter metallireducers* alone; however, AQDS and Fe(III) both increased cell-mediated DNAN degradation.

In all cases, DNAN was reduced through intermediate 2-methoxy-5-nitroaniline (MENA) to 2,4-diaminoanisole (DAAN). Finally, a photosynthetic culture, *Rhodobacter sphaeroides*, reduced DNAN to MENA quickly when light was present, suggesting that photobiological degradation is possible and may be an effective surface water strategy. DNAN was also reduced by *Rhodobacter sphaeroides* in dark conditions, however this reaction was slower. Experiments currently being run test DNAN reduction by different bacteria known to degrade similar compounds and by Fe(II) adsorbed to different mineral surfaces.

Back to Contents

Geochemistry of Chromium: Mechanisms for Natural Attenuation and In Situ Treatment

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Background/Objectives. Historical anthropogenic releases of hexavalent chromium have occurred at industrial sites that used chromium for wood preservation, metal plating, and as an anti-corrosive agent. However, chromium is also a common trace metal in iron/magnesium-rich rock forming minerals, including pyroxenes and amphiboles. Although these minerals are found in most rocks, they are most plentiful in ultra-mafic and mafic rocks. The trivalent form of chromium found in common rock minerals is subject to oxidation to the hexavalent form in surrounding water with close contact with manganese oxide minerals. The natural concentration of hexavalent chromium in groundwater is dependent upon the parent rock composition and the prevailing redox conditions. Hexavalent chromium is readily reduced back to trivalent chromium when groundwater conditions become mildly reducing. Under normal pH conditions, trivalent chromium forms insoluble solids that reduce groundwater chromium levels to very low or non-detect levels. The geochemistry of two historical chromium release sites was evaluated, including a detailed evaluation of soil cores for potential reduction capacity, to support site remediation activities. The results of this assessment, including an understanding of geochemical mechanisms, is presented.

Approach/Activities. Two sites with historical chromium releases are used as examples of differing background concentrations and degrees of natural attenuation based on differing natural geochemical conditions. Trace metal and general geochemical data were collected over a number of years at each site to characterize plumes, establish background concentrations, and distinguish geochemical reactions that govern the fate and transport of chromium in the two different environments. Soil core samples from this environment were collected and analyzed for their chromium reduction capacity in an anoxic laboratory environment. In situ treatment technologies are being applied or designed for both sites to enhance the natural reduction process to remove chromium from groundwater.

Results/Lessons Learned. Hexavalent chromium is stable in waters of high oxidation-reduction potential, and is readily reduced to insoluble trivalent chromium when conditions become slightly more reducing. This effectively removes chromium from solution, as demonstrated at one site where the plume entered a more reducing river floodplain environment. Soil core analysis from this area showed that a significant portion of the chromium plume can be removed by the natural reducing capacity of floodplain sediments. Quantification of reduction capacity is complicated by potential oxidation of reduced soil samples in the field and the natural heterogeneity of soil redox properties in fluvial environments. In situ applications are planned to enhance and expand the area of this natural tendency by introducing organic carbon sources to the subsurface, resulting in reductive removal of chromium from groundwater. At the second site, the plume extends into a different geological environment, which may contain a higher natural background concentration. This makes definition of the leading plume edge more difficult, and new geochemical tools will be applied to address this issue.

Reduction of Cr(VI) in Mine Effluents using Ascorbic Acid

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Background/Objectives. Chromite ore ($FeCr_2O_4$) is one of the principal ores of the element chromium. South Africa holds approximately two thirds of the world's viable chromite resources, dominating the global production of ferrochrome. Although completely unintended, small amounts of Cr(VI) are formed during ferrochrome production. The most commonly applied treatment strategy remains the aqueous reduction of Cr(VI) with ferrous iron.

Approach/Activities. In this study, the reduction of Cr(VI) by ascorbic acid (AsA) was compared to the use of biodegradable reductants such as glucose, fructose, galactose, citric and tartaric acid. Potassium dichromate solution was used as the model pollutant. During batch optimisation tests, the effects of AsA concentration, pH and source of AsA on Cr(VI) reduction were evaluated. Using the optimised conditions, the reduction process was scaled up to a continuously operated 2 stage reactor system during which the effect of residence time on Cr(VI) reduction was determined.

Results/Lessons Learned. The results obtained indicated that AsA was the most promising biodegradable reductant tested, reacting with nearly instantaneous kinetics. Cr(VI) (50ppm) reduction of >99% could be achieved at a residence time of 15 minutes using 0.03% AsA. A cost analysis, comparing the use of AsA versus conventional Fe^{2+} as reductant, indicated that it would be cheaper to reduce Cr(VI) with Fe^{2+} rather than AsA. However the use of Fe^{2+} would mean the introduction of an environmental pollutant. AsA, whilst more expensive, is environmentally friendly as it is biodegradable and the dosage required is low enough to base a decision between Fe^{2+} and AsA on the environmental impact rather than the cost of reductant.

Combined Nano-Biotechnology for In Situ Remediation of Hexavalent Chromium in Groundwater

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Background/Objectives. Chromium, especially the highly toxic and reactive hexavalent form, Cr(VI), is one of the most abundant heavy metals causing pollution of groundwater and soil due to its frequent industrial exploitation. The vast majority of adverse environmental effects attributable to the hexavalent Cr(VI) form are due to its significant aqueous solubility, environmental mobility, reactivity, and toxicity. This study combines *in-situ* chemical reduction and immobilization by nanoscale zero-valent iron (nZVI) and subsequent bioreduction, supported by whey, to treat source area and plume concentrations of Cr(VI) in groundwater. Combining these two remedial approaches takes advantage of features from both – fast nZVI-mediated decrease of Cr(VI) concentrations in source area groundwater to prevent the further spread of the contamination followed by more economical treatment of the lower Cr(VI) concentrations in the plume by microorganisms.

Approach/Activities. The combined technology was tested in laboratory column experiments as well as in the field at two pilot sites that differed from each other by the level of Cr(VI) contamination. In the laboratory, the chemical reduction of Cr(VI) by nZVI (0.5g nZVI/kg of soil) was studied in columns packed with soil from the contaminated site and fed with groundwater containing 20 mg/l of Cr(VI). After 35 days the column input was changed to whey (2.7 g TOC/column), an organic substrate for biological reduction. The inlet Cr(VI) concentration in this phase was set to 8 mg/l. A similar approach was applied in the field. At the Hradek site the initial Cr(VI) concentration in the groundwater was 0.9 - 2.5 mg/l. 120 kg nZVI was injected as a 2 g/l suspension via 3 wells into the aquifer developed in sandy gravel with a saturated thickness of 5 m. Nine months after the nZVI injection, whey was added in an amount achieving 300 mg TOC/l of groundwater to stimulate bioreduction. At a second confidential field site, the initial Cr(VI) concentration ranged from 1.8 to 38 mg/l. 20 kg of nZVI was injected using direct push technology into the gravelly-sandy aquifer with a saturated thickness of 4 m. Two months after the nZVI injection, whey was added in order to achieve 60 mg TOC/l in the groundwater.

Results/Lessons Learned. The column tests showed a high efficiency (>95%) for the removal of Cr(VI) from the aqueous phase using nZVI, without any deleterious effects on the microorganisms (based on both the microbiological cultivation tests and the PLFA analysis). The subsequent bioreduction phase exhibited an even higher removal efficiency (>99%). During the pilot tests, the application of nZVI rapidly pretreated the aquifer without any substantial effect on the content of inorganic constituents in groundwater or negative impact on the composition or abundance of indigenous bacteria. Stimulation of bioreduction using whey resulted in a further decrease in Cr(VI) concentrations in the groundwater to below detection limits throughout the treated areas without any significant rebound of Cr concentrations after substrate depletion. At the Hradek site, where a larger amount of nZVI was applied, microbial populations also reduced the spent nZVI from Fe(III) to soluble Fe(II), which can act as a Cr(VI)-reducing agent. This finding is supported by characterization of the bacteria using 454 pyrosequencing, which identified genera belonging to iron-reducing representatives. Thus, the successive combination of the two geofixation methods - chemical reduction and bioreduction of Cr(VI), seems to be an efficient and sustainable remedial approach.

In Situ Bio-Precipitation of High Concentration Cr(VI) in Groundwater Related to Chromate Ore Processing Residue

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Background. Chromate ore processing residue (COPR) used as historic backfill material at a site located in Jersey City, New Jersey has contributed to elevated Cr(VI) concentrations (above 200 milligrams per liter [mg/L]) in underlying groundwater. Following the excavation of COPR material, a potential approach to treat groundwater in situ via bio-precipitation was selected for evaluation. This is an established treatment technology that works by reducing Cr(VI) through reaction with multiple biologically generated reductants or direct anaerobic respiration with Cr(VI) serving as the terminal electron acceptor. The reduction of Cr(VI) produces trivalent chromium [Cr(III)] which provides three clear benefits from a treatment perspective. First, Cr(III) is less toxic and therefore typically has higher permissible environmental concentrations. Second, Cr(III) is less soluble under typical groundwater conditions and is generally immobilized in the form of a hydroxide mineral, that can be incorporated in a matrix of carbonate, sulfide, and other precipitates generated during the treatment process. Finally, insoluble Cr(III) phases tend to be resistant to re-oxidation to Cr(VI) phases under typical soil and groundwater conditions. These factors combine to make Cr(VI) treatment via in situ bio-precipitation an attractive remedial technology.

Approach. A pilot study was conducted to evaluate the feasibility and effectiveness of organic carbon delivery to mediate anaerobic Cr(VI) bio-precipitation for treatment of groundwater with high Cr(VI) concentrations due to the presence of COPR. A dilute solution of molasses was injected via wells as the organic carbon substrate into two distinct geological formations to promote reducing conditions favorable for Cr(VI) reduction. Two injection events were completed within a 6-month period and coupled with ongoing performance monitoring to generate design parameters necessary for site-wide groundwater treatment and to evaluate the effectiveness of the bio-precipitation approach for treatment of the elevated groundwater Cr(VI) concentrations.

Results. Organic carbon injection promoted a reduction of Cr(VI) by up to four orders of magnitude where substrate delivery was achieved. Elevated total organic carbon (TOC) concentrations observed within the monitoring well network were sustained over the course of the sampling program and fostered the required geochemical bio-precipitation reactions to provide sustained Cr(VI) treatment. Cr(VI) reduction at well locations where reagent delivery was achieved (8 out of 14 wells) was at least 73%, 94% and 96% after one, two and four months following injection, respectively. The maximum treatment observed was 99% or greater in all three sampling events. Similar trends were also observed in several locations where increased TOC was not observed. Chromium treatment in these areas may be the result of migration of reductants (e.g. Fe, sulfide) or low levels of TOC from the injection area. The results of the field pilot test clearly demonstrate the effectiveness of the bio-precipitation technology, and its applicability to address elevated (200 mg/L) Cr(VI) in groundwater.

Full-Scale Treatment of Hexavalent Chromium in Shallow Aquifer Using Emulsified Vegetable Oil

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Background/Objectives. In November 1986, a train derailment resulted in the release of significant quantities of methanol, sodium dichromate, ethylene glycol and chromic acid. Much of the substances released were contained through emergency response activities and removal of impacted soil and track ballast; however the shallow aquifer was impacted by hexavalent chromium (Cr(VI)) dispersion from the sodium dichromate and chromic acid. A groundwater recovery and treatment system consisting of an ion exchange system was constructed and operated from 1990 through 1996. From 1997 through 2008, monitored natural attenuation was implemented as the remedial alternative. In 2014, a full scale remediation system was implemented to demonstrate enhanced bioremediation using emulsified vegetable oil (EVO).

Approach/Activities. Chromium can persist in the environment as Cr(VI) and trivalent chromium (Cr(III)), which have widely different toxicity and transport characteristics. Cr(VI) tends to be more mobile in the environment as it partitions weakly to solids in soils and groundwater; whereas, Cr(III) has limited solubility and forms strong complexes with the soil matrix making it relatively immobile. Cr(VI) can be reduced by both biological and chemical processes which may be coupled with the reduction of microbial metabolites such as iron and sulfate. *In situ* biological treatment using EVO begins with lowering the ORP so that the soluble Cr(VI) is converted to Cr(III). Cr(VI) undergoes biologically mediated reduction to Cr(III) under anaerobic conditions. Indigenous micro-organisms utilize the EVO as a carbon source for biomass generation and as an electron donor for energy production. The process to reduce Cr(VI) may occur in a single step or in multiple steps. In the single step process, electrons are directly transferred from electron donor to Cr(VI) resulting in the oxidation of the electron donor to Cr(III). In the two step process, the anaerobic conditions brought about by the addition of EVO result in the reduction of iron and sulfur which then reduce the Cr(VI) to Cr(III). The two primary pathways for the conversion of Cr(VI) to Cr(III) are as follows:

Direct microbial oxidation of a generic carbohydrate coupled with reduction of Cr(VI).

$$C_3H_6O_3 + 4CrO_4^{2-} + 8H^+ \rightarrow 3CO_2 + 4Cr(OH)_3 + H_2O$$

$$CH_2O + 4CrO_4^{2-} + 8H^+ \rightarrow 3CO_2 + 4Cr(OH)_3 + H_2O$$

Indirect microbial reduction of Cr(VI) via iron hydroxide reduction.

$$C_3H_6O_3 + 12FeOOH + 24H^+ \rightarrow 12Fe^{2+} + 3CO_2 + 21H_2O$$

$$3Fe^{2+} + CrO_4^{2-} + 8H_2O \rightarrow 4Fe_{0.75}Cr_{0.25}(OH)_3 + 5H^+$$

Results/Lessons Learned. Approximately 440,000 gallons of EVO solution were injected into 35 injection well pairs to treat the shallow aquifer. Two post-injection sampling events have been conducted to evaluate reduction of Cr following the injection. Results indicate a significant decrease in Cr(VI) and total Cr in the treatment area; Cr(VI) concentrations decreased approximately 50% in high concentration areas and approximately 90% in outlying areas. The results indicate that EVO has been successful in converting Cr(VI) to Cr(III) and decreasing total aqueous concentrations of total Cr in the aquifer.

Back to Contents

Overcoming Challenges Caused by Previous Remedial Actions to Remediate a Chromium and TCE Contaminant Plume

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Background/Objectives. Air Force Plant 4 (AFP4), located in Fort Worth, Texas, is used for the production of military aircraft. Historical manufacturing operations at AFP4 resulted in the release of various hazardous wastes, including spent solvents. As a result, the underlying Terrace Alluvium groundwater has become contaminated, primarily with trichloroethene (TCE). Chrome Pit 3 (CP3) is located to the southwest of the Main Assembly Building at AFP4. Barium chromate sludge, diluted metal solutions, and drums of unidentified liquids were disposed of in this pit from about 1957 until 1973. Between December 1983 and January 1984, approximately 8,900 cubic yards of contaminated soil was excavated from CP3. Soil testing conducted during the excavation indicated that the most highly contaminated soils had been removed; however, TCE was still present in the groundwater.

To remediate residual TCE in the groundwater at CP3, a series of in situ chemical oxidation (ISCO) injections were performed between 2008 and 2009 using potassium permanganate ($KMnO_4$). Immediately after the injections, TCE concentrations declined; however, an increase in chromium concentrations was observed. TCE concentrations began to rebound in 2010, after which lactate injections were performed to try to reduce both the TCE and chromium. In October 2011, continued rebound in the TCE concentrations was observed, with an average TCE concentration of 11,500 mg/L in site monitoring wells. In addition, little change in chromium concentrations was observed more than a year after the lactate injections. The average chromium concentration was approximately 4,600 mg/L.

Approach/Activities. A pilot study is being conducted at CP3 to determine the feasibility of using in situ chemical reduction (ISCR) to reduce dissolved chromium concentrations and enhanced reductive dechlorination (ERD) to degrade chlorinated volatile organic compounds (cVOCs). To date, fifty-three (53) direct-push technology (DPT) injection points have been used to inject calcium polysulfide (CPS) into the shallow groundwater to create reducing conditions in the aquifer and precipitate dissolved chromium. An additional 24 DPT injection points were used to inject EHC-L® and KB-1® to enhance biodegradation of residual TCE.

Results/Lessons Learned. As of July 2014, the total dissolved chromium concentrations have declined in 11 of the 14 pilot study monitoring wells and TCE concentrations have declined in 9 monitoring wells compared to the baseline monitoring event in April 2012. The analytical results show that the zone of affected groundwater is more reduced than compared to baseline conditions; however, the redox conditions are generally not suitable for precipitation of dissolved chromium or biological reductive dechlorination. $KMnO_4$ still persists in two of the monitoring wells and hinders progress toward creating reducing conditions and precipitating chromium in these areas; however, it is not as pervasive as it was at the beginning of the pilot study when it was noted in at least five monitoring wells. The results to date suggest that the CPS has been effective, however, additional amendments are needed to overcome the demand presented by the residual $KMnO_4$.

Use of Stable Chromium Isotopes to Assist in Distinguishing Anthropogenic and Natural Sources in Groundwater

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Background/Objectives. Hexavalent chromium is present at elevated concentrations in groundwater at three sites due to historical releases. The distinction between the downgradient edges of the anthropogenic groundwater plumes and natural background levels is unclear due to the variability of chromium concentrations and differing geologic parent materials. Various geochemical tools have been applied to groundwater data to help make this distinction. Chromium-53 is a stable isotope of chromium that is slightly heavier than the common chromium-52 isotope; experimental data have demonstrated a preference for chromium-52 to participate in reactions that reduce hexavalent chromium to insoluble trivalent chromium, thus enriching the remaining water in chromium-53. Stable chromium isotope analysis was added to the list of assessment tools for three sites with the objective of differentiating the chemical signature of the anthropogenic chromium source from the naturally occurring chromium.

Approach/Activities. Stable chromium isotope analysis was performed on groundwater samples from three sites, along with analyses for hexavalent chromium, other trace metals, a suite of general chemistry parameters, and natural tracers. Naturally-occurring reductants in an aquifer with chromium-containing minerals may result in a gradual increase in the δ^{53}Cr along the long, natural groundwater flowpath that begins in upland recharge areas. In contrast, hexavalent chromium from contaminated sites have relatively short flowpaths, which would suggest little opportunity to increase the δ^{53}Cr value above zero.

Results/Lessons Learned. The reductive fractionation/isotopic enrichment data assisted in understanding processes occurring within and near the plume margins that were useful in delineating the extent of contamination at the three sites. However, the chromium isotope data did not in themselves consistently provide positive identification of the anthropogenic versus natural chromium. At one of the two sites, one edge of the plume encounters a distinctly reducing zone, resulting in rapid natural attenuation that is so abrupt that there is not enough measurable chromium for an isotopic sample. At the third site, natural reductive fractionation was more distinct, making this plume more suitable for study of gradual, natural attenuation without a distinct change in overall redox conditions. For all three sites, the isotopic data, when combined with other geochemical parameters, contributed to an improved understanding of the interaction between reductive and mixing processes that occur within and near the edges of chromium contamination plumes.

Pinning Down Site Specific Sorption (K_d) of Hexavalent Chromium: Evaluation of Desktop, Benchtop, and Field Investigations

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Background/Objectives. A dilute hexavalent chromium plume at an active manufacturing facility is currently controlled by a pump and treat (P&T) system. In order to improve site management decisions, a combination of desktop, benchtop, and field investigations were conducted to estimate the length of time that the P&T system would need to operate to meet cleanup goals for the site. The evaluation also included timeframe estimates for alternative remedial options and endpoints. Sensitivity analysis determined that of particular importance to timeframe estimates is the site-specific partitioning coefficient (K_d) of hexavalent chromium, which controls the rates of both advective transport and matrix back-diffusion.

Approach/Activities. Multiple lines of evidence were used to determine the site-specific (and formation-specific) hexavalent chromium K_d values. These included high-resolution site characterization, which identified within the larger dilute plume a “slug” of contaminant mass advecting and dispersing through groundwater. Investigation results were used to parameterize a model of contaminant transport. In order to further refine timeframe estimates, a laboratory chromium leaching study was also conducted.

Results/Lessons Learned. Sorption isotherms generated from laboratory studies indicate that K_d values are highly variable across the observed concentration range and across different geologic formations present on site. Estimates of the timeframe required for hexavalent chromium to flush out of the site were more using lab developed data compared to field data. The laboratory study showed an increasing tendency for hexavalent chromium to sorb to soil as concentrations decrease. These results indicate that understanding the multi-faceted and variable nature of hexavalent chromium Kd is both complex, and crucial to the development of an accurate conceptual site model.

Methane Prevention during Bioremediation of Chromium (VI) in Fractured Bedrock

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Background/Objectives. At a former printing facility within a residential area, chromium (Cr) VI were detected above 1,000 milligram per kilogram (mg/kg). Limited or no overburden is present in the subsurface. The impact of Cr is limited to the fractured sandstone and its associated aquifer. Two calcium polysulfide injections were conducted to remediate Cr in the source and majority of the site to below the NJDEP Groundwater Quality Standard (GWQS). The first injection targeted the source area using pneumatic fracturing, and the second injection targeted an off-site well via gravity feed through existing wells located on site. Because the groundwater velocity in the fracture bedrock is more than 1 foot per day, calcium polysulfide injected during the second event attenuated and Cr concentration rebounded in the off-site wells after nine months. Bioremediation using emulsified vegetable oil (EVO) coupled with a methane generation inhibitor was proposed to reduce the Cr concentration in the off-site well to below NJDEP GWQS. Ultimately, the remedial objective is to close the site and convert it non-restricted use.

Approach/Activities. EVO was selected as substrate because of its longevity and resistance to the high groundwater flow velocity in the subsurface. EVO with large droplet size will be applied for this site because large droplets show superior resistance to the high groundwater flow than the small droplets. Limited overburden is present at the site, so the methane generated by EVO and lactate fermentation may not be effective scavenged at this site. Methane can migrate through fractured bedrock in the vadose zone, and cause adverse impact to the residential buildings within the treatment area. To avoid methane generation with the residential area, a methane inhibitor, statin, was proposed to be injected with EVO. The methane inhibitor, developed by Provectus Environmental Products, Inc, interferes with the metabolism of methanogens, and bench-scale studies showed that the methane inhibitor at 50 milligram per liter was able to reduce methane production over 95%. However, a field implementation of the inhibitor in conjunction with EVO was not demonstrated previously.

Results/Lessons Learned. The bioremediation using EVO and methane inhibitor is expected to occur in the spring of 2015, and the preliminary results will be available before May 2015. The preliminary results will confirm the effectiveness of Cr reduction, and prove whether methane inhibitor can effectively reduce the methane production in subsurface, practically in the fractured bedrock with fast groundwater flow. The results will also provide information on the fate and transport of the methane inhibitor in the subsurface. If the methane inhibitor is approved to be effective at reducing methane without interfering with bioremediation, the methane inhibitor should be considered for the bioremediation site in an urban and residential environment.

Back to Contents

Optimization of Metals Bioremediation Using Column and Microcosm Studies

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Background/Objectives. Metals remediation can be complex given the sensitivity of metal speciation to geochemical conditions, in particular, pH and redox potential. Remedial approaches, such as the addition of electron donors, can alter the redox state of an aquifer, thereby affecting the solubility and mobility of metal species. Furthermore, metals are often toxic to microorganisms and may be inhibitory to bioremediation of other compounds, such as chlorinated solvents, with implications for sites with comingled contaminants. Mobilization of naturally occurring metals by amendments may also be of concern at some sites.

Approach/Activities. Laboratory treatability studies are commonly used to evaluate remedial options prior to field implementation for a wide variety of contaminants, including metals such as: arsenic, chromium, zinc and nickel; chlorinated volatile organic compounds (cVOCs), petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). Treatability studies are used to assess the impact of amendments (electron acceptors [e.g., sulfate], electron donors, oxidants, zero valent iron [ZVI] and pH adjusting agents) on various remediation technologies under different design scenarios. Laboratory scale studies are performed in both batch microcosms and continuous flow through columns. Batch microcosms offer the advantages of low cost and the ability to practically test numerous treatments simultaneously.

Flow through column studies offer the advantages of simulating the movement of groundwater through an aquifer or permeable reactive barrier (PRB) and are ideal for understanding the impact of geochemical gradients.

Results/Lessons Learned. This presentation will focus on the use of treatability studies to evaluate treatment options for metals. Case studies of laboratory batch and column treatability studies will be presented. In one study, effective dechlorination of trichloroethene (TCE) was not observed until hexavalent chromium concentrations were reduced, at which point TCE dechlorination commenced, providing valuable information for managing the full scale remediation. Another study involved amending microcosms with emulsified vegetable oil (EVO) as a carbon source and comparing ferrous sulfate and potassium sulfate amendments as sulfate sources to evaluate dissolved arsenic removal. Under anaerobic conditions, arsenic can be reduced and precipitated as arsenic-iron-sulfides, which is a microbially-mediated process. A higher removal rate was achieved with the ferrous sulfate amendment suggesting that an iron source was beneficial in removing arsenic from solution.

Zinc Complexation by Chitosan and the Effects on Aquatic Biota

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Background/Objectives. Chitosan, a biopolymer used in cosmetic formulations, as a food additive and in wastewater treatment, exhibits high affinity for metal ions. Extensive research has been done on the uptake of metal ions by chitosan. However few works have been focused on the use of chitosan in natural aquatic systems and on its impact on components of the food chain, such as the larvae of insects and aquatic Oligochaeta. The toxicity of some substances such as metals causes sublethal effects, especially at low concentrations. These effects may occur at the molecular level and thus can cause damage to the exposed populations, as well as to alter its role in the ecosystems. Recent studies demonstrate the high potential of the use of chitosan in sequestering metal. Therefore, the aim of this study was to evaluate the effects of solid chitosan on aquatic biota, to evaluate the potential of chitosan to complex zinc ions Zinc and to act in the bioremediation of the aquatic biota

Approach/Activities. The potential use of chitosan in bioremediation was evaluated by using larvae of *Chironomus xanthus* (Diptera, Chironomidae) and the aquatic worm *Allonais inaequalis*(Annelida, Oligochaeta) by carrying out chronic toxicity tests (10 days) using different zinc concentrations in aquatic systems: 0.18 mg/l, 5.0 mg/l and 7.0 mg/l in presence/or absence of chitosan. Biochemical analysis of macromolecules such as RNA and proteins will be performed to evaluate the deleterious effects of metals in organism

Results/Lessons Learned. . The results show that solid chitosan at a concentration of 1.0 mg/l, reduced in 60% the mortality of the aquatic biota. The results will provide the basis for enabling the use of biopolymers in remediation activities impacts on aquatic environments contaminated by metal ions.

Arsenic in Groundwater at Geochemical Extremes: Acidic and Reducing Conditions May Confound Analysis

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Background/Objectives. Sources of arsenic to groundwater include its natural presence in aquifer soil minerals, as well as anthropogenic sources such as residues from energy generation, mining or chemical processing. Its incorporation into iron minerals limits arsenic solubility in groundwater, however reductive iron dissolution, acidic conditions, or alkaline conditions can increase its solubility. Conventional analytical methods including inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and mass spectrometry (ICP-MS) are typically used to quantify arsenic concentrations in groundwater to part per billion (ppb) levels. We have discovered inaccuracies associated with these methods in the presence of other trace elements namely rare earths (lanthanides), including lanthanum, neodymium and samarium.

Approach/Activities. Lanthanides are naturally-occurring elements and, when present, can cause false-positive results for arsenic due to spectral and isobaric interferences. We evaluated conditions that lead to enhanced solubility of soil minerals (including pH extremes and geochemically-reducing conditions) and identified alternative methods for arsenic analysis. These include arsenic speciation to quantify individual arsenic species (As(III), As(V) and others) or the use of methods that separate arsenic from the sample matrix (hydride generation). Evaluation was also performed of the presence and concentration of arsenic in soils (through digestion or extraction methods) and methods were identified to limit interferences from lanthanides.

Results/Lessons Learned. Strategies for characterizing arsenic in groundwater at sites that exhibit extreme geochemical conditions should employ greater diligence when selecting analytical methods. Alternative methods were identified for delineation and remediation of potential arsenic impacts.

Biotransformation Pathways of Dimethylarsinic (Cacodylic) Acid in the Environment

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Background/Objectives. Historically, dimethylarsinic acid DMA(V) and its salts have been used as herbicides and defoliants. Between 1962 and 1971, an estimated 1.2 million gallons of Agent Blue (a mixture of DMA(V) and sodium cacodylate) were applied as a defoliant during the Vietnam conflict. By the 1970 to 1980s, DMA(V) was the most popular herbicide worldwide. It is estimated during that time 10 to 12 million acres were treated annually with 2.1 million kilograms of monomethylarsonic acid (MMA[V]) and DMA(V) in the United States. Due to the potential for organic arsenicals to transform into inorganic forms of arsenic (which are more toxic), the EPA banned the use of organic arsenicals after December 31, 2013. Given the widespread use of DMA(V), understanding the potential biotransformation pathways of organoarsenicals within the environment as well as the fate, transport, and risk associated with the various arsenic species is vital for guiding remediation strategies at sites contaminated with DMA(V).

Approach/Activities. This presentation is a literature review and will discuss the following items:

- **Chemical properties and toxicity**. DMA(V) is an amphoteric compound (exhibiting properties of both an acid and base) with an acid dissociation constant (pKa) value of 6.4. It is comprised of a single arsenic atom connected by three single covalent bonds (two methyl groups and one hydroxyl group) and a double bond to oxygen resulting in a +5 oxidation state for arsenic.
- **Biological transformation processes.** Biotransformation of DMA(V) is a significant part of the arsenic biogeochemical cycle and can produce a variety of end products. Site specific conditions, in particular the redox condition, will direct the forms of arsenic species present.
- **Fate of these compounds in the environment.** The fate of DMA(V) in the environment is difficult to quantify because of the number of interrelated abiotic and biological processes that occur simultaneously. These combinations include phase transfer, advection, diffusive transport, methylation, demethylation, oxidation and reduction.

Results/Lessons Learned. Biotransformation of DMA(V) is a significant part of the arsenic biogeochemical cycle and can produce a variety of end products. Under oxic conditions, DMA(V) is predominately demethlyated to inorganic As(V). As pentavalent As species are generally immobile, maintaining an oxic environment may aid in reducing transport of arsenic in the environment. Under anoxic conditions, DMA(V) is also demethylated to inorganic arsenic. Although the transformation pathways incorporate a variety of intermediate compounds, both inorganic As(V) and As(III) can be produced. These results indicate that transitioning from oxic to anoxic conditions may increase the toxicity and mobility of arsenic in the environment.

Back to Contents

Antimethanogenic ISCR Reagent for Improved Heavy Metal Immobilization

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Background/Objectives: Trace metals constitute a significant class of groundwater contaminant, originating from mining effluents, industrial solid waste and wastewater, landfill leachate, agricultural wastes and fertilizers, and fossil fuels. Conventional reagents for *In Situ* Chemical Reduction (ISCR) developed over a decade ago (Mueller *et al*., 2003) make use of synergistic interactions between various biotic (*e.g.,* microbial fermentation of organic carbon sources) and abiotic processes (*e.g.,* zero-valent iron [ZVI] chemistry) to encourage dehalogenation of organic compounds as well as reductive precipitation of various heavy metals (Dolfing *et al,* 2008). These common ISCR amendments have been modified to include (when needed): a source of sulfur, (powdered activated carbon (PAC)/charcoal, buffering agents, and/or other additives to further encourage the immobilization of heavy metals.

Despite these efforts, ISCR processes are often confronted by an inability to meet stringent regulatory requirements, especially for arsenic (MCL < 10 µg/L in water intended for human consumption). One likely explanation for this phenomenon is that, with the possible exception of lead, almost all Group IV, V and VI elements can be biomethylated. These methylmetal(loids) are usually volatile and more toxic than their inorganic counterparts due to increased water solubility and hydrophobicity. For example, methylmercury is one of the most potent toxins known to man. Hence, the biosynthesis of organo-metals as a potential by-product of conventional ISCR treatment is likely a factor contributing to the difficulty associated with meeting remedial action objectives. It is known that microorganisms are primarily responsible for the biosynthesis of organo-metals (Challenger, 1945), and that the activity of methanogens (directly and/or indirectly) is a main source of their production.

Approach/Activities: The generation of methylated arsenic species is suspected to have occurred at a Florida golf course. Groundwater samples arsenic impacts were partially mitigated following multiple applications of ERD (lecithin) and conventional/modified ISCR amendments (EHC® and EHC-M™), site where agricultural applications of arsenic resulted in groundwater contamination. The post-remedy sampling found that the aqueous arsenic concentrations did not decrease. Speciation analyses found that a significant fraction of the arsenic was methylated forms.

We supplemented a modified ISCR Reagent with a source of Monacolin K and other natural statins to inhibit the growth and proliferation of Archaea *i.e*., methanogens (Scalzi *et al*, 2013, 2014) in soil and groundwater from a site where In theory, this should reduce the biosynthesis of highly toxic, mobile methylated arsenic species.

Laboratory studies have demonstrated that the addition of statins can significant decrease the production of methane. In the absence of site-specific samples from Florida, microcosms were prepared with manure, soil, groundwater to assess the effect of statins on methane production. A 4-fold decrease in methane was noted with the addition of the statin. The microcosms were also spiked with tetrachloroethene and a *Dehaloccocoides* innoculum. We found that the reduction in methanogenesis was accompanied by a 30-fold increase in PCE degradation. Inhibiting methylation is expected to inorganic metal species to be more quickly sequestered for safe, long-term, stable immobilization via adsorption and precipitation reactions. Moreover, the overall toxicity of the site is not expected to increase via the generation of methylmetal(loids) as a consequence of the treatment process.

In addition methane inhibition mitigates the safety issues associated with elevated methane in groundwater, soil gas, and indoor air, the antimethanogens also promote more efficient use of the hydrogen donor yielding more cost-efficient remedial actions.

Groundwater Arsenic Contamination in Raghunathganj Area of Murshidabad District, India: Causes, Effects and Remediation

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Background/Objectives. Arsenic is a chemical element (metalloid, atomic number-33, periodic group 15) that occurs in conjugation with sulfur and metals and also as pure elemental crystal. The permissible limit as defined by WHO for maximum concentrations of arsenic in safe drinking water is 0.01 mg/L. WHO has defined the areas under threat: Seven Districts of West Bengal have been reported to have ground water arsenic concentrations above 0.05 mg/L. The total population in these seven districts is over 34 million while the number using arsenic-rich water is more than 1 million (above 0.05 mg/L). That number increases to 1.3 million when the concentration is above 0.01 mg/L. Acute illness due to arsenic poisoning involves fever, anorexia, melanosis, cardiac arrhythmia and eventually cardiovascular failure.

Approach/Activities. The present study is aimed to focus on the isolation and characterization of arsenic resistant microorganisms from arsenic (As) contaminated groundwater for its ultimate use as a bioremediation agent. This study initially involves the isolation, biochemical and molecular characterization, protein profiling, specific gene and its product identification of arsenic resistance microorganism surviving in the arsenic containing water sample collected from a tube well in Raghunathganj, Murshidabad District of West Bengal, India). Further the positive outcome of these mentioned tasks will lead us to primer designing, molecular mechanisms for gene isolation and its amplification, gene sequencing, homology modeling and the gene product causing arsenic accumulation / conversion of oxidation or reduction state; to use these confirmed potent arsenic resistant microorganism for bioremediation of arsenic contamination from drinking water (groundwater).

Results/Lessons learned. Gram negative bacteria were isolated by serial dilution of arsenic contaminated water samples. Two bacteria showing good growth in medium supplemented with high concentrations of arsenic (Sodium arsenate and Sodium arsenite) were chosen. The isolates were named SSPS-R2 and SSPS-R7. Protein profiling of the bacteria grown in presence and absence of arsenic revealed arsenic induced protein bands. 16 S rDNA sequence of SSPS-R2 GenBank accession number **KP987528**) showed 100% homology to *Clostridium botulinum* while 16 S rDNA sequence of SSPS-R7 (GenBank accession number **KP987529**) matched 100% to *Bacillus cereus*. These isolates were found to tolerate arsenic concentrations upto 13000mg/l and 1000 mg/l respectively. The novel step of this study is the finding of microorganism for microbial conversion of arsenic compounds and its derivate into other compound(s) so that it does not compete for phosphates and become unable to utilize the phosphate transporters (e.g., Pit, Phosphate transporter and Pst, Phosphate specific transporter) to enter the cells in arsenic non-resistant organisms.

Keywords: Arsenic, bioremediation, protein-profile, primer-designing, gene-sequencing, microbial conversion.

Back to Contents

A Case Study and Data Gap Analysis of Possible Biotransformation of Perfluoroalkyl Acids (PFAAs) Precursors

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Background/Objectives. Perfluoroalkyl or polyfluoroalkyl substances (PFASs) comprise a large group of chemicals. Aqueous film forming foams (AFFFs) were developed in 1966 containing multiple classes of PFASs, such as perfluoroalkyl acids (PFAAs), with a wide variety of presumed PFAAs precursors as well. Military bases used them in extinguishing fires involving flammable liquid fuels and conducted fire-training exercises on a weekly to monthly basis. Many of these fire-training areas (FTAs) have undergone extensive remedial activities to addressed fuel and/or chlorinated solvent contamination, but very little work has been done to address PFASs contamination. The potential biotransformation of polyfluoroalkyl precursors present in AFFFs, is known to result in higher levels of PFAAs. At the Former Wurtsmith Air Force Base (WAFB) over 10,000 people either worked or lived on the base, with B-52 bombers and KC-135 support airplanes that operated at the base until its closure in 1993. Operations at the base resulted in numerous releases of hazardous substances to the environment. These sites resulted in large plumes of chlorinated solvents, fuel constituents, and landfill leachates.

Approach/Activities. As of 2010, significant progress has been made to characterize and remediate site contamination, with only a handful of sites left to have remedial actions implemented. In 2010, the Michigan Department of Environmental Quality (MDEQ) along with United States Air Force (AF) contractors began sampling the entire base for PFASs, randomly picking a few groundwater samples from each Installation Restoration Program (IRP) site that had active monitoring. A total of 20 different PFASs have been found so far at WFAB. Biological samples have also been taken. A total of 9 different fish (filet and liver) species were also analyzed from the marshes and Au Sable River, and Tree swallows (plasma, egg, and diet) from nest boxes located close to the base. The AF has moved quickly to address the most contaminated plume identified at the base — a fire training-area (FTA-02), which discharges a great deal of PFASs to the marsh system and the Au Sable River. The AF will begin capturing and treating this plume by early 2015, with the first system to be installed on a former AF base for treating PFASs.

Results/Lessons Learned. Out of 67 groundwater wells sampled on base or down gradient of the base, only 3 did not show any PFASs contamination. The data collected so far shows the extent and complexity of PFAS contamination at AF Bases and demonstrates that FTAs are not the only significant sources of PFASs contamination at former military sites. Many samples at WAFB from groundwater, soil, sediments, fish, and birds showed some of the highest concentrations reported in literature. The analysis of the fish resulted in a “Do Not Eat” fish advisory for the marshes and the Au Sable River. The extent, contaminant fate, transport, and bioaccumulation and magnification of PFASs from WAFB will be presented as a case study. Initial data of the past and current remedial investigations indicating possible biotransformation of PFAAs precursors, along with data gap analysis of the existing data, will be presented. Evidence of remediation-induced biotransformation has already been shown to be present on at least one military site contaminated with AFFFs. The WAFB can be used as a reference site for other military or non-military contaminated sites, providing insight into the types of studies required, data gap analysis, and potential for future scientific enquiry on the fate, transport, and risks of exposure from such sites.

Lessons Learned from Characterizing Several Dozen Sites Impacted by Perfluorinated Compounds

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Background/Objectives. Perfluorinated compounds (PFCs), such as perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), are a class of compounds widely used in diverse applications, such as carpet protection, surfactants, and shampoos. In particular, PFC-based surfactants have been used in aqueous film-forming foams (AFFF) that have been routinely used in both civilian and US military fire-fighting. Historically, effluents from AFFF fire-fighting activities were neither impounded nor pre-treated prior to discharge to water treatment systems or to the environment. Widespread environmental presence of PFCs has been identified. PFCs are persistent, bioaccumulative, toxic, and are not readily degradable by conventional biological and abiotic treatment technologies. Thus PFCs have drawn increasing public and regulatory concerns including being listed on US EPA's Unregulated Contaminant Monitoring Rule-3 (UCMR-3) list. The UCMR-3 listing requires that large Public Water Systems sample and analyze six PFCs and has already revealed PFC impacts to some of these systems. These impacts and other PFC related regulatory initiatives around the globe have resulted in a dramatic increase in the number of sites characterized for PFCs.

This paper presents lessons learned from characterizing several dozen PFC impacted sites and highlights a number of unique concerns and protocols that must be followed due to the characteristics of PFCs and significant potential for sample contamination. The high solubility of PFCs and associated resulting large dilute plumes, low laboratory detection limits and Health Advisory Levels (HALs), presence of PFCs in many of the products routinely used during groundwater sampling, and potential for non-point sources of PFCs (e.g. dust) all create the need for unprecedented care to ensure an accurate Conceptual Site Model on PFC impacted sites.

Approach/Activities. Data and experiences from several dozen PFC sites was gathered via AECOMs PFC Working Group, which collaborates on technical issues to improve our overall understanding of PFCs. The data was then evaluated to identify both common and unique results. Special sampling protocols were also captured from the experience of the PFC Working Group, available literature on the topic, and recommendations provided by analytical laboratories. The experience was then combined to develop a detailed list of sampling protocols and procedures. The site data was also evaluated to identify any trends and outliers or unique situations.

Results/Lessons Learned. The results of this evaluation and associated lessons learned provide valuable insight into: sources of background and non-point sources of PFCs, common fate and transport characteristics of PFC soil, groundwater, surface water, and sediment impacts, and reinforce that PFC characterization activities must be very rigorous and involve new protocols and procedures.

Remediation of Perfluroalkyl Compounds by Oxidation Using Ferrate (IV), (V) and (VI)

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Background/Objectives. The perfluoroalkyl substances (PFAS), perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are stable, recalcitrant compounds and therefore extremely persistent in the environment. They have been found globally in the aquatic environment, including drinking water and treated wastewater effluent. The compounds may bioacculmulate and are therefore a potential threat to both human health and the environment. The U.S. EPA has developed provisional health advisories for drinking water. Therefore, effective remediation methods must be developed to remove PFAS from water.

Approach/Activities. In this work we demonstrate the potential for removal of PFAS from aqueous solution using three high-valent iron compounds (ferrates). These compounds are appealing for degrading PFAS due to their high oxidation potentials. Ferrates are also expected to have little impact on the environment both during *in*-situ and *ex*-situ applications as their reductive by-products are non-toxic and naturally occurring (i.e., ferric oxy/hydroxides).

Results/Lessons Learned. Each PFAS was treated at three pH levels using doses of solid sodium and potassium salts of Fe(IV), Fe(V) and Fe(VI) in buffered deionized water. PFAS removal was dependent on both pH and ferrate dose. Efficient removal occurred at lower pH using lower valence ferrates. This work illustrates the potentials of ferrates to remove PFAS.

Degradation of Perfluorinated Compounds by Fungal Pure Cultures and Groundwater Microcosms

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Background/Objectives. Perfluorinated compounds (PFCs) are used in over 200 consumer and industrial products, including aqueous film forming foams (AFFF), non-stick coatings, stain-resistant textiles, insulation, and surfactants. PFCs have a long carbon-fluorine chain, which makes them highly stable and resistant to decomposition. The production and discharge of PFCs are regulated in Europe and Australia. In the United States, there are federal and state guidelines for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), two persistent PFCs that are suspected endocrine disrupters, and reproductive and developmental toxicants. Current methods available for removing PFCs from environmental media, such as sonodegradation, photodegradation, and reverse osmosis, are cost- and energy-intensive, and not suitable for cleaning up widespread contamination. In contrast, in situ biodegradation may be a more cost-effective method for remediating PFC-contaminated sites. In this study, the nature and extent of PFC contamination at several Air Force sites and the biodegradation of PFCs were examined.

Approach/Activities. Laboratory pure cultures of the wood-decaying fungus, Phanerochaete chrysosporium, were tested for their ability to biodegrade PFOA, PFOS, and 6:2 FTOH with growth on nutrient supplements such as lignocellulosic powder, yeast extract, cellulose, and glucose. Sediment and groundwater from two sites impacted with PFCs via fire-training and fire-containment operations were used to construct microcosms. Experimental conditions included autoclaved killed controls, simulated natural attenuation, and bioaugmentation with P. chrysosporium. Experimental controls included an autoclaved, sterile control and a live matrix control to account for physico-chemical factors and background levels of poly- and per-fluoroalkyl acids, respectively. Triplicate bottles were sacrificed on days 0, 7, 14, and 28 for LC/MS/MS quantitative analysis and high-resolution mass spectrometry analysis to qualitatively measure PFCs and their biodegradation products.

Results/Lessons Learned. Three novel bacteria and 5 fungi capable of degrading PFCs were isolated from this site based on their capability to degrade other xenobiotics and to tolerate high concentrations (~1 g/L) of PFOA and PFOS. Three fungi were found to tolerate at least 1 g/L PFOA, and when exposed to 0.5 and 1 g/L PFOA, biomass increased (~3–5 mg, dry weight) compared to the PFOA-free control, 0.01 g/L PFOA, and 0.1 g/L PFOA. In one set of the bioaugmented microcosms, a 53% decrease in PFOA was observed after 360 days. Studies are underway to characterize these isolates, and measure biodegradation kinetics. Within 28 days, P. chrysosporium degraded 6:2 FTOH towards poly-fluorocarboxlic acids with lower PFCA yields compared to microbial consortia in various environmental matrices, such as soils and sediments. PFCAs, including perfluoropentanoic acid (PFPeA) and perfluorohexanoic acid (PFHxA), accounted for only 5.7 mol% of initially applied 6:2 FTOH, whereas previous studies using environmental matrices have detected a total of 16–40 mol%. This study demonstrates that fungi such as P. chrysosporium drive biodegradation pathways of PFOA precursors towards more readily degradable poly-fluorocarboxylic acids. These results will be immediately useful to environmental professionals and researchers to determine the applicability of natural and engineered biodegradation processes at PFC-contaminated sites.

Potential Treatment Train Options for Persistent Per/Polyfluoroalkyl Acids

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Overview: The heat stability of per/polyfluoroalkyl substances (PFASs) and their ability to block oxygen and suppress volatile vapors from flammable solvents have resulted in their common use as components of aqueous film-forming foams (AFFFs) amenable to fighting even the toughest fires. Most military facilities that routinely service aircraft maintain fire-fighting training areas to allow emergency personnel to train with AFFFs. Training with AFFFs for more than 30 years has resulted in repeated short-term releases of AFFFs at fire-fighting training areas. When PFASs have been included in the monitoring at military sites, PFASs were found in the groundwater associated with military fire-fighting. In addition, potable water groundwater sources in the United States (e.g., AZ, MN, WV) as well as globally (e.g., England, China, etc.) have been found to be contaminated with persistent of per/polyfluoroalkyl acids (PFAAs) such as of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) for which there are already USEPA Provisional Health Advisory values established as well as state-specific values. Suspected PFAS sources in water supplies range from land applied biosolids, storm runoff, leaky landfills, public fire-fighting activities, and industrial spills and dumping. Many PFAAs including PFOS and PFOA are recalcitrant to biological degradation and also extremely resistant or remain untouched by many traditional abiotic technologies especially those amenable to in-situ remediation. Currently, capture (e.g., activated carbon) is the only technology currently being used for removal of PFAAs in contaminated groundwater; however, this approach commonly results in only limited remediation and typically requires decades of operation.

Approach/Activities: Over the past decade, scientists have begun to address the potential for abiotic destruction of PFAAs. Persulfate oxidation at relatively low temperatures 40-50 °C have been shown successful in laboratory-based aqueous studies for mineralizing per/polyfluoroalkyl carboxylates (e.g., PFOA) and other fluoroalkyl compounds when an ethylene spacer between the perfluorinated tail and the terminal polar functional group (known as telomer-based compounds such as 8:2 fluorotelomer sulfonate, 8:2 FTS). We measured effective mineralization of PFOA and 6:2 FTS with heat-activated persulfate at 40- 50 °C and 2000 – 10,000 mg $Na_2S_2O_8$/L; however, no transformation of PFOS was observed even at 90 °C. PFOS and related compounds appear resistant to oxidation, but some reductive approaches with in-situ potential have shown potential to remove fluorine or the sulfonate group. Preliminary research on using nanoscale-ZVI with Pd, Al, and Ni catalysts or Vitamin B12 systems show promising results for reductive transformation of PFOS. Fluoride, sulfite/sulfate, and preferential loss of different PFOS isomers is being quantified. Intermediates resulting from partial transformation are being quantified with liquid chromatography time of flight mass spectrometry.

Results/Lessons Learned: Transformation of PFOS from 25 to 70% has been achieved in the different reductive systems. Bimetal systems may be appropriate for use in permeable reactive barriers whereas the nZVI/B12 systems have the potential to also be used for in situ injection technologies. Transformation products, although only marginally changed, now have an increased potential to be oxidized, thus highlighting the need to consider treatment train options. Current reductive technologies being explored, oxidation of potential intermediates, and plausible treatment trains will be presented.

Back to Contents

Emerging Contaminant False Positives from Standard Groundwater Sampling Equipment and Procedures

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Background/Objectives. Emerging contaminants are generally characterized by lower health advisory levels and lower analytical quantitation limits than the environmental industry has customarily dealt with over the past several decades with typical site contaminants. Established standards for common groundwater contaminants (e.g., trichloroethene, benzene) are in the range of 5 micrograms per liter (µg/L or parts per billion - ppb). In contrast, several emerging contaminants have health advisory levels that are in the 10's to 100's of nanogram per liter (ng/L or parts per trillion - ppt) range. Attaining these much lower standards in laboratory analysis has the potential to introduce false positive results due to interference from sampling equipment or decontamination detergents containing trace levels of target compounds. False negative analytical results could also result from sorption of the target compounds on either sampling or lab analytical equipment. This presentation will identify sources of false positive and false negative results that may impact findings and conclusions for two of the most well-known emerging contaminants: 1,4-dioxane and per- and poly-fluorinated alkyl substances (PFAS).

Many sampling pumps contain or are coated with fluoropolymers and fluorotelomers, such as polytetrafluoroethylene (PTFE). Internal parts include O-rings, seals, impellers, bladders, and wire jackets. Sample tubing is often coated as well. Many of these parts contact the groundwater sample during collection and have the potential to introduce low-level contamination that may be incorrectly attributed to the facility or aquifer. With potential regulatory standards in the sub-ppb range, such as New Jersey's 0.04 µg/L preliminary health based guidance for drinking water, introduction of low levels of PFAS into a sample could lead to unnecessary regulatory or stakeholder concern.

In a leaching sample from a common environmental detergent that was collected in February 2013, 1,4-dioxane was identified at 760 J µg/L. This sample was not representative of the concentrations that would be present if a manufacturer's recommended 1% solution was prepared, and then triple-rinsed off the sampling equipment. But it still raises a concern that low level 1,4-dioxane detections could be due to residual soap on the sampling device.

Approach/Activities. Equipment blanks were created using the most common sampling equipment by exposing the equipment to Type II Reagent Grade distilled water, collecting the water in PTFE-free sample bottles, and analyzing the samples for a defined list of PFAS at Oregon State University's analytical laboratory. 1,4-Dioxane levels were analyzed in a 1% solution and more dilute mixtures of multiple manufactured batches of powdered and liquid environmental detergent. Analysis was performed in CH2M HILL's Applied Sciences Laboratory.

Results/Lessons Learned. Detections of some of the six PFAS that are on the US EPA's Unregulated Contaminant Monitoring Rule 3 (UCMR3) were noted at the 10's of ng/L level, high enough to raise some concern. Additionally, 1,4-dioxane levels were present in dilute mixtures above the sub-ppb range of several state's regulatory standards.

Field Deployable PFCs Sensors for Contaminated Site Screening

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Background/Objectives. Perfluorinated compounds (PFCs), are emerging and ubiquitous environmental contaminants that have been found at low concentrations in waste water, surface water, soil, and animal tissues. Because they are bio-accumulative, extremely persistent and toxic, several states have established analytical methods and emission limits. Furthermore, there is a huge effort surrounding remediation of PFCs contaminated areas. Considering the impacts on both the environment and public health, there is an acute need for rapid, selective, low cost, and field portable PFCs sensing. Although there are established LC/MS/MS methods to measure PFOA and PFOS at low levels, the methods are tedious and the equipments are expensive and are not field portable.

Approach/Activities. Ion-selective electrodes (ISEs) with fluorous anion-exchanger membranes for the potentiometric detection of perfluorinated compounds, inlcuding perfluorooctanoate ($PFO^–$) and perfluorooctanesulfonate ($PFOS^–$), were developed [1]. The developed ion sensors exhibits exceptionally high selectivities for $PFO^–$ and $PFOS^–$ over interferents that commonly present in environment and trace level detection limits for $PFO^–$ and $PFOS^–$, 1.7×10^{-10} M (0.070 ppb) and 8.6×10^{-10} M (0.43 ppb), respectively. These values are comparable with results obtained using well established techniques such as GC/MS, LC/MS, and LC/MS–MS, but the measurement with ISEs avoids lengthy sample preconcentration, can be performed in-situ, and is less costly.

Results/Lessons Learned. Real life application of these electrodes was demonstrated by in-situ measurements of the adsorption of $PFOS^–$ onto Ottawa sand and detection of $PFOS^–$ in a background of surface water. The results obtained are consistent with those from an earlier LC–MS study, validating the usefulness of these sensors for environmental studies. With a glass-free solid contact reference electrode, a field-deployable sensor system was fabricated. The sensor system was successfully applied for rapid and direct screening and detecting of $PFO^–$ and $PFOS^–$ and providing “Yes” or “No” answer in contaminated soil, surface water and drinking water, demonstrating the fast, easy, sample pretreatment-free, selective and economical nature of $PFO^–$ and $PFOS^–$ detection with fluorous membrane ISEs.

[1] Fluorous Membrane Ion-Selective Electrodes for Perfluorinated Surfactants: Trace Level Detection and In-Situ Monitoring of Adsorption onto Sand; Chen, L. D.; Lai, C.-Z. ; Granda, L. P. ; Fierke, M. ; Mandal, D.; Stein, A.; Gladysz, J. A.; Bühlmann, P., *Anal. Chem.* **2013**, *85,* 7471–7477.

Back to Contents

Bioremediation of 1,4-Dioxane and Mixed Chlorinated Solvents Using Monooxygenase-Expressing Bacteria

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Background/Objectives. 1,4-dioxane was extensively used as a stabilizing agent in chlorinated solvents such as 1,1,1-trichloroethane. This compound has the potential to create large contaminant plumes because 1,4-dioxane is poorly retarded in aquifers. Due to the widespread use of chlorinated solvents as cleaning solvents, many chlorinated solvent contaminated sites likely are contaminated with 1,4-dioxane.

Approach/Activities. An emerging groundwater remediation practice area to address groundwater impacts with 1,4-dioxane is cometabolic bioremediation. Cometabolism is the simultaneous degradation of two compounds, in which the degradation of the second compound (the secondary substrate) depends on the presence of the first compound (the primary substrate). This underappreciated bioremediation strategy has been successfully used on some of the most recalcitrant contaminants, e.g., trichloroethene, dichloroethene, vinyl chloride, 1,4-dioxane.

In aerobic cometabolic bioremediation indigenous bacteria are stimulated by adding oxygen and a cometabolic growth substrate to trigger the production of enzymes. These enzyme then oxidize or degrade the target pollutant via cometabolism. Alkane gases such as methane, propane or ethane are commonly used as the primary substrate. Indigenous mircroorganisms while oxidizing the primary substrate for energy and growth express a monooxygenase enzyme that fortuitously degrades the contaminant (the secondary substrate). The enzyme is a protein-like substance that acts as a catalyst for degradation of the contaminant. Contaminant degradation provides no apparent benefit to the microorganism involved. The biodegrader is not dependent on the contaminant for carbon or energy therefore can perform at low levels of contamination.

This method is most useful for bioremediation of pollutants that are not themselves good aerobic growth substrates for bacteria. Bioremediation strategies that employ cometabolism have the advantage of being able to degrade contaminants to trace concentrations, very low parts per billion levels and actually to parts per trillion.

Results/Lessons Learned. Nutrients are critical to supporting biomass growth and contaminant and cosubstrate metabolism. The addition of nutrients such as diammonium phosphate and water-soluble molybdenum (Mo) increases the kinetics of the degradation reactions and growth of monooxygenase-expressing bacteria. *In situ* cometabolism requires monitoring groundwater nutrient levels, and measuring oxygen and cosubstrate utilization rates as indicators of *in situ* biological activity.

This presentation will present results and lessons learned from several 1,4-dioxane / chlorinated solvent cometabolism laboratory treatability studies and field demonstration projects.

Understanding and Improving Attenuation of 1,4-Dioxane: Data Mining and Treatment Trains

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Background/Objectives. The overall objective of this SERDP-sponsored project is to develop site-specific management approaches for 1,4-dioxane-contaminated sites through applied research on novel in situ treatment technologies, modifications to existing technologies, and a better understanding of plume transport and attenuation characteristics. Currently, there is limited technical information the efficacy of various natural and engineered attenuation processes for 1,4-dioxane. As a result, the prevailing view is that 1,4-dioxane does not readily attenuate and is difficult to treat, particularly using in situ methods.

Approach/Activities. A multi-faceted approach is being used to address these knowledge gaps. This includes intensive data mining to provide information on the rates of 1,4-dioxane attenuation observed at a large number of contaminated sites. Existing long-term 1,4-dioxane site records are being used to evaluate the general hypotheses that 1,4-dioxane attenuation is slow relative to co-occurring chlorinated solvents and that 1,4-dioxane attenuation is influenced by site characteristics. Secondly, a laboratory-based evaluation of the natural biological attenuation potential of 1,4-dioxane under a range of conditions and in tandem with other treatment methods is being conducted. By examining various “treatment train” approaches for 1,4-dioxane and CVOC co-contaminants, the goal is to determine potential enhancements or incompatibilities that might be expected when technologies are combined.

Results/Lessons Learned. Based on a comparison between historic and recent maximum site concentrations, 1,4-dioxane has decreased by a median value of 74% over time at > 100 field sites that were part of the data mining efforts. This is comparable to the reductions observed for TCE and 1,1-DCE but significantly less than that for 1,1,1-TCA. Using site-by-site and well-by-well data, a number of site characteristics have a small but statistically significant impact on 1,4-dioxane reduction and/or plume length, including hydraulic conductivity and the maximum dioxane concentration. The data indicate that vinyl chloride negatively impacts 1,4-dioxane attenuation, but that the presence of other chlorinated solvents have little to no apparent impact. Based on sites where a statistically significant first-order attenuation rate could be calculated, 1,4-dioxane attenuation is occurring at the majority of sites (half-life = 3 years), and non-parametric trend analyses suggested that most plumes could be classified as stable (42%) or decreasing (36%). Similar data have been compiled for co-occurring chlorinated solvents. Studies evaluating the performance of combinations of in situ technologies are also underway using soil and groundwater from a site in Oklahoma contaminated with both 1,4-dioxane and chlorinated solvents. The focus is on examining the potential efficacy and impacts of various “treatment train” approaches for 1,4-dioxane and CVOC co-contaminants, including enhanced biodegradation, in situ chemical oxidation, and catalysis. Results presented here will include comparisons of degradation rates and by-products/end-products of technologies used individually and in tandem. In addition, the impact of high and low concentrations of 1,4-dioxane and co-occurring chlorinated solvents are being tested to understand how inhibition and/or preferential utilization might influence the performance of individual technologies. A specific goal is to understand how site conditions and technologies impact the abundance and expression of 1,4-dioxane degradative capabilities of native and/or introduced microorganisms.

Cometabolic Biodegradation of Comingled 1,4-Dioxane and Chlorinated Solvent Plumes

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Background/Objectives. 1,4-Dioxane (1,4-D) is often found as a co-contaminant at Air Force chlorinated solvent sites due to its historical use as a stabilizer for 1,1,1-trichloroethane (TCA) and possibly other chlorinated solvents (CVOCs). The standard approach for treatment of 1,4-D in groundwater is extraction followed by advanced oxidation (AO) using UV, hydrogen peroxide and/or ozone. AO systems, however, are very expensive to build and operate due to high energy, chemical, and labor costs. One potential approach for 1,4-D treatment is *in situ* aerobic cometabolism in the presence of a cosubstrate such as methane, ethene, and ethane. Studies in literature have demonstrated 1,4-D biodegradation under laboratory conditions and confirmed the presence of cometabolic biomarkers (e.g., methanotroph activity and monooxygenase generation) at 1,4-D field sites. This AFCEC-funded project builds upon this concept by evaluating the use of a fermentable organic substrate to produce methane, combined with sequential oxygen addition, to enhance *in situ* cometabolic biodegradation of 1,4-D and CVOCs in groundwater.

Approach/Activities. The technology demonstration design consists of two treatment barriers. An upgradient permeable reactive barrier (PRB) formed by injecting an emulsified oil substrate through a line of wells and a downgradient oxygen releasing barrier, to create distinct geochemical zones (anaerobic/aerobic) within a comingled 1,4-D and CVOC plume. Area of Concern 1 (AOC1) at Former Air Force Plant 3 (AFP 3) in Tulsa, OK was selected for the field demonstration. Trichloroethene (TCE) and 1,4-D concentrations in groundwater of up to 30,000 µg/L and 660 µg/L, respectively, were observed within the test area. In August 2013, approximately 330 gallons of diluted emulsified oil and chase water were injected to create the upgradient barrier, followed by a commercial dechlorinating bacterial consortium to enhance CVOC treatment performance and accelerate methane production.

Results/Lessons Learned. To date, performance results have been promising. Eight months after substrate injection, increased biological conversion of TCE was observed, as evidenced by the increased concentrations of *cis*-1,2-dichloroethene, vinyl chloride and ethene in all injection wells and up to 40 ft downgradient of the PRB along with significant methane generation from oil fermentation within the subsurface groundwater. Unexpectedly, around 40 to 60% decrease in 1,4-D concentrations was also observed in almost all injection and monitoring wells after 6 months. To better understand possible mechanisms for the observed 1,4-D decrease, Bio-Trap® samplers baited with C-13 1,4-D were installed in selected wells in August 2014. Analysis of Bio-Trap® samplers is currently underway. Data obtained from the Bio-Traps® can be valuable for better understanding 1,4-D biodegradation potential and also be used to adjust the final design and location of the oxygen barrier.

Remediation of 1,4-Dioxane using a Thermophilic Aerobic Bacteria and its Cell-Free Extract

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Background/Objectives. 1,4-dioxane has emerged as a contaminate of concern in groundwater due to its high mobility and acute toxicity. Methods using oxidation to accelerate degradation are currently the dominant remediation approach. Dioxane is chemically similar to pollutants such as dibenzo-dioxins and dibenzo-furans that we have treated successfully in the past with bioremediation. We report here on the application of a similar protocol for the degradation of dioxane. Pollutants such as dibenzo-dioxins and dibenzo-furans share an aryl ether structure with dioxane and were expected to be susceptible to degradation by *G. miduosuji*, a thermophile isolated from compost. Prior work indicated that the dibenzo-dioxins and dibenzo-furans could be rapidly degraded using both slurry-phase and solid-phase incubation approaches. The present work extends the application of the *G. miduosuji* to dioxane contaminated media.

Approach/Activities. Prior work with *G. miduosuji* allowed us to define its nutrient requirements and to optimize the temperature and oxidative conditions. At 60°C, over 50% of the total dibenzo-dioxins and dibenzo-furans in fly ash were destroyed over a 48 hour period. To evaluate the efficacy of this bacterium for dioxane degradation, the live cells were grown on glass beads and used as the stationary phase in a packed bed column. The contaminated ground water or laboratory test samples were then pumped through the columns and flow rates were varied to determine the relationship (if any) between sample exposure time and degradation efficiency. Additional experiments were done with *G. miduosuji* cell extracts to assess the ability to degrade dioxane in cell-free systems. In all cases, parallel control treatments having the same conditions as the treatment except for the presence of the Geobacilli were done.

Results/Lessons Learned. The results of the initial packed column studies demonstrated a degradation rate of 7% at a residence (flow through) time of about 1 minute. Additional experiments are being carried out to characterize a full range of flow and temperature conditions. In prior solid phase tests on dibenzo-dioxins and dibenzo-furans the degradation rates of the individual homologs varied and in general, degradation rates were greater for the penta- and hexa-chlorinated dioxins and furans (0.8 day-1) than for the tetra-chlorinated forms (0.15-0.2 day-1). We also will report on work with cell extracts that maintain enzymatic activity. The themophilic nature of the organism means it can't be introduced directly into the environment so the main application will be in pump and treat related BioGAC systems; these have worked with MTBE another GAC recalcitrant ether. Also, we envision possible treatment modalities in bioreactor systems and compost piles for excavated sediments and soils.

Field Application of Biomarker-based Tools to Validate 1,4-Dioxane Biodegradation

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Background/Objectives. 1,4-Dioxane is an emerging contaminant of concern, which is commonly associated with chlorinated solvent plumes. Due to its high solubility in water, resistance to biodegradation under natural conditions and ineffective removal by technologies applicable for chlorinated solvents, 1,4-dioxane plumes typically extend beyond chlorinated solvents plumes. 1,4-Dioxane biodegradation, catalyzed by monooxygenase enzymes, has been reported in a number of laboratory studies, and *Pseudonocardia dioxanivorans* CB1190 (hereafter CB1190) was identified as a bacterium capable of using 1,4-dioxane as a sole carbon and energy source under aerobic conditions. However, molecular biological tools to validate the occurrence of 1,4-dioxane biodegradation have not yet been established. The project team has recently identified 1,4-dioxane biomarkers and designed primer sets to amplify monooxygenase genes for 1,4-dioxane biodegradation. To validate the 1,4-dioxane biomarkers, the project team constructed various microcosms with contaminated groundwater or activated sludge samples. In these microcosms, the abundance of the following genes was significantly correlated with dioxane degradation ($r = 0.75 – 0.92$, $p<0.01$): phenol (PHE), propane (PrMO), alcohol dehydrogenase (ADH) and aldehyde dehydrogenase (ALDH) and dioxane (DXMO) monooxygenase enzymes. A field validation step was therefore conducted to further confirm the applicability of 1,4-dioxane biomarkers for site investigation and remediation.

Approach/Activities. 1,4-Dioxane biomarkers were applied at sites to evaluate 1,4-dioxane natural attenuation potential and the effectiveness of enhanced 1,4-dioxane biodegradation via biostimulation and bioaugmentation. This effort included the collection of groundwater and BioTrap^{TM} samples from three sites to evaluate natural attenuation potential and from one site to evaluate enhanced 1,4-dioxane biodegradation by supplying propane and propanotrophs. Additionally, a series of groundwater and baited BioTrap^{TM} samples were collected from one well where BioTraps^{TM} were amended with CB1190 and a slow release oxygen source followed by deployment in a well for 6 months. The collected 1,4-dioxane biomarker data were reviewed with the site chemical, geochemical and hydrological data to determine the applicability of 1,4-dioxane biomarkers as a line of evidence that supports MNA and enhanced biodegradation.

Results/Lessons Learned. This is the first field application that quantifies the abundance as well as expression of 1,4-dioxane degrading monooxygenase genes, and relates the 1,4-dioxane biomarker responses to natural attenuation, biostimulation and bioaugmentation.

Sustainable Phytoremediation of 1,4-Dioxane: 10 Years of Success

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Background/Objectives. The project site is an established example of effective sustainability in long term remediation of a 1,4-dioxane plume. Phytoremediation was implemented in 2004 as a remedy for 1,4-dioxane in groundwater at a closed landfill facility. The project site was used in the past to dispose of general waste and byproducts of polyester resin. These byproducts included 1,4-dioxane.

Historically, the contaminated groundwater at the site was extracted and treated by an ultraviolet/hydrogen peroxide oxidation process and discharged under an NPDES permit. Groundwater extraction was suspended in 2002 due to an extreme drought in the area. However, soon after the deactivation of the extraction system, a groundwater seep manifested itself as surface flow traveling from a surface water and toe-drain collection sump to the receiving river. A combination of monitored natural attenuation and phytoremediation were approved for groundwater remediation and seep control.

Approach/Activities. A pilot program was installed in March 2004. Subsequently, a full-scale phytoremediation system was designed with the combined purposes of hydraulic control and removal of 1,4-dioxane from the groundwater. Upon state regulatory agency approval, the full scale phytoremediation system was installed at the toe of the landfill in an area of approximately 8,000 sq. ft. A total of 106 14-foot tall rooted poplar trees were planted 6 feet below ground in 12 rows. The tree rows were planted perpendicular to the surface drainage flow and the general groundwater flow direction. Construction of the full scale system was completed in December of 2005.

After initial review of the system performance and health, a supplemental planting was completed in April 2007. Since 2007 routine monthly inspections and periodic maintenance, including pruning, minor supplemental plantings, and application of fertilizer have been the primary activities, in addition to semi-annual monitoring. A significant pruning and supplemental planting effort was completed in the spring of 2012. Further significant maintenance activities are expected to occur once every five years. The result is a low-cost self-sustaining treatment system capable of maintaining the remedial and administrative objectives for the site.

Results/Lessons Learned. Through 2014, the system has remained healthy and intercepted the groundwater seep as expected. Surface water sample locations of the seep are usually dry, as a direct result of the water uptake capacity of the trees. Samples have demonstrated a decrease in 1,4-dioxane concentration of 50% or better. The mechanism of decreased concentration is uptake of the 1,4-dioxane into the trees. Bench studies have indicated that the fate of the 1,4-dioxane is volatilization after a minimal period of residence in the tree body. Decreased concentrations result from removal of the highest concentration water and increased flow of lower concentration water into the area.

The phytoremediation system continues to be inspected, maintained and monitored in compliance with regulatory requirements.

Bench-Scale Testing Of Various AOPs For Removal of 1,4-Dioxane versus Bioremediation and MNA

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Background/Objectives. Tetra Tech, Inc. (Tetra Tech) is designing a pump-and-treat containment system for treatment of impacted groundwater at a 30-acre former dump site located in the State of Maryland. Environmental issues at the site (which is located adjacent to a water body that is a tributary of the Chesapeake Bay) were originally discovered in the 1990s. Numerous investigations have been conducted to ascertain the size and orientation of the contaminant plume. The groundwater is predominantly impacted by chlorinated volatile organic compounds (*CVOC),*1,4-dioxane, and heavy metals. The treatment system will utilize a number of treatment processes including advanced oxidation for the treatment of 1,4-dioxane which has a treatment goal of 6 parts per billion (ppb). The objective of this study was to compare the bench-scale test results to less energy-intensive, more environmentally sustainable alternatives such as bioremediation and monitored natural attenuation (MNA).

Approach/Activities. Bench-scale treatability testing was performed to assess the treatment efficiency and limitations of different types of advanced oxidation processes (AOP), including (1) ultraviolet (UV)-titanium dioxide, (2) ozone-hydrogen peroxide, and (3) UV-hydrogen peroxide. AOP bench-scale tests were performed in 2012 and 2013 in accordance with a work plan jointly developed by Tetra Tech and the system suppliers. Fifty gallons of groundwater from the most contaminated well was collected and shipped to each of the system suppliers for the bench-scale testing. The groundwater was pretreated by pH adjustment, anionic polymer addition, mixing, settling, and filtration prior to shipping to each of the AOP facilities. Each system supplier performed bench-scale testing using their equipment with varying parameters relevant to their systems. Some of the parameters included UV dose, hydrogen peroxide concentration, ozone dose, and hydrogen peroxide-to-ozone molar ratio.

Results/Lessons Learned. UV-Titanium Dioxide: Results of the treatability testing suggest that the size of the AOP system and energy input requirements are controlled by the degradation rate of 1,4-dioxane. The process degraded 1,4-dioxane and other Contaminants of Concern (COCs) to the required degree.

Ozone-Hydrogen Peroxide: Results for the bench-scale test established that the process is able to achieve discharge criteria for 1,4-dioxane and other COCs. However, the process produces bromate at concentrations above its MCL (10 micrograms per liter [µg/L]). The process is more complex; three variables (ozone dose, hydrogen peroxide to ozone molar ratio, and number of injectors) require adjusting to meet discharge standards and simultaneously control bromate formation.

UV-Hydrogen Peroxide: Samples were sent to two system suppliers for testing. One supplier used medium-pressure lamps and spiked groundwater, while the second supplier used low-pressure lamps and unspiked groundwater. Both system suppliers were successful at treating 1,4-dioxane and other COCs to the required degree.

The bench-scale test results were compared to more sustainable alternatives such as bioremediation and MNA monitored natural attenuation. Because limited data exists on bioremediation and MNA of 1,4-dioxane in particular, and the client required a system to contain

In Situ Thermal Remediation of 1,4-Dioxane and Advances in Heat-Enhanced Bioremediation

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Background/Objectives. 1,4-Dioxane resists in situ treatment by conventional advective flow based technologies. Effective remediation is limited to expensive, ex situ treatment by advanced chemical oxidation using processes that produce hydroxyl radicals. However, significant concentration reductions (>99%) in 1,4-Dioxane were recently observed at two electrical resistance heating (ERH) projects where ERH was used for treatment of chlorinated solvents in groundwater.

The efficacy of combining ERH and bioremediation technologies to reduce contaminant mass flux from source zones and enhance reductive dechlorination in the downgradient plume has moved from concept to field application. Remedial designs are more frequently including the combination of these approaches into the site wide conceptual model.

Approach/Activities. The field observations lead to further bench testing to evaluate the effects of 1,4-Dioxane treatment by steam stripping. The tests showed that the vapor-liquid equilibrium mass fraction ratios of 1,4-Dioxane to water increase substantially as the system approaches the boiling point of water. The mass fraction of 1,4-Dioxane in steam produced during ERH is an order of magnitude higher than in the water being boiled. When the steam and 1,4-Dioxane vapors are combined with sufficient air, the bulk of the 1,4-Dioxane remains in the vapor phase where it can be readily treated using vapor phase activated carbon.

Results/Lessons Learned. Recent results and lessons learned from full scale field applications including ERH remediation of 1,4-Dioxane and heat enhanced bioremediation of chlorinated solvents including engineering design elements and costs will be presented.

Using Aerobic Cometabolic 1,4-Dioxane Biodegradation and Groundwater Recirculation to Treat 1,4-Dioxane and Co-Contaminants in a Dilute Plume

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Background/Objectives. Treatment of groundwater contaminated with 1,4-dioxane (1,4-D) and chlorinated solvent compounds is a requirement at many Air Force cleanup sites. The presence of 1,4-D in a chlorinated solvent plume often forces the selection of a more costly pump-and-treat remedy during the Feasibility Study process. Due to the high costs of ex-situ treatment, viable in-situ treatment technologies for 1,4-D are desired. Although numerous studies on aerobic cometabolic biodegradation (ACB) of 1,4-D have been published, most of them have been laboratory studies at high 1,4-D concentrations, not the low 1,4-D levels typically found at Air Force sites. To better evaluate the potential of using ACB to treat 1,4-D and co-contaminants in a dilute plume, the project team has been funded by the Air Force Civil Engineer Center to conduct a field test using groundwater recirculation to deliver substrates and bioaugmentation to enhance 1,4-D biodegradation in situ.

Approach. The project consists of three key phases: (1) laboratory testing, (2) biostimulation, and (3) bioaugmentation. For Phase 1, numerous aerobic propane-oxidizing bacteria were tested to assess their ACB potential towards 1,4-D. Two bacterial strains were selected for further testing using groundwater from a candidate site to evaluate whether these bacterial strains can grow and perform biodegradation under site-specific groundwater conditions. After the conclusion of the laboratory testing, an injection/extraction well pair, a monitoring network, and an above-ground substrate delivery system will be constructed. The substrate delivery system will add propane and oxygen to extracted groundwater. Extracted groundwater will then be re-injected to support the growth of propane-oxidizing bacteria in situ. During Phase 2, a conservative tracer test will be conducted to characterize the travel times from the injection well to individual monitoring wells, followed by biostimulation of indigenous propane-oxidizing bacteria in order to assess the background ACB activity. In Phase 3, promising bacterial strains selected in Phase 1 will be used to bioaugment the recirculation zone and the performance enhancement due to bioaugemetation will be evaluated. The project team plans to track transport and in-situ activity of the bioaugmentation culture through various microbial molecular methods.

Results. The laboratory tests conducted so far have indicated that, out of the 5 commercially available strains, only one organism, Arthrobacter sp. has exhibited robust 1,4-D-transformation activity in our screening procedure. In contrast, all of the isolates obtained from Dr. Hyman's laboratory from previous MTBE and TBA degradation studies appear to have substantial 1,4-D transformation activities, and a pure culture of Mycobacterium sp. was found to degrade 1,4-D to a level below 1 □g/L. All of the test strains grow on propane and likely utilize monooxygenase enzymes to initiate propane (and 1,4-D) degradation, our results suggest that there are a variety of propane-oxidizing monooxygenases that are unreactive towards 1,4-D.

Microbially-Driven Fenton Reaction for Simultaneous Degradation of 1,4-Dioxane and Co-Located Contaminants Tetrachloroethylene (PCE) and Trichloroethylene (TCE)

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Background/Objectives. Hazardous contaminants of heightened concern include the chlorinated solvents tetrachloroethene (PCE) and trichloroethene (TCE) and the solvent stabilizer 1,4-dioxane. Recent concern over these contaminants in surface waters and groundwaters is driven by several factors, including widespread use and improper disposal practices by industry, high miscibility in water, recalcitrance to conventional degradation processes, and classification as probable human carcinogens. Current remediation technologies entail carbon absorption, distillation, UV based advanced oxidation processes and ex situ pump-and- treat procedures that are neither cost effective nor able to effectively remove co-contaminants such as 1,4-dioxane, PCE, and TCE. The objective of this study is to degrade 1,4-dioxane simultaneously with co-located contaminants PCE and TCE via a microbially driven Fenton reaction that operates at circumneutral pH and does not require continual addition of the Fenton reagents Fe(II) and peroxide.

Approach/Activities. *Shewanella oneidensis*, an iron respiring facultative anaerobe was used as a biocatalyst for the generation of hydroxyl radicals via the Fenton reaction. Hydroxyl radical were produced by providing *S. oneidensis* batch cultures with Fe(III) and alternating between aerobic/anaerobic conditions with lactate as the electron donor. The system was initially tested under different aerobic/anaerobic cycling frequencies of 0.75, 1.5, 3, and 6 hours to optimize the degradation of 10 mM 1,4-dioxane. The system was subsequently applied to simultaneously degrade 1,4-dioxane in the presence of 500 μM TCE and 500 μM PCE in a fed-batch reactor design.

Results/Lessons Learned. Based on our findings, the generation of reactive hydroxyl radicals through the microbially driven Fenton reaction effectively degraded 1,4-dioxane generating intermediates identified as acetate and oxalate through chromatographic methods at an optimal cycling time of 3 hours. The modified fed-batch reactor system also degraded 1,4-dioxane, TCE and PCE in combination as co-contaminants. The contaminants were not degraded in control experiments in the absence of bacterial cells (abiotic control) or Fe(III). This system is currently being optimized to improve rates of co-contaminant degradation by examining effects of varying bacterial cell density and the concentrations of Fe(III), oxygen, and the three co-contaminants in fed-batch reactor configurations.

Bench-Scale Assessment of Monitored Natural Attenuation and Bioremedial Treatment Alternatives of 1,4-Dioxane at a Contaminated Site

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Background/Objectives. 1,4-Dioxane (Dioxane) is an emerging groundwater contaminant that is commonly found at sites impacted by chlorinated solvents, typically 1,1,1-TCA. However, the hydrophilic nature of dioxane precludes efficient physical and chemical treatments. Recent ?ndings by our lab and others suggest that indigenous bacteria that can degrade dioxane might be more widespread than previously assumed [1-6]. Here, we seek to evaluate the performance of various *in situ* biological remedial alternatives to mitigate dioxane at a site located in west Texas through a long-term microcosm study.

Approach/Activities. Groundwater and aquifer materials were collected at a total of four monitoring wells at the site, representing different dioxane contamination levels (i.e., source, middle, leading-edge of the dioxane plume, and background control). Triplicate microcosms were prepared with the components for treatments mimicking natural attenuation, bioaugmentation (with the archetype dioxane degrader, *Pseudonocardia dioxivorans* CB1190), and biostimulation (with 1-butanol, methane, propane, and tetrahydrofuran [THF]). All microcosms were incubated at room temperature under aerobic conditions. Dioxane concentrations were monitored using a frozen micro-extraction method followed by GC/MS [7], and initial (time 0) and final (16 weeks later) copy numbers of *thmA/dxmA* and 16S rDNA genes were measured by real-time qPCR using *Taqman* (5' nuclease) assays [8].

Results/Lessons Learned. This microcosm study demonstrates that dioxane can be degraded by indigenous microorganisms in groundwater and aquifer materials collected near the source and middle zone area at the site located in west Texas. Three converging lines of evidence have been provided to indicate the presence of indigenous microbes that are capable of utilizing dioxane as a sole carbon source: i) considerable dioxane removal was observed in biologically active microcosms but bot in sterile controls; ii) genes encoding large hydroxylases of THF/dioxane monooxygenases were abundant and enriched while incubation; and iii) ^{14}C dioxane was oxidized to $^{14}CO_2$ and a significant correlation between ^{14}C recovery as CO_2 and dioxane degradation activity was observed ($p<0.05$). Bioaugmentation with CB1190 significantly enhanced dioxane removal compared to natural attenuation. Biostimulation with some auxiliary carbon sources was either ineffective (e.g., with methane) or only marginally beneficial (e.g., with 1-butanol) compared to natural attenuation or bioaugmentation. For biostimulation with THF, dioxane degradation occurred after more than half of the initial THF (300 ppb) was consumed in source-zone microcosm, suggesting THF may not be a good auxiliary candidate to facilitate dioxane removal at this site. In contrast, dioxane degradation was stimulated (perhaps cometabolically) by propane, albeit after a three-month lag period. Thus, further research is recommended to assess the feasibility of this approach and to enhance and optimize the performance of indigenous propanotrophs to mitigate dioxane plumes.

Effect of Hexavalent Chromium on the Biodegradation of 1,4-Dioxane

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Background/Objectives. 1,4-Dioxane is a probable human carcinogen and an emerging contaminant in groundwater at many military and industrial contaminated sites. Biodegradation of 1,4-dioxane has been successfully established in laboratory studies, which show that aerobic bacteria use monooxygenase enzymes to catalyze the oxidation of 1,4-dioxane. A lack of comprehensive understanding of site biogeochemical influences has prevented the successful transition of 1,4-dioxane biodegradation in the laboratory to the field. Co-contaminant metals can potentially serve as inhibitors to microbes carrying out *in situ* biodegradation of 1,4-dioxane. At Air Force installations, hexavalent chromium was found at levels above remediation goals in 25% of all groundwater samples tested. In this study, we report the effects of hexavalent chromium (Cr(VI)) on 1,4-dioxane biodegradation.

Approach/Activities. Biodegradation of 1,4-dioxane by *Pseudonocardia dioxanivorans* CB1190 was investigated in the presence of different concentrations of Cr(VI). All experiments were conducted in 100 mL bottles containing bacteria cultured in 25 mL ammonium mineral salt medium (AMS) with the initial 1,4-dioxane concentration of 1 or 100 mg/L. In order to determine the half maximal inhibitory concentration (IC_{50}) of Cr(VI) for CB1190, Cr(VI) concentrations tested included 1, 2, 5, 10, 25, 50, 100, 200, 350, or 500 mg/L In addition to pure culture studies, microcosms were established using groundwater from sites contaminated with 1,4-dioxane as well as Cr(VI). Concentrations of 1,4-dioxane were quantified over time using Agilent 6890 Chromatograph (GC) equipped with a Flame Ionization Detector (FID) and a Restek Stabilwax-DB capillary column (30 m x 0.53 mm id x 1 µm). Biodegradation rates obtained from the various experiments were statistically compared to determine the effects of Cr(VI) on biodegradation of 1,4-dioxane.

Results/Lessons Learned. Our results demonstrated that Cr(VI) had a pronounced inhibitory effect at concentrations as low as 50 mg/L on pure cultures of CB1190, with an IC_{50} of 95.5 mg/L ($R^2 = 0.91$, $p < 0.05$). Complete biodegradation of 1,4-dioxane required an additional 48 hours in the presence of 5 mg/L Cr(VI) compared to the chromium-free control. At 50 mg/L Cr(VI), 43% of the initial 100 mg/L dioxane was degraded over 72 hours. 1,4-Dioxane was not biodegraded in the presence of 500 mg/L Cr(VI) for the full duration of these experiments. Quantification of 16S rRNA genes using qPCR confirmed that 5 mg/L Cr(VI) extended the lag phase by 72 hours more than the Cr-free control, however a significant difference in cell yields could not be determined. These results suggest that Cr(VI) inhibits dioxane biodegradation rates despite having little effect on the bacterial population responsible for degradation of dioxane. In our early results, only 43% of 1,4-dioxane was removed in the presence of 50 mg/L Cr(VI) in the 11 days, however those results were obtained with low initial biomass concentrations of approximately 1×10^5 cells/L. Increasing the initial biomass concentrations by 10-fold was able to remove 85% of the initial 1,4-dioxane concentrations in the presence of 50 mg/L Cr(VI) within 12 hours. These results lend further support that Cr(VI) is an inhibitor of 1,4-dioxane biodegradation; however, inhibition on 1,4-dioxane biodegradation rates could be mitigated by a robust microbial community. Results obtained from this study will be useful for environmental professionals in selecting biodegradation as a remedial technology for certain groundwater resources contaminated with 1,4-dioxane as well as hexavalent chromium.

Back to Contents

Programmatic Approaches for Management of Emerging Contaminants

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Background/Objectives. The identification of chemicals of emerging concern (CECs) at established remediation sites can have a significant effect on real or perceived liabilities associated with these sites. CECs can come onto regulatory radar due to toxicity re-evaluation (e.g., TCE), discovery (e.g., PFCs), new exposure pathways to humans (e.g., hexavalent chromium), or lower detection limits (e.g., 1,4-dioxane). There are also “emerging issues”, which represent increasing concerns for society, regulators, manufacturers or property owners, such as vapor intrusion, emerging technologies (e.g., nanotechnologies) and sustainability. CECs require diligence and awareness on the part of facility owners and engineering consultants to ensure that no one is blindsided by new issues. Programmatic management of CECs in large portfolios is often an efficient approach to addressing CECs.

Approach/Activities. Federal agencies have employed a wide variety of approaches to the identification and assessment of CECs and CEC-impacted sites, ranging from case-by-case evaluation in response to direct regulatory inquiry, to enterprise-wide investigation of major installations in their portfolio. Examples of programmatic approaches to management of emerging contaminants will be provided from the US Air Force, US Navy, and the Australian Department of Defence.

Results/Lessons Learned. This presentation will present guidance and policy, technical approach, and lessons learned from these various programmatic approaches.

Laboratory Treatability Studies to Assess Degradation Processes for 1,2-Dichloropropane

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Bella Bakrania (O'Brien & Gere, Philadelphia, PA)

Background/Objectives. There is little available information in the literature on the treatability of 1,2-dichloropropane (1,2-DCP), a compound with groundwater and surface water quality standards in the state where the Site is located. 1,2-DCP-impacted Site groundwater is also characterized by high and low pH (4 – 10 s.u.) and high sulfate concentrations (1,000 mg/l). In-situ remedial measures including source injections and a Permeable Reactive Barrier (PRB) are under consideration. Due to the lack of studies on this compound, O'Brien & Gere performed several treatability studies using Site groundwater. Tests were designed to capture potential remedial design data where possible.

Approach/Activities. O'Brien & Gere retained a laboratory to perform a treatability study to assess the potential for enhancing in situ bioremediation of 1,2-DCP (Test A). Test A involved biostimulation of the indigenous microbial population using sodium lactate as an electron donor and bioaugmentation using three commercially available bacteria cultures. The potential for enhancing degradation through the addition of microscale zero-valent iron (ZVI) and an emulsion of ZVI (surfactant, soybean oil, and water) were also evaluated. In addition, O'Brien & Gere evaluated accelerated hydrolysis through heating as a mean of transforming 1,2-DCP to propylene glycol abiotically. O'Brien & Gere later retained a different laboratory to assess the abiotic reduction of 1,2-DCP by ZVI (Test B). Test B included an evaluation of several commercially available ZVI products for possible use in a PRB. The objectives were to identify potential intermediate and final products, calculate a degradation rate for 1,2-DCP, and estimate a residence time for 1,2-DCP reduction by ZVI emplaced in a PRB. O'Brien & Gere retained a third laboratory to test ZVI (Test C) on 1,2-DCP-spiked deionized water instead of Site groundwater to eliminate geochemical variables identified in Test B. In addition, O'Brien & Gere requested this laboratory also assess the potential for chemically oxidizing 1,2-DCP (Test D) using a commercially available activated persulfate.

Results/Lessons Learned. Test A: The rate and extent of intrinsic degradation of 1,2-DCP in Site groundwater is limited likely by the lack of available nutrients at the Site. Indigenous bacteria present at the Site are capable of completely degrading 1,2-DCP (up to 160 mg/L) via the dichlorelimination pathway to form propylene with the addition of lactate as an electron donor. High concentrations of sulfate do not inhibit the biodegradation of 1,2-DCP. Extreme pH's inhibit the ability of the indigenous bacteria to reduce 1,2-DCP to propylene. Test B: The ZVI microcosm testing did not provide a conclusive, proof of concept demonstration that ZVI treatment can be effective in a PRB application in reducing 1,2-DCP in Site groundwater. Tests C and D are in progress. Early Test D results appear favorable. All results will be available for presentation by the May 2015 conference.

A Case for the Development of a Pentachlorophenol Degrading Consortium

Duane Graves and Andrew Montgomery (Geosyntec)
Ernest Mott-Smith (mott-smithe@bv.com), Ed Hicks, and Cal Butler
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Background/Objectives. PCP is a common contaminant on hazardous waste sites. Over 300 of the approximately 1600 National Priorities List sites in the United States have been impacted by PCP. The chemical was used as a biocide and wood preservative and is typically a major contaminant of concern for wood treating facilities. Toxicologically, PCP is a threat to the liver, kidneys, blood, lungs, nervous system, immune system and gastrointestinal tract and is deemed a probable human carcinogen by EPA. PCP is an engineered chemical, not occurring naturally. Consequently, the degradation of PCP is inconsistent from site to site because microbes appear to have not evolved common enzymes that efficiently catalyze the steps needed to degrade the compound either through respiratory or assimilatory pathways. To date, no well-documented commercially available microbe consortiums are available for PCP degradation, although there has been some limited effectiveness using KB-1® Plus.

State of the Practice. The argument for developing a PCP degrading consortium will be presented followed by a proposed pathway for accomplishing this goal. First, the physicochemical and biological properties of PCP will be reviewed and the relative magnitude and distribution of PCP contamination worldwide will be discussed. The current understanding of the PCP aerobic and anaerobic degradation pathways will be presented along with the relative effectiveness of natural strains of bacteria that can degrade PCP (e.g., *Sphingomonas chlorophenolicum*). Site specific data from EPA wood treating sites will be compared to evaluate the variable treatment success of natural and enhanced biodegradation.

Technical Path and Impetus for a PCP Degrading Consortium. A proposed technical path for identifying, enriching, and commercializing a viable consortium will be outlined. Screening level studies of existing PCP sites will be used to select the most robust degraders. Samples from these sites will then be put through a selection and dilution process followed by growth and enrichment phase to produce a useable consortium. The estimated cost and timeframe for development of the consortia will also be presented. The value of a robust PCP degrading consortium will be evaluated for potential savings relative to existing treatment technology.

Phased Sustainable Bioremediation Obtains Closure of a Perchlorate Contaminated Site

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Background/Objectives. Multiple releases of perchlorate from a process building occurred over a period of approximately 50 years at a small manufacturing facility in the Midwest. Perchlorate had impacted both shallow soils and groundwater at the facility above state recommended guidance levels with concentrations in groundwater as high as 1,100 µg/L and soil at 28,000 µg/kg. A phased sustainable remedial approach was determined to be the most comprehensive solution to address the perchlorate source area and reduce perchlorate concentrations in soil and groundwater.

Approach/Activities. The phased sustainable remedial approach included the following; establishing an in situ injection biobarrier in groundwater, decontamination and demolition of the process building and finally, shallow soil-mixing in the former building footprint to introduce an electron donor/carbon source to generate an in situ bioreactor. The first phase involved installation of the biobarrier immediately down gradient of the process building in August of 2010 to assure that the reducing conditions and carbon/electron donor was introduced to groundwater prior to beginning the soil remediation phase. The injections were conducted starting at approximately 23 feet below ground surface (bgs) (at the top of the aquitard) up to seventeen feet bgs. Two thousand gallons of a five percent emulsified vegetable oil solution (100 gallon solution injected into each point for a total of 1,500 gallons of ESO in a solution of 30,000 gallons. The next phase included the decontamination and demolition of the process building that was conducted in September 2010. The final phase was conducted immediately following the decontamination and demolition of the building that included introducing an electron donor/carbon source into the soils to stimulate the microbial degradation of perchlorate. Approximately 12 yards of hardwood mulch and municipal yard waste, obtained locally, was mixed into the top 48 inches of soil over an area 30 feet by 30 feet just inside the footprint of the former building. Drip irrigation lines were then placed in the furrows created by the soil/mulch tilling to introduce 12,000 gallons of a 1% solution of calcium magnesium acetate as an additional water soluble electron donor/carbon source.

Results/Lessons Learned. Perchlorate in groundwater has reduced from 1,100 µg/L to < 10 µg/L in the performance monitoring well immediately downgradient of the biobarrier. Perchlorate in soil reduced from an average of 19,000 µg/kg to an average of 500 µg/kg in 6 months. These significant reductions in perchlorate concentrations observed in both groundwater and soils have met the remedial goals and have facilitated the request for closure of the Site under the State voluntary remediation program in the fall of 2014. The sustainable remedial strategy included minimal low-carbon footprint subsurface injections and shallow soil mixing with a locally and on-site obtained carbon source that required no additional energy expenditure and minimal monitoring over the 3-year remediation program. No further action is currently being negotiated with the state regulator for both soil and groundwater.

Back to Contents

Laboratory Treatability Study to Assess the Aerobic Biodegradation Process for Propylene

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Cindy Schreier, Ph.D., President (PRIMA Environmental, El Dorado Hills, CA)

Background/Objectives. There is little available information in the literature on the treatability and degradation of propylene, a volatile organic compound (VOC) that is regulated in the state where the Site is located. Propylene-impacted Site groundwater is also characterized by high (10 s.u.) and low (4 s.u.) pH and high sulfate concentrations (1,000 mg/l). In-situ remedial measures including a permeable reactive barrier and biobarrier are under consideration. Due to the lack of studies on this compound, O'Brien & Gere retained PRIMA Environmental (PRIMA) to perform a treatability study to identify if propylene is aerobically biodegraded and if so, to identify if the biodegradation is enhanced with the addition of nutrients.

Approach/Activities. The test evaluates aerobic biodegradation of propylene in Site groundwater in contact with oxygen in the headspace. Impacted soil samples were collected from the Site analyzed for total organic carbon (TOC) and VOCs (including propylene). Impacted Site groundwater was collected and analyzed for VOCs (including propylene), alkalinity, anions (ammonia, nitrate, nitrite, phosphate, and sulfate), dissolved organic carbon (DOC), oxidation reduction potential (ORP), and pH. A total of three (3) reactors were setup: 1) Sterile Control; 2) Air Only; 3) Air + Nutrients. The reactors contain Site soil and groundwater, and the control additionally contains azide to sterilize the microcosm. The nutrient is a commercially-available plant food which contains both macro- and micro-nutrients. Reactors were sized and filled such that headspace accounts for approximately 50% of the total volume, to ensure adequate oxygen for aerobic biodegradation of propylene and minimize pressure build-up due to bioactivity. Microcosms are being maintained in darkness at room temperature (about 20°C) and are shaken briefly three (3) times per week for the first two (2) weeks, then weekly thereafter. Headspace in each reactor is being tested for propylene gas, at four time points (0 days, 7 days, 14 days, and one later date to be determined). Oxygen in the headspace is being measured approximately weekly using a fiber optic probe. If the oxygen level drops significantly, PRIMA and O'Brien & Gere will determine whether additional oxygen should be supplied. If propylene does not appear to be biodegrading or if degradation appears to stall, water may be collected and analyzed for anions (nitrate, phosphate, and sulfate), aerobic heterotroph plate counts, and pH.

Results/Lessons Learned. The test is in progress; however, results will be available for presentation by the May 2015 conference.

TPH–What Is The Right Cleanup Level?

Panel Discussion Tuesday/Track C

Moderator
Sara Mcmillen (Chevron)

Panelists
Deb Edwards (Exxon Mobil)
Mala Pattanayek (Integral Consulting)
Rob Scofield (GSI Consulting)
Fred Vreeman (Alaska Department of Environmental Conservation)

Cleanup requirements for TPH in soil range widely, from 10 to 10,000 mg/kg depending on location and perceived risk. In addition, analytical methods used to evaluate TPH in soil can give different results depending on the laboratory used. This adds challenge to remediating oil-contaminated soil to acceptable levels. This panel will provide an overview of the documents produced and decisions made by the previously held Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). Any new approaches and developments in TPH regulations and analytical techniques at the state level will be discussed. Differences between approaches used by USEPA and various states will be discussed. The panel will include the perspective of oil and gas personnel who know firsthand the challenges of dealing with petroleum-contaminated sites every day. The goal of the panel is to reinitiate the conversation about managing petroleum sites and identify data gaps and next steps to standardizing the approach to managing petroleum-contaminated sites.

Back to Contents

Comparative Trials of Oil Sorbent Products for Removing Crude Oil from Water

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(Shell Pet. Dev. Co. Nigeria Ltd, Port Harcourt, Nigeria)

Background/Objectives.A significant number of Companies have approached Shell Petroleum Development Company of Nigeria Ltd (SPDC) in connection with products and services they can provide to assist in the recovery of crude oil from surface waters. Free oil containment and recovery is an essential first phase in mitigating environmental impact associated with spills. The objective of the trial was to measure the relative performance of various oil sorbent products to remove crude oil from water

Approach/Activities. In order to test the performance of various products, standard test methods for sorbent performance of adsorbents were applied to 10 different sorbent materials belonging to two categories; polypropylene-based materials and organic products. Six petroleum sorbents made from cotton sheets or inert, synthetic fibers principally polypropylene and polyester (Type I adsorbents), as well as, four unconsolidated particulate organic products which are either plant-based or made from recycled polyurethane (Type II adsorbents) were tested.

The comparative trial was designed and executed over a five week period at the SPDC Remediation Centre of Excellence, at Obigbo, Rivers State in Nigeria. The trial commenced on 17th September, 2014 and was completed on 20th October 2014.

Results/Lessons Learned. The Type I adsorbents, made principally from synthetic fibers performed well in the buoyancy testing and better in comparison to the Type II adsorbents, which tended to sink particularly under simulated wave conditions. This would make oil adsorbed by these materials much more difficult to recover in the field and so could lead to greater environmental impact. The Type II particulate adsorbents also tended to discolor the clean test water during the buoyancy testing.

The Type I adsorbents also performed better than the Type II adsorbents in the oil absorbency capacity testing, retaining more oil per gram of adsorbent used in both wet and dry testing conditions. Of the Type I adsorbent tested for oil capacity, the polypropylene-based pads performed better in the longer duration testing in comparison to the cotton based pads. Overall, it was concluded that the Type I adsorbents made in the form of polypropylene-based pads, were most efficient at recovering free oil under the test conditions.

Microbial Biofilms and Bioremediation of Metals from Oil Sands Tailings Ponds

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Raymond J. Turner Ph.D. and Howard Ceri, Ph.D,
(University of Calgary, Calgary Alberta, Canada)
Lyriam Marques, Ph.D. (HydroQual Laboratories Ltd., Calgary Alberta, Canada)

Background/Objectives. The oil sands tailing ponds in northern Alberta are composed of complex slurries of residual bitumen, oil organics, naphtha diluent, water, sand, clay, and metals, and constitute unique and challenging environments for remediation. Tailings ponds have very active microbial populations, which makes the application of bioremediation a possible tool in tailings remediation and reclamation. Remediation of organic contaminants in soils and water occurs naturally by abiotic and biotic mechanisms, but can be accelerated through bioremediation applications such as biostimulation, bioventing, and bioaugmentation, which act to stimulate and enhance microbial activities. However, metals are often inhibitory to organic biodegradation processes, and thus selection of metal resistant organisms for use in bioremediation strategies can be vital.

The objective of this study was to use an *in vitro* mixed species biofilm model developed at the University of Calgary to study the indigenous microorganisms of an oil sands tailings pond, and evaluate their bioremediation potentials. Multispecies biofilms were grown under a variety of culture conditions and their communities characterized by molecular method such as quantitative PCR (qPCR), denaturant gradient gel electrophoresis (DGGE) and 454 pyrosequencing.

Approach/Activities. Metal resistance of biofilms isolated from tailings ponds were studied by exposing them to a series of common metal pollutants and measuring biofilm activity through an ATP (adenosine triphosphate) assay. Microbial activity was found to remain elevated even after exposure to concentrations of 1000 mg/L of strontium and 2000 mg/L of nickel. Through scanning electron microscopy (SEM), metal bioprecipitates were found on the extracellular matrix of the biofilms, identifying a method of metal removal and immobilization from metal contaminated waters.

Results/Lessons Learned. This study demonstrates an *in vitro* biofilm growth approach that can be used to study environmental microbial communities and a method of assessing the bioremediation potential of these unique oil sands tailings microorganisms.

Ozone Enhances the Bioavailability of Residual Hydrocarbons in Soil

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Background/Objectives. Petroleum spills at oil-extraction sites and refineries may result in long-term liability because of the persistence of weathered heavy hydrocarbon (HH) residuals. Heavier residuals can take the form of hundreds or thousands of aliphatic and heterocyclic isomers, most of which are recalcitrant to biological and chemical degradation in situ. These fractions of total petroleum hydrocarbons (TPH) typically remain in the vadose zone long after lighter components have volatized, biodegraded, or otherwise naturally attenuated.

Ozone holds promise as a means for stimulating the biodegradation of heavy hydrocarbons in unsaturated soils by achieving a small degree of HH oxidation that improves solubility and bioavailability of these contaminants. We used ozone gas at the bench scale to determine the efficacy of pre-oxidation for making HH residuals in unsaturated soils more bioavailable.

Approach/Activities. We treated 250 grams of soil containing weathered petroleum hydrocarbons (10 g TPH/kg) with ozone gas (inlet concentration 2300 ppmv, outlet concentration 230 ppmv) for 1.5, 2, 2.5, and 3 hours. We measured soluble chemical oxygen demand (SCOD), 5-day biochemical oxygen demand (BOD5), dissolved organic carbon (DOC), and total petroleum hydrocarbons (TPH) before and after ozone treatment. We also assessed hydrophilic ozonation byproducts by gas chromatography linked to mass spectrometry (GC-MS).

Results/Lessons Learned. Ozonating soil containing ~1% (w/w) residual petroleum hydrocarbons with a dose of up to 1.5 kg O3/kg TPH achieved nearly 50% TPH reduction simultaneous with greater than an >20-fold increase in soluble COD, but ≤ 12% loss of total organic carbon (TOC). The TPH molecules were converted to partly oxidized products, ten of which were identified as n-monocarboxylic acids that were readily biodegraded, since ozonation resulted in a 4-fold increase in biochemical oxygen demand (BOD5). BOD5 results after ozonation were the same with or without a microbial seed, which suggests that bioaugmentation following ozonation may not be necessary.

The large changes in SCOD, DOC, BOD5, and the formation carboxylic acids were proportional to the ozonation time up to 2.5 h, although the changes from 2.5 h to 3 h were small. This makes 2.5 h of ozonation of 250 g of soil with 10 g TPH/kg soil a good benchmark for ozonation treatment to enhance biodegradation. Our results so far show the promise of gas-phase ozonation and justify more studies to optimize the dose and determine field-application strategy.

Biodegradation of Buried MC252 Oil on a Coastal Headland Beach

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Background/Objectives. Coastal headland beach in southern Louisiana were disproportionately impact by MC252 oil in 2010.Since 2011, over 60% of oiled material removed during cleanup activities in the Gulf were removed from Fourchon Beach, Louisiana, a 9-mile coastal headland beach in southeastern Louisiana. Efforts to protect more sensitive marsh areas using hard structures on these beaches created conditions for accumulation and burial of significant quantities of oil across an 8 feet deep beach profile. Oil persists in these areas due to the natural anaerobic conditions of tidal groundwater on these beaches. The objectives of these field and laboratory studies are to determine factors controlling the rate and extent of biodegradation of 3-ring PAHs in crude oil trapped in the subsurface.

Approach/Activities. This study was performed at the far eastern end of Fourchon Beach, LA. Field samples were removed from 2011-2014 from the area including oil sampled from depth with a Geoprobe, surface residue balls (oil-sand aggregates distributed over the surface of the beach), free oil floating on the groundwater surface and oil recovered during excavations used as part of a remedial approach in late 2013. Crude oil PAHs in the oil samples were extracted with hexane/acetone (50/50) using accelerated solvent extraction and analyzed for alkylated PAHs using a gas chromatograph with a mass selective detector. Terminal electron acceptors and nutrient were evaluated based on repetitive groundwater analysis of oxygen, sulfate, sulfide, nitrate, nitrite, ammonium and orthophosphate. Biodegradation of PAHs was estimated based on weathering ratios of alkylated phenanthrenes and dibenzothiophenes to poorly biodegradable chrysenes and C30-hopanes. A serum bottle microcosm study is being conducted using oiled sands from this site to determine whether small O_2 additions are capable of driving PAH biodegradation when compared with anaerobic treatments.

Results/Lessons Learned. In field samples removed from the site, the ratio of total PAHs/C30 hopane ranged from 24 to 634 with lowest values were observed in SRBs from the surface where O2 limitations are absent. In the samples removed from depth with borings or during excavation, total PAHs/C30 hopane was significantly higher coincident with submergence in anaerobic groundwater. In the groundwater, high levels of sulfate (400 to 1500 mg/L) and sulfide (0.1 to 4 mg/L) were measured coupled with non-detectable dissolved oxygen (less than 0.02 mg/L). Groundwater pH is close to neutral, alkalinity ranged from 750 to 1400 mg/L, with ammonia and phosphate levels greater than 1.0 mg/L, suggests nutrient conditions favorable for biodegradation in the subsurface. Salinities in the groundwater are generally hypersaline routinely exceeding 50 ppt. However, persistence of alkylated forms of phenanthrenes, dibenzothiophenes and chrysenes even 4 years after the spill, suggests that biodegradation rate at the site under sulfate reducing conditions are too slow to serve as an effective natural recovery process.. O_2 can only penetrate when low tides reduce the saturated portion of the beach profile Additional laboratory microcosm studies using oiled sand and groundwater from the study site are in progress to evaluate if aerobic conditions would enhance biodegradation rate and to estimate te minimum oxygen levels required to increase the biodegradation rate for active bioremediation to be a feasible strategy. These will be completed by the May 2015 conference.

Retail Petroleum Site Remediation: A Case Study of How We Can Make Things Worse

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Background/Objectives. Remedial actions are intended to produce positive results on the environment. However, when remedial actions are not properly designed and/or implemented, the contamination problem can be enhanced producing deleterious effects. These effects can increase the magnitude, distribution, and longevity of initial contamination. The environmental field often retreats from evaluating mistakes, yet recognizing our mistakes is an important part of professionalism. This paper outlines an example where multiple mistakes made by different entities can lead to a “perfect storm” whereby the initial contamination is made worse.

Approach/Activities. Litigation brought forth by abutting property owners produced an investigation of two retail petroleum sites. Prior to the litigation, the environmental conditions at each site were characterized and remediated independently. As such, a comprehensive understanding of the hydrogeologic conditions within the area was never fully recognized. Utilizing the technical data collected from both sites, a full understanding of the interaction of the sources, hydrogeologic conditions, and impacts of remedial actions could be recognized. Enhanced visual imaging, geophysics, and modeling were applied to the existing data set to explain how patterns of contamination could be readily explained.

Results/Lessons Learned. The analyses conducted document how contamination can be enhanced when site complexities are not recognized. Moreover, the analyses document that retail sites, although small in area, are technically complex due to data limitations both spatially and temporally. Cooperative remedial actions to address adjacent contamination problems should be considered by the industry to enhance public safety and mitigate environmental impacts.

Back to Contents

Numerical Simulation of Low Temperature In Situ Thermal in DNAPL Source Zone Remediation

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Background/Objectives. Remediation of dense nonaqueous-phase liquid (DNAPL) source zones caused by perchloroethylene (PCE) and trichloroethylene (TCE) releases is often considered "technically impracticable" to achieve typical soil and groundwater cleanup target levels. One innovative approach to address this challenge is the use of in situ thermal (IST) technologies (i.e., Electrical Resistance Heating (ERH), Steam Injection (SI), and Thermal Conductive Heating (TCH)), as they have the potential for quicker and more thorough treatment of NAPL source zones than conventional remediation technologies. The major limitation of the IST technologies, however, lays in the high electricity demand to raise subsurface temperature to approximately the boiling point of water. Moreover, a proportional amount of energy is also required to cool the extracted off-gas and groundwater to allow for contaminant recovery.

Approach/Activities. To explore a more sustainable delivery of the IST technology, the effect of low temperature IST (i.e., 50°C to 90°C) combined with a Soil Vapor Extraction (SVE) and a Multi-Phase Extraction (MPE) system has been evaluated for various DNAPL (i.e., PCE) site conditions using the TMVOC and iTOUGH2 suite of nonisothermal multiphase flow simulators. The results of the numerical simulation help better understand the physical processes of mass removal under low temperature in situ heating, and investigate the feasibility of employing such technologies for DNAPL source zone treatment. Using the inverse modeling capability of the iTOUGH2 simulator, the optimum Return on Investment (ROI) in terms of total mass removal and remediation cost in relationship of temperature settings of IST has also been pursued.

Results/Lessons Learned. Simulation results indicate that significantly more PCE mass can be removed and off-site contaminant fluxes can be reduced even with the temperature of ISTs set as low as 50°C. The remedial effectiveness of various low temperature settings of ISTs has been evaluated to determine the IST temperature for an optimum ROI of a DNAPL source zone remediation.

Comparative Trials of Proprietary Additives, Organic Manure and Inorganic Fertilizers on the Bioremediation of Crude Oil-Impacted Soil

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(Shell Pet. Dev. Co. Nigeria Ltd, Port Harcourt, Nigeria)

Background/Objectives. A significant number of Companies have approached Shell Petroleum Development Company of Nigeria Ltd (SPDC) in connection with products and services they can provide to assist in the remediation of oil spills, many claim that their products and methodologies can remediate oil impacted soil and groundwater very quickly and efficiently.

The objective of the trial was to measure the relative performance of various proprietary additives, organic manures and inorganic fertilizers in the ex-situ bio remediation process used by SPDC to remediate of crude oil impacted soils. The measurement of performance was relative to a control where no additives or products were used, such that the marginal effect of the additive or product could be isolated

Approach/Activities. In order to test the performance of various products against a control, a comparative trial was designed and executed over a 15 week period at the SPDC Remediation Centre of Excellence, at Obigbo, Rivers State in Nigeria. The trial commenced on the 7th of May and was completed on the 27th of August 2014.

Results/Lessons Learned. Significant (83%), TPH degradation was observed in the control test cell. Eight of the ten additives/products being tested produced more degradation than the control; the rest produced the same or less degradation. The greatest additional degree of degradation over control was +12%; the worst was -27%. The mass of product added in comparison to the mass of oil to be degraded in each test cell varied significantly, due to the vendor’s recommendations.

In order to determine the efficiency of the products, a unit mass correction was applied to normalize the results, thereby removing effects due to bulking/dilution. On this basis it was observed that the inorganic fertilizer was the most efficient in terms of mass of product required, the least efficient was chemical surfactants and bio enhancement products. Scaling up the comparative trial product quantities to the field scale for typical spills observed in SPDC, would indicate substantial quantities of the products would be required using the vendors recommendations with only the inorganic fertilizers being of practical consideration.

Chromatographic analysis indicates that weathered crude used to spike the host garden soil had been effectively degraded across the majority of the carbon range.

Back to Contents

Selection of an Optimal Site-Specific Method for the Measurement of LNAPL Transmissivity

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Background/Objectives. LNAPL transmissivity is rapidly gaining acceptance as a preferred metric to measure the hydraulic recoverability of mobile light non-aqueous phase liquid (LNAPL). However, to date no detailed analysis of test or analytical methods relative to controlling site-specific factors has been conducted. This study was performed at a variety of petroleum industry facilities in a variety of geologic and hydrogeologic environments in order to evaluate multiple LNAPL transmissivity measurement methods to identify guidelines for the selection of optimal methods relative to site-specific factors.

Approach/Activities. The approach consisted of the field testing and measurement of LNAPL transmissivity using baildown testing, manual skimming testing, and oil/water ratio testing methods. LNAPL transmissivity was calculated using a variety of analytical tools including the API LNAPL transmissivity baildown test analysis spreadsheet and custom-designed spreadsheet analytical tools. Comparison of test success and results by test method was conducted to determine the conditions under which each test method might be preferable.

Results/Lessons Learned. Results demonstrate that the preferred LNAPL transmissivity test method is strongly correlated with the magnitude of groundwater fluctuation relative to the magnitude of available LNAPL drawdown, as well as the duration of LNAPL recharge relative to the duration of groundwater fluctuations observed at a given test well. LNAPL drawdown tends to increase with the progression of test methods from baildown testing to manual skimming testing to oil/water ratio testing. Each method is capable of repeatable test results within its given range of optimal site-specific factors. However, each method also clearly demonstrated an optimal set of conditions under which it performed. Based on the results of the work performed, guidelines for the selection of an optimal LNAPL transmissivity test method are provided.

A Comparison of Natural Source Zone Depletion and Active Remediation Rates

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Background/Objectives. After a subsurface release, the mass of petroleum hydrocarbon light non-aqueous phase liquid (LNAPL) is degraded by the intrinsic processes of volatilization, dissolution, and biodegradation. These collective processes have been termed natural source zone depletion (NSZD). Recent published literature indicates that NSZD is significant and may contribute to NAPL pool stability. Several methods to monitor NSZD rates have been developed including the gradient method (P.Johnson et. al., 2006), soil flux system (N.J.Sihota et. al., 2011), and traps (K.McCoy et. al., 2014). Results of field measurements using these new methods generally confirm the initial literature reports that NSZD rates are significant; however, there is some concern that the measured NSZD rates are too significant and unbelievable. This doubt casts a shadow over the new methods thereby stalling their application. This presentation seeks to discuss NSZD rates within a practical context by comparing measured NSZD rates to mass removal rates achieved by other remedial technologies. The intent is to clarify the meaning of NSZD rates and demonstrate that the majority of the field measurements reasonably lie within the spectrum of remediation. Practical information will be presented that will allow the audience to evaluate the potential use of carbon dioxide (CO_2) efflux monitoring methods at their sites.

Approach/Activities. The theory behind intrinsic petroleum depletion processes will first be discussed including the range of potential volatilization, dissolution, and biodegradation rates within variable subsurface environments. As performed by P.Johnson et. al. (2006), this will establish a spectrum of theoretically possible NSZD rates.

The theoretical rates will be compared to measured NSZD rates; results of CO_2 efflux measurements from at least five sites using both the soil flux system (LI-COR BioSciences, Inc.) and traps (E-Flux, LLC) will be presented to show the range in measured NSZD rates at sites with diverse subsurface conditions. A rationale will be provided to explain the range in results at each site.

The theoretical and measured NSZD rates will be compared to mass removal rates from active remediation systems as a point of comparison. Remedy mass removal rates from the above five sites where CO_2 efflux monitoring was performed will be reported along with data from an additional 15 petroleum remediation sites. Methods of measurement and mass removal rates will be reported for remedies including LNAPL skimming, trench recovery, bioventing, soil vapor extraction, air sparging, multiphase extraction, and pump and treat.

Results/Lessons Learned. The theoretical and actual measured NSZD rates fell within the range of active remediation mass removal rates and prove that the methods of CO_2 efflux monitoring are producing reasonable results. Site-specific conditions such as climate, LNAPL source mass, geology, and on-going remediation activity will explored as rationale for the observed variation in NSZD rates.

Sustainable Thermally Enhanced LNAPL Attenuation (STELA) Using Soil Solarization

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Background/Objectives. Based on knowledge of aerobic and anaerobic biodegradation processes and emerging data from carbon dioxide emission studies from hydrocarbon sites, Sustainable Thermally Enhanced LNAPL Attenuation (STELA) can be an effective bioremediation strategy. The technology involves increasing subsurface temperatures to between 20 ºC and 35 ºC in order to increase degradation rates at light non-aqueous phase liquid (LNAPL) sites. Recent research results from Colorado State University suggest several-fold increase in hydrocarbon degradation rates with temperatures greater than 20 ºC (68 ºF) (Sale, 2012). Various technologies to heat the subsurface exist, though this study focuses on a low-cost, passive method. Soil solarization involves a surface cover that will absorb and/or trap solar energy, heating the surface soil. This heat will be conducted downward to the LNAPL zone, thereby enhancing biodegradation.

Approach/Activities. Two small-scale pilot studies will be conducted at two locations (Colorado and New Jersey) for one year in order to determine the heating efficiency of various soil solarization treatments. Data from four different small plots will help assess the impact of: i) different soil cover materials (i.e., chipped asphalt, plastic cover, and combination of both), ii) geographical locations/availability of solar energy, and iii) seasonal effects on heating. At each pilot test location, detailed temperature monitoring with depth will be obtained over time within the treatment area, and compared to background (untreated) temperature data. Additionally, comparisons to the theoretical heat transfer Hillel model will be performed.

If the pilot indicates that the approach will be successful, data from the small-scale pilot tests, along with gas permeability studies, and thermal modeling will be used to design a full-scale pilot test of the STELA technology. The full-scale pilot test will involve soil and groundwater characterization, and assessment of biodegradation rates both before and after heating.

Results/Lessons Learned. The small-scale pilot tests will be conducted for one year from Fall 2014 to Fall 2015. To date, combined plastic and asphalt performed slightly better than the plastic only, and significantly better than asphalt only. The plastic and asphalt combination increased subsurface soil an average of 4 ºC to 1 ºC, and maximum of 6 ºC and 2 ºC for depths at 1 ft and 10 ft bgs, respectively. Due to the installation time period in late fall, additional subsurface heating is expected in the upcoming warmer months of spring and summer.

Jet A Fuel Recovery Using Micellar Flooding: Design and Implementation

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Background/Objectives. Surfactants offer two mechanisms for recovering NAPLs. The first method is to mobilize NAPL by reducing NAPL/ water interfacial tension and increase the NAPL's aqueous solubility–called 'solubilization'–as an enhancement to pump & treat. The second approach has been well-studied and applied successfully in several pilot-scale and a few full-scale tests within the last 15 years, known as Surfactant Enhanced Aquifer Remediation (SEAR). A useful source of information for this second approach is the "Surfactant–enhanced aquifer remediation (SEAR) design manual" from the U.S. Navy Facilities Engineering Command. Few attempts have been made at recovering NAPLs using the mobilization approach presented in this paper.

Approach/Activities. Our goal is the design and implementation of a surfactant flood that will recover an LNAPL, Jet A fuel, from a surficial sand aquifer located in Denmark, using as few pore volumes of surfactant solution as possible. The approach will rely on mobilizing the LNAPL (the second approach identified above) with the incorporation of foam as a means of directing the injected solution to the LNAPL contaminated zone. Hydraulic control wells will be incorporate in the design of the project to ensure capture.

Results/Lessons Learned. This paper will review the laboratory work that has been performed as part of the design for a full-scale implementation of a micellar flood that will include mobility control using foam. Completed lab work includes phase behavior screening of surfactants and detailed studies of the most promising formulations. Our on-going lab work will include measurements of viscosity, surface tension, and a 1-D column test. These results will be used in numerical simulations of the 1-D column experiments, followed by three-dimensional simulations of the site in order to design the implementation and optimize performance.

Innovative Surfactant System Formulations for LNAPL Recovery

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Background/Objectives. Based mostly on empirical experience, practitioners have concluded that NAPL solubilization was a necessary first step in the mobilization process and that surfactant concentration, up to a point, was generally proportional to performance. It is now understood, as evidenced by trends seen in the detergent industry that high efficiency products at lower concentrations meet the industry's requirements. These lower concentration formulations are not only as effective but work well at a variety of temperatures and water hardness conditions. That said, surfactants typically found in household cleaning systems, such as laundry detergent or shampoo, lower the interfacial tension (IFT) by about an order of magnitude. This is sufficient because mechanical energy can be added to laundry or shampooing to mobilize the trapped oil. In a porous medium, however, we must reduce the IFT by three or four orders of magnitude to reach our goals.

Approach/Activities. Technology developed at the University of Oklahoma, originally focused for enhanced oil recovery at petroleum reservoirs and subsequently adapted to the environmental arena, can lower the IFT sufficiently to allow physical mobilization of residual LNAPL with the limited production of thermodynamically stable emulsions. This talk will focus on the use of artfully formulated surfactant blends that reduce solubilization and simply allow LNAPLs in saturated soils to become mobile.

Results/Lessons Learned. The presentation will include results and lessons learned from the latest field implementation where selecting an optimized surfactant blend minimized required flush water and costs for produced effluent fluids treatment.

Overcoming Problematic LNAPL Recovery Sites in Montana

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Background/Objectives. This presentation evaluates 3 petroleum release sites in Montana with significant light non-aqueous phase liquid (LNAPL). Each site is noteworthy due to: 1) complex hydrogeologic conditions, 2) the nature of impacts and the current usage of affected areas, 3) multiple potential source areas, and 4) funding constraints limiting the amount of assessment and cleanup completed to effectively address LNAPL and dissolved plumes. In each case, LNAPL recovery alternatives were evaluated based on site-specific conditions, implemented first on a pilot scale, then scaled up based on the success of results.

Approach/Activities: A large weathered gasoline release was discovered in Harlowton, MT in 1999 based on the presence of petroleum contamination in a private water supply well. Subsequent investigation of dissolved contaminants confirmed the presence of MTBE, benzene, and 1,2-DCA in a fractured sandstone aquifer underlying the study area and a widespread LNAPL plume under a large portion of the town. Several monitoring wells contained 4-10 feet of LNAPL. Drinking water for the town is provided through several groundwater supply wells including one well proximal to the LNAPL plume that contained low concentrations of 1,2-DCA. Investigation activities culminated in the selection and installation of a LNAPL recovery system in the center of the main plume area in 2013. The LNAPL recovery system has been highly successful, recovering 18,500 gallons of leaded gasoline over a 12 month timeframe.

Beginning in 1994, extensive remediation work was completed at a site in Ronan, MT to address a large release of gasoline. Remediation was extremely challenging due to tight, clayey soil conditions and the difficulty of addressing a cleanup at an active service station. In addition, high concentrations of MTBE and benzene were discharging to a stream on the downgradient edge of the plume. Subsequent closure of the business allowed access to the entire site for complete evaluation and remediation. Following many years of investigation and standard engineering applications for remediation, an innovative approach using electrical resistance heating (ERH) was utilized. Three separate applications of ERH resulted in almost complete removal of the LNAPL plume. 13,341 gallons of gasoline have been removed from the site.

At a third site in Miles City, MT explosive gasoline vapors were detected in the Lewis and Clark Apartments in October 2010. The fire department responded and evacuated residents. The owner of an adjacent gas station estimated the loss of 9700 gallons of unleaded gasoline from an 8,000 gallon dual-compartment gasoline UST. Other buildings were impacted: the U.S. Post Office was evacuated in November 2010 and petroleum vapor intrusion was detected in three nearby businesses. Ventilation and/or sub-slab SVE systems were installed in all of the impacted businesses and in the UST basin. Routine pumping of recovery wells with a vacuum truck resulted in the recovery of over 8,500 gallons of gasoline. Combined treatment from the SVE system network resulted in the recovery of an additional 6100 gallons of gasoline, for a total of 14,600 gallons.

Results/Lessons Learned: LNAPL recovery at all three sites was critical to address each large volume release and mitigate impacts to nearby residents and downgradient receptors. In all cases, aggressive recovery of LNAPL has expedited remediation by many years. The Miles City site may achieve DEQ cleanup standards for closure in 2015.

Back to Contents

In Situ Geochemical Stabilization (ISGS) for Nonaqueous Phase Liquid Treatment: Technical Assessment

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Background/Objectives. ISGS (In Situ Geochemical Stabilization) technology entails the use of modified permanganate solution that targets mass removal and flux reduction of the NAPL. The introduction of the permanganate solution results to the migration of the oxidant through the treatment area and consequently to geochemical reactions that destroy the targeted contaminants that are present in the dissolved phase. As a result the NAPL starts to steadily lose its more labile components and “chemical weathering” or “hardening” occurs. Subsequently a net increase in viscosity of the organic material is observed, which yields a more stable, recalcitrant residual mass.

Additionally, both the insoluble manganese dioxide precipitate, that results from permanganate oxidation, and other mineral species included in the ISGS formulation accumulate along with the NAPL interface, resulting in the physically coating of the NAPL and thereby reducing the flux of dissolved-phase constituents of interest into the groundwater.

Approach/Activities. ISGS was implemented at a site located in northern New Jersey in order to decrease the source area NAPL present. Based on the post remedial data, the ISGS technology was found to be very effective in addressing the groundwater and the free product contamination in all five targeted monitoring wells (MW-11, MW-12, MW-13, MW-14 and MW-15).

In MW-11, the concentrations of almost all SVOC compounds decreased to levels below the laboratory detection limits, total BTEX concentrations decreased by 85%, while the concentrations of total alkanes have also reached non-detect levels. In MW-12 the concentrations of the SVOCs and total alkenes reached levels below the laboratory detection limits, while BTEX compounds overall decreased by 68%. In MW-13 the concentrations of all targeted SVOC compounds decreased considerably, while naphthalene was the compound that was massively affected with the concentration decreasing from 1,920 μg/L in August 2013 to 1.18 μg/L in January 2014. In MW-14 the concentrations of all targeted compounds have decreased to levels below the laboratory detection limits except for benzene that decreased by 43%. Finally, in MW-15 the concentrations of almost every SVOC and BTEX compound have decreased to levels below the laboratory detection limits.

Results/Lessons Learned.
The free product that was present in the five wells, disappeared within 30 days of the implementation of the injection event. The historic changes in the thickness of the free product lawyer in each monitoring point are presented in the table below.

Table 1. Injection Thickness of Free Product (ft).

Well ID	**Sampling Date**					
	05/25/2012	**06/07/2012**	**03/14/2013**	**10/16/13**	**10/18/13**	**01/15/14**
TW-1/MW-14	4.16	3.90	4.24	**ND**	**ND**	**ND**
TW-2/MW-15	5.34	4.98	5.31	**ND**	**ND**	**ND**
TW-3/MW-11	5.26	5.12	5.37	**ND**	**ND**	**ND**
TW-5/MW-12	5.60	4.99	4.64	**ND**	**ND**	**ND**
TW-8/MW-13	3.43	3.07	3.26	**ND**	**ND**	**ND**

Colloidal Ferrofluids Revisited:
Current Research in Magnetic NAPL Recovery

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Overview. A synthetic magnetic fluid consisting of a colloidal suspension of nanoscale magnetic particles, or domains, in an oil-miscible carrier fluid, when combined with another non-aqueous phase liquid (NAPL), renders the resultant mixture to also be magnetic. NAPL may also be doped with specially treated nanoscale magnetic domains, rendering the carrier NAPL also to be a magnetic fluid (in general “ferrofluids”). Use of a surfactant encapsulation prevents magnetic particle agglomeration. Brownian motion prevents particle sedimentation in gravitational or magnetic fields. Ferrofluids are mobilized or rendered stationary by magnetic fields that easily overcome gravity and capillary forces.
Initial uses of ferrofluids included mobilization of fuels in zero gravity. Modern applications are broadly lumped into four categories, including 1) theoretical/physical studies, 2) electronic applications, 3) medical/pharmaceutical, and 4) environmental/engineering. Current research related to magnetic NAPL recovery is hereby presented.

Background/Objectives. Modern NAPL recovery techniques are almost entirely predicated upon our exploitation of gravity and understanding of NAPL behavior in the realm of Newtonian physics. The objective of this presentation is to introduce environmental professionals to historical and current research in magnetic NAPL recovery.

Approach/Activities. Historical uses of colloidal ferrofluids are varied and include uses as pump seals, liquid dampers, as ferromagnetic liquid cores for speakers, as inoculates for magnetic mobilization of fuels, for sub-surface sensor, and as delivery agents for pharmaceuticals. A history of ferrofluid research is presented including a summary of prior art and modern environmental applications. A bench-scale study is discussed showing magnetic manipulation and immobilization of Non-Aqueous Phase Liquid (NAPL) residing in macro-pore spaces, including simulated crustacean burrows. Potential and realistic environmental applications of magnetic LNAPL recovery are discussed with case-study examples.

Results/Lessons Learned. Historical research on the application of manipulating magnetically responsive colloidal dispersions for changing fluid behavior peaked in the early 1970’s with approximately 150 papers published per year. Modern on-line search engines suggest that approximately 100 research papers are published a year on the specific topic of “ferrofluids”. Modern research includes considerable bench-scale studies on use of ferrofluids to recover NAPL. Some of the challenges for effectively using ferrofluids that early researchers discovered are still viable today. Limitations for practical magnetic NAPL recovery include:

1. Energy requirements to generate sufficient magnetic field requirements for recovery
2. Ferrofluid viscosity increases with magnetic field induction
3. LNAPL body must be inoculated with magnetic domains
4. Technology may not be improvement upon existing technologies
5. Negative public and regulator perception of nanotechnology

Remedial Design Characterization and High-Resolution Sampling to Design Pilot Scale Injection for LNAPL Remediation

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Background/Objectives. The site is located south of Copenhagen, Denmark. After extensive remedial effort and cost (greater than $1 million) free product continues to be observed in 5 monitoring wells. Benzene and other petroleum hydrocarbons in groundwater, in the majority of the on-site monitoring wells within the impacted area, remain at significant concentrations greater than allowable levels. LNAPL is observed in 5 monitoring wells (B113, B106, B105, KB5, and B108) within a 1,000 ft2 area of the site. B113 contained 2 feet of NAPL in February 2011.

Approach/Activities. A Remedial Alternatives Analysis (RAA) was prepared by the primary consultant for the site. In the RAA, Trap & Treat® technology involving injection of BOS 200® was identified as a feasible remediation approach at the site. The owner and primary consultant decided to first conduct an in-situ pilot test at the site to explore the feasibility and applicability of the technology at the site. They chose the area of the site where the greatest amount of LNAPL was present (B113). The pilot area was approximately 1,000 s.f. Prior to installation, a Remedial Design Characterization (RDC) high density sampling event was conducted in the Pilot Area. The high resolution sampling event was used to develop a three dimensional conceptual model of the hydrocarbon mass within the pilot area. The high resolution sampling included: the installation of two well clusters, two continuous soil borings completed with samples collected and analyzed every 2-vertical feet, and four MIP borings. The soil and groundwater results from the RDC were used to calculate the vertical and horizontal distribution of hydrocarbon mass in the pilot test area. The hydrocarbon mass was used to develop the pilot test injection design loadings

Results/Lessons Learned. A total of 178 injections were installed in 18 injection points using high flow and high pressure. A discussion will be provided on methods and procedures used to overcome short circuiting issues. As much as 5 feet of LNAPL accumulated in one of the new well clusters installed in the center of the pilot area. The well clusters and sentinel wells were monitored for six months. The monitoring confirmed that the LNAPL has been successfully removed. The owner and primary consultant have chosen to move forward with full-scale treatment of the site based on the success of the pilot test. Results from the full-scale treatment will be available in May 2015.

Nationwide (USA) Statistical Analysis of LNAPL Transmissivity

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Background/Objectives. LNAPL transmissivity is rapidly gaining acceptance as a preferred metric to measure the hydraulic recoverability of mobile light non-aqueous phase liquid (LNAPL). However, to date no widespread collection or analysis of LNAPL transmissivity data on a large-scale geographic basis has been conducted. This study was designed to collect measured LNAPL transmissivity values across a range of facilities, geographies, geologies, and LNAPL types, and to statistically analyze the collected data to determine the distribution and dependent correlations among the data collected. In particular, the study was intended to capture a clear understanding of the statistical distribution of LNAPL transmissivity in order to provide a context for site evaluations, regulatory rulemaking, and remediation decisions dependent upon LNAPL transmissivity.

Approach/Activities. The approach consisted of the development of a standardized nationwide database for collection of LNAPL transmissivity and supporting data, dissemination of this database to a range of petroleum industry corporations and their environmental engineering and consulting contractors, collection and QA/QC of the databases from multiple companies, and statistical analysis of the combined datasets that resulted from this nationwide data collection effort. Critical data collected included LNAPL physical properties, geologic and hydrogeologic parameters of relevance, LNAPL transmissivity values, test and analytical methods, and geographic and temporal scales of measurement. Descriptive and inferential statistical analyses were performed to understand the distribution and dependent correlations of LNAPL transmissivity and related data.

Results/Lessons Learned. Results demonstrate that the distribution of LNAPL transmissivity across a broad range of facilities, geologies, measurement methods, and NAPL types is strongly right-skewed, approximating log normality. Detailed analyses of LNAPL transmissivity values by geology, permeability type, measurement method, analytical method, NAPL type, NAPL physical properties, and other relevant parameters were performed and will be presented. The results of this research project provide a broad understanding of LNAPL transmissivity occurrence nationwide, and provide a context within which future LNAPL transmissivity values may be interpreted and evaluated to determine their significance.

Improving Petroleum Remedy Sustainability by Coupling Biological and Physical Remediation Technologies

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Background/Objectives. An active gas station was impacted by a 7-acre free-phase product (product) plume, with a thickness up to 2.1 feet, and associated dissolved phase contaminants. Since the site is located in an agriculturally dependent, high desert community, there were several environmental and business concerns regarding traditional remediation approaches. Further complicating the remedy, the product was present in a lower-permeability silty sand horizon just above a highly transmissive sandy gravel horizon. The objective of the remedy was to provide an effective and resource-conscious approach for this site using a very limited budget.

Approach/Activities. The final remedial approach was designed to both minimize small-town business impacts during the onset of a recession (March 2008), reduce non-beneficial groundwater waste, and take advantage of regional aquifer geochemistry to provide a more sustainable remedy. By using existing investigation wells as strategic extraction points and relying on directional drilling for conveyance installation, impacts to the downtown business corridor were minimized and permitted uninterrupted use of a state highway extending across the plume, a major local grocery store, and the subject gas station. A centrally located liquid ring pump (LRP) reduced total system costs by not requiring a separate vapor control system and sharply reduced groundwater removal by preferentially extracting from within the product-saturated silty soil horizon. As the product plume retracted, the pump-and-treat system with stormwater discharge was converted to recirculation and a low-nutrient version of the AnoxEA® AQ biological oxidant was periodically dosed into re-injected groundwater beginning at +18 months of operation. Over the next 36 months, extraction and injection locations were strategically modified to support microbially mediated desorption of the product. Elevated nitrate and dissolved oxygen in the regional gravel aquifer effectively limited migration of dissolved phase products outside of the treatment zone during the mobilization process, further preserving the regional groundwater.

Results/Lessons Learned. Despite the distribution and mass of the free-phase plume, extraction mass removal rates had become asymptotic within 18 months. Periodic dosing of re-injected water with Low Nutrient AnoxEA® AQ resulted in a gradual microbially mediated increase in dissolved petroleum. We will present analytical data from across the plume that shows dissolved BTEX at source area monitoring wells increasing by 3,100% with total extraction BTEX recovery rates improved by 300% across the entire extraction system. The accelerated recovery technique and overall extraction approach reduced the anticipated remedy duration from 15 to 20 years down to meeting cleanup goals and entering MNA in less than 5 years. This process has also mitigated the effects of concentration rebound, with only 1 well (in the source area) out of 27 rebounding to slightly above the cleanup level in the nearly 3 years since the site entered MNA.

Compared to conventional treatment approaches, this approach is estimated to have reduced granulated activated carbon usage by up to 200,000 pounds, saved 800 megawatt hours of electricity, and preserved over 150,000,000 gallons of groundwater for this arid agricultural area.

Back to Contents

The Lifecycle of MTBE in Public Water Supply Wells in California

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Background/Objectives. MTBE was removed from gasoline in California effective January 1, 2004 based largely on concerns regarding the impact of MTBE on public water supplies. At the time, MTBE had been detected in a small number of public water supply wells, however, many wells had never been tested for MTBE so the full extent of impacts to public water supplies was not known and it was feared that future testing would show greater impacts. Since 2004, the number of public water supply wells tested for MTBE has greatly increased. In addition, there is a significant population of wells that have been tested frequently for MTBE over an extended period of time. The unique usage history of MTBE makes MTBE monitoring results valuable for understanding the longer-term fate and transport within groundwater.

Approach/Activities. We have utilized the California Department of Public Health (CDPH) database, which contains results for almost 250,000 water samples analyzed for MTBE, to evaluate the extent of MTBE in public water supply wells in California and to evaluate how impacts have changed over time.

Results/Lessons Learned. These data show that MTBE has never been detected in over 98% of 13,183 public water supply wells tested for MTBE. Although the total detection frequency has remained relatedly stable since 2000, the number of wells with first-time detections of MTBE peaked in 2001 and has decreased by 80% since that time. For the 188 wells where MTBE has been detected, MTBE was detected only once in 85 of these wells even though most of the wells were tested for MTBE more than five times. MTBE was not detected in the most recent analysis for 142 (76%) of these wells. We analyzed trends over time in 21 individual frequently analyzed wells where MTBE has been detected more than 10 times, MTBE concentrations are stable or decreasing over time in 18 of these 21 wells. In 13 (62%) of these 21 wells, current MTBE concentrations were below analytical detection limits in the most recent sample and for 9 of these wells, there have been 10 or more consecutive non-detect results since the most recent detection of MTBE. These results suggest that MTBE impacts to many public water supply wells are temporary in nature. Taken as a whole, the available data indicate that the impact of MTBE on public water supply wells in California has peaked and will likely continue to decrease over time.

Optimized Remedial Strategy to Manage an Extensive MTBE Plume

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Background/Objectives. The Naval Facilities Engineering Command (NAVFAC) Base Realignment and Closure Program Management Office West (BRAC PMO West) was able to negotiate a successful remedial strategy for a large-scale, complex methyl tert butyl ether (MTBE) plume with the California Department of Toxic Substances Control (DTSC) and San Francisco Bay Regional Water Quality Control Board (Water Board) at the Former Department of Defense Housing Facility (DoDHF) Novato in Novato, California. The key elements of the strategy included: 1) the definition of target treatment areas (TTAs) within an extensive MTBE plume; 2) the documentation and acceptance of performance metrics prior to remedy implementation by all stakeholders; and 3) continuous optimization efforts for system operation and long-term monitoring.

Releases associated with two former Navy gas stations had produced a commingled plume of gasoline-related constituents. Prior to remediation, MTBE concentrations in groundwater were measured as high as 200,000 ug/L, compared to a final cleanup goal of 13 ug/L (i.e., the maximum contaminant level [MCL] for MTBE). Additionally, further characterization determined that dissolved MTBE had migrated approximately 0.5 mi. downgradient of the former source area, with a substantial portion of the plume extending beyond the former Navy property boundary, including underneath an area that was to be developed with housing.

Approach/Activities. The remediation strategy was developed based on a robust conceptual site model that relied upon three-dimensional visualization of surface topography, site geology, hydrogeology, and contaminant distribution extending from the source area to the leading edge of the MTBE plume. In order to effectively remediate such a large dissolved MTBE plume, a treatment train approach was implemented starting with air sparging and biosparging of on-site source area TTAs, transitioning to an off-site hot spot TTA, and finishing with monitored natural attenuation (MNA).

Results/Lessons Learned. This presentation will discuss the overall remedial strategy including the treatment objectives, performance goals, evaluation techniques, and lessons-learned. Of particular importance was the development of quantifiable performance goals that were agreed upon by all project stakeholders prior to treatment system installation and start-up. The performance evaluation framework was used to govern decision-making related to continued system operation, optimization, system shutdown, and potential system re-start. Ultimately active remediation of the MTBE plume is complete and the Navy is in the long-term monitoring phase. Currently the project stakeholders are considering a potential transition to no further action because MNA mechanisms have stabilized the MTBE plume over time and there are no unacceptable risks to human health and the environment.

Significance of Enhanced Aerobic Biodegradation for Accomplishing Aggressive BTEX, MTBE, and TBA Endpoints in a Large Gasoline Source Zone

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Background/Objectives. Treatment of an eight-acre oxygenated-gasoline LNAPL body was required to reach California-drinking-water-based endpoints within an aggressive time frame.

Approach/Activities. Dual-phase extraction – soil vapor extraction to extract volatile hydrocarbons and enhance aerobic biodegradation accompanied by dewatering – was the selected remedial approach. Remedial progress was tracked by monitoring hydrocarbon concentration and composition in soil vapor and LNAPL (soil), monitoring leachability of COC from LNAPL, and estimating rates of volatile hydrocarbon mass extraction. The rate of in-situ aerobic biodegradation of hydrocarbons was estimated using respirometry tests and by monitoring oxygen and carbon dioxide concentrations in extracted soil vapor. Confirmation monitoring at the end of remediation included soil vapor rebound monitoring of hydrocarbon concentration, hydrocarbon composition, and oxygen and carbon dioxide concentrations.

Results/Lessons Learned. Clear understanding of volatile extraction and in-situ aerobic biodegradation processes was important for continually adapting progress tracking and remedial operations to achieve cleanup goals. Early in remediation, concentrations of hydrocarbons in soil and extracted soil vapor were high and included a significant fraction of light hydrocarbons. Oxygen and carbon dioxide concentrations and respirometry testing showed significant aerobic biodegradation. During this stage of remediation, LNAPL in active airflow channels is stripped of the more volatile hydrocarbon constituents, and aerobic biodegradation is consuming the more soluble hydrocarbon constituents. Remedial effort was concentrated on areas with the highest hydrocarbon, light hydrocarbon, and carbon dioxide concentrations and lowest oxygen concentrations. As remediation progressed, hydrocarbon concentrations in soil and soil vapor decreased, lighter hydrocarbons were depleted, and oxygen and carbon dioxide concentrations, as well as respirometry testing, demonstrated that the rate of hydrocarbon destruction by aerobic biodegradation exceeded the rate of volatile hydrocarbon extraction. During this stage of remediation, volatile extraction of hydrocarbons is diffusion limited and aerobic biodegradation is active throughout the LNAPL zone. Remedial effort was concentrated on areas where the light hydrocarbon depletion trends were slowest and where oxygen consumption was highest. In the late stages of remediation, the rate of volatile hydrocarbon extraction had significantly decreased, but hydrocarbon destruction through aerobic biodegradation remained at rates more comparable to those observed earlier in remediation and continued to destroy the least volatile COCs such as xylenes and TBA. By continually adapting remedial operations to observed conditions, cleanup goals were achieved, including aggressive California-drinking-water-based leachability goals for TBA.

Closing a Large Oxygenate Plume with a Multiple-Line-of-Evidence Approach; A California Low-Threat UST Case Closure Policy Success Story

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Background/Objectives. A methyl *tert*-butyl ether (MTBE) plume and isolated benzene, toluene, ethyl benzene, and xylenes (BTEX) plumes have been identified and monitored in groundwater at an active gasoline refueling station (the site) at Marine Corps Recruit Depot, San Diego since 1996. Historic site characterization and monitoring have documented benzene and MTBE concentrations in groundwater up to 14,000 and 17,000 micrograms per liter (µg/L), respectively. Limited active remediation has been performed to reduce concentrations. Four underground storage tank (UST) areas, including 15 individual USTs, and distribution piping to former and current pump islands have been identified as potential source areas. Potential pathways and receptors of site contaminants include 1) vapor intrusion to indoor air that may impact commercial/industrial workers in buildings within and adjacent to the site, and 2) groundwater migration and discharge to San Diego Bay that may affect aquatic organisms. With the adoption of the Low-Threat UST Case Closure Policy (LTUSTCCP) in California, the site was identified as a candidate for “no further action” (NFA) closure with land-use restrictions. However, definition of action levels and further evaluation of contaminant concentrations, distribution and transport potential were warranted.

Approach/Activities. A comprehensive site assessment using a multiple-line-of-evidence approach was performed between June 2011 and April 2013 to:

- Identify all subsurface utility corridors that have the potential to affect the distribution of chemicals of potential concern (COPCs) at the site;
- Evaluate concentrations of COPCs near former and existing USTs and their associated pipelines in the vicinity of the site to determine the source of COPCs in groundwater;
- Delineate the spatial extent and evaluate concentration trends of COPCs in groundwater;
- Assess the potential for natural attenuation across the site;
- Define regulatory action levels consistent with the intended land use, applicable receptors and complete exposure pathways;
- Determine if COPCs in groundwater and soil gas pose risk to human health or the environment; and
- Determine if site assessment results support a recommendation for NFA.

The initial investigative phase utilized a direct push technology (DPT) membrane interface probe (MIP) coupled with an on-site direct sampling ion trap mass spectrometer (DSITMS) to: 1) identify subsurface utility corridors; 2) delineate the nature and extent of groundwater contamination; and 3) optimize the location and design of permanent groundwater and soil gas monitoring points. The second phase included two years of groundwater and soil gas monitoring to evaluate concentration trends and plume stability. Finally, using the data collected in the above two phases and in prior investigations, a simple fate and transport model was developed to assess risk to aquatic receptors.

Results/Lessons Learned. The site assessment activities resulted in a revised conceptual site model that demonstrates site conditions satisfy the criteria for NFA established in the LTUSTCCP. The results obtained during the site assessment activities will be presented.

Client approval pending.

Back to Contents

Bioremediation of Tert Butyl Alcohol (TBA) in Low-Permeability Soil

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Background/Objectives. At an active gas station in Northern New Jersey, the groundwater is impacted with benzene, toluene, ethylbenzene, xylene (BTEX), methyl tert-butyl ether (MTBE), and tert butyl alcohol (TBA) from a historical gasoline release. The site geology is consists of sandy and silty clay. Six rounds of sodium persulfate injections were performed at this site, and sulfate reduction was observed after the last persulfate injection. Currently, TBA is the primary contaminant exceeding NJDEP groundwater quality standard (GWQS) throughout the site, and benzene only exceeds NJDEP GWQS at the area that was never influenced by persulfate injection. Thus, an aerobic bioremediation was proposed to address the remaining contaminants at this site.

Approach/Activities. The aerobic bioremediation was selected because TBA is not readily degraded under anaerobic oxidation pathway like sulfate-reduction. The aerobic bioremediation will entail injecting Oxygen Release Compound (ORC) Advance via Direct Push Technology (DPT) and injection trench. DPT injection will be completed through more than 19 points, which will encompass the source and the area that was not influenced by previous injections. The treatment will target the overburden aquifer and smear zone. Because the overburden has low permeability, delivering of ORC Advanced could encounter difficulty. Three tiers of injection strategy was developed to delivery all the required amendment to the target zone and into the soil matrix.

Results/Lessons Learned. The baseline monitoring was completed in August 2014, and the injection will be completed in October 2014. The performance monitoring will be completed by July 2015, and at least one monitoring event will be conducted before May 2015. The baseline monitoring results showed that the aquifer is under anaerobic and reductive conditions, which can be inhibitory for TBA degradation. During the ORC Advance injection, the tiers of injection strategy will be tested to identify the optimum delivery technology for the low permeability soil. Although aerobic bioremediation can effectively degrade TBA and benzene, the effectiveness of the remediation will be greatly impacted by the site hydrogeological conditions, which determine the oxygen diffusion and transport rate.

Back to Contents

Molecular Characterization of a Biosparging Site

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Background/Objectives. At a site undergoing biosparging, a characterization of the microbial community was conducted by functional gene analysis and stable isotope probing. The site is impacted by releases of fuel hydrocarbons. Constituents of concern include benzene, methyl tert-butyl ether, and tertiary butyl alcohol. These constituents are in groundwater in saprolite and the fractured rock beneath it. The area undergoing biosparging is a highly permeable fractured rock zone. It is in transition from a weathered soil/rock mixture called saprolite to the parent bedrock. The saprolite zone underwent air sparging previously and because of observations made during that work, an understanding of the capabilities of the microbial community was important.

Approach/Activities. Samples for molecular and microbial analyses were collected at baseline, which is before the initiation of sparging activities, and will be collected one month and three months after sparging begins. The locations sampled include wells screened in the transition zone in the source area, side gradient and downgradient. Wells screened in the shallow saprolite were also sampled to determine vertical extent of influence. Groundwater was analyzed for benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene and methyl tertiary butyl ether (MTBE) concentration. Dissolved oxygen (DO), pH, temperature, specific conductance, oxidation-reduction potential (ORP) and pressure data were also collected. Functional gene analysis and microbial characterization and stable isotope probing were performed with QuantArray^R , a quantitative polymerase chain reaction (qPCR) method and BioTraps^{R,} respectively. The Petroleum QuantArray evaluates functional genes for both aerobic and anaerobic biodegradation of a broad range of compounds, including alkanes/TPH, naphthalene and other polynuclear aromatic hydrocarbons (PAHs), and BTEX and MTBE. The BioTraps^R are baited with ^{13}C –labeled benzene, MTBE, and tertiary butyl alcohol (TBA) to determine uptake of these key compounds and phospholipid fatty acid analysis (PLFA) will determine community structure.

Results/Lessons Learned. The baseline qPCR data have been received and show a diverse set of functional genes. Very low numbers of microbial populations were detected in some transition zone (fractured rock) samples. The shallow saprolite samples and some source area transition zone samples had large and diverse microbial populations. Performance of the biosparge system will be examined against these microbial results.

The Use of Metaproteomics to Characterized North Slope Sediments Exposed to Crude Oil

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Background/Objectives. Microbes are vital to ecosystems by serving as a direct food source and by performing essential processes (e.g., oxygen cycling, nitrogen fixation). Microbes can serve to remove pollutants (e.g., oil) through the process of bioremediation and/or carbon utilization. We had previously characterized North Slope sediment samples exposed to crude oil using metagenomics. The purpose of this project was to characterize these sediments using metaproteomics. Further, we sought to develop protein extraction methods and perform proteomic data analyses to compared oil and non-oil sediments to determine if proteomes are unique.

Approach/Activities. Sediment samples from the coast of Barrow AK were collected and exposed to crude oil (North Slope Crude). Proteins were extracted from three samples exposed to crude oil (0.1% for 4 weeks) and three not exposed to oil (“baseline”) using MoBio’s new NoviPur soil protein kit. Extracted proteins were digested and analyzed by LC-MS/MS analysis at Battelle using an optimized gradient and C18 column. Proteins were identified using a metagenomic database previously developed and Mascot. The two sample groups were compared with MarkerView and functionally classified using the Krypto Encyclopedia of Genes and Genomes (KEGG) Database.

Results/Lessons Learned. After optimization, we were able to get reproducible LC-MS traces of protein digests (3 exposed to oil and 3 unexposed). Using Mascot, we identified a higher number of proteins from oil degrading species from oil exposed samples. Using unsupervised Principal Component Analysis (PCA) revealed some separation of groups when all peaks were considered and good separation when only peaks with significant differences ($p<0.05$) were considered. Supervised PCA allowed complete separation and allowed identification of putative biomarkers of oil exposure. Using MarkerView, we identified several potential biomarkers of interest. Further, a larger number of protein involved in lipid and xenobiotic metabolism were identified from the oil exposed samples, suggesting metaproteomics may be used as markers for oil degradation. In general, our analyses showed that when exposed to crude oil, microorganisms within sediment samples responded in a measurable way.

Identifying Active Microbial Communities during In Situ Hydrocarbon Degradation in Cold Soils using Heavy Phosphate

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Background/Objectives. As part of the Sustainable In Situ Remediation Cooperative Alliance (SIRCA), novel forms of phosphorus fertilizer are being developed to stimulate residual hydrocarbon degradation in the clay rich, cold, calcareous soils of Western Canada. However, identifying the microbial community interacting with these novel forms of phosphorus is a challenge. Stable isotope probing of microbial communities involves the labelling of microbial DNA by a heavy isotope of C, N or O. This labelled DNA can then be separated from non-labelled DNA using a density gradient centrifugation and then this labelled DNA interrogated using a variety of molecular approaches, e.g. sequencing, quantitative PCR analysis, etc. While methods to label microbes using nitrogen fertilizers have been reported, no methods exist for phosphorus fertilizers. The objective of this project is to develop and validate the use of PO_4^{18} as a means of labelling a wide variety of anaerobic and aerobic microorganisms.

Approach/Activities.
To validate this hypothesis, *Bradyrhizobium elkanii, Psychrobacter arcticum, Micrococcus luteus and Desulfomonile tiedjei* were utilized as they have varying GC content and gram positive/gram negative morphology. A molecular weight difference can be determined by the GC content of the microbes and the gram positive and gram negative strains provide an idea of the uptake of phosphate based on their cell wall and membrane structure. The heavy phosphate they are grown in is synthesized by mixing 97% atom ^{18}O and PCl_5 together. Media containing either light phosphate or the synthesized heavy phosphate is used to grow the microbe which results in the uptake of either heavy or light phosphate into cellular structures in the microbe. The DNA is extracted and put into caesium chloride (CsCl) gradients of low GC content microbes with a light or heavy phosphate label and high GC content microbes with a light or heavy phosphate label to separate the labelled heavy DNA from light DNA. The gradients spin in an ultracentrifuge and the tubes are fractioned into smaller aliquots to illustrate how the DNA has separated in the tube. DNA is precipitated and then presence/absence tests are run on the fractions by PCR to determine if separation based on weight occurred.

Results/Lessons Learned. Preliminary testing has begun in the lab using traditional C and N labelling to ensure that the methodology is successful before labelling with heavy phosphate. A range of concentration densities for CsCl was run for the N label and results from this test are pending.

Microorganisms Indicative of Anaerobic Benzene Degradation Potential in Groundwater Systems

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Background/Objectives. Benzene is a prevalent groundwater contaminant due to its natural occurrence in petroleum hydrocarbons and broad industrial application. As a known human carcinogen, it causes considerable concern regarding drinking water safety. Although benzene is more persistent in anaerobic aquifers than other similar compounds (e.g. toluene), monitored natural attenuation remains a cost-effective method, used extensively to deal with its contamination. Such a process may take years to decades to decrease concentrations of the contaminants. In this context, relatively slow rates of biodegradation can still have tremendous impact on plume longevity and concentrations. Therefore, having a means to evaluate and track bioremediation of benzene in anaerobic aquifers would be extremely valuable. In the current work, we propose DNA biomarkers as a novel tool for identifying the presence or absence of the potential benzene degraders.

Approach/Activities. Our laboratory has enriched several anaerobic benzene-degrading microbial consortia that are capable of degrading benzene under different terminal electron-accepting conditions. We conducted 16SrRNA sequence analysis of the primary benzene degraders using clone libraries and metagenome analyses. These sequences were then aligned with 16SrRNA sequences from other benzene-degrading microorganisms established in other labs around the world. A phylogenetic tree was then constructed to represent variability among the benzene degraders. 16SrRNA sequences from any organism reported to carry out anaerobic benzene degradation were compiled to create a comprehensive reference database, to which DNA sequences from samples from field sites can be compared.

Results/Lessons Learned. Different benzene-degrading microorganisms were identified in cultures grown under different terminal electron-accepting conditions, even for cultures originated from the same sites. Cultures enriched from different contaminated sites seem to converge to similar microbial communities when they are cultivated with the same electron acceptor. When benzene degradation is coupled to low potential electron acceptors such as sulfate or carbon dioxide, members of the *Deltaproteobacteria* were identified as the primary benzene degraders. When benzene degradation is coupled with nitrate or iron reduction, however, microbes associated with the *Clostridia*les were enriched. Reported pure cultures of anaerobic benzene degraders, including Azoarcus and Dechloromonas, however, fall into neither clade. The reference database of all 16SrRNA sequences documented in some way to be involved in anaerobic benzene degradation is useful to suggest potential specific biomarkers for assessment of benzene biodegradability prior to a monitored natural attenuation or biostimulation study. Cultures mentioned in this study also have potential for bioaugmentation as a cost-effective tool for remediation of benzene in anoxic groundwater.

Development and Application of an RT-qPCR Assay Targeting Anaerobic Benzene Carboxylase (*abcA*) Gene Expression in Hydrocarbon-Contaminated Groundwater

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Background/Objectives. Benzene is an organic compound commanding high regulatory and public-health concern. Benzene is broadly distributed in hydrocarbon-contaminated sites, many of which are anaerobic. Because of substantial interest in benzene's fate in the environment, there is a need for tools that can be applied to field sites to document anaerobic benzene biodegradation. This investigation was designed to: (i) utilize existing DNA sequence information to develop an mRNA-based assay to quantify expression of anaerobic benzene-degradation genes in microbial communities native to hydrocarbon-contaminated groundwater and (ii) apply this newly developed biomarker assay during a controlled, hydrocarbon-release experiment conducted in conjunction with researchers of the University of Waterloo and University of Neuchatel at the Borden research site (Ontario, Canada).

Approach/Activities. Using a previously reported gene sequence of a putative anaerobic benzene carboxylase (*abcA*) (Laban et al., 2010), we developed an assay targeting a 287-bp fragment of the *abcA* gene. This assay was applied to microbial DNA extracted from a reference petroleum-contaminated site in South Glens Falls, NY. Amplified DNA of the expected size was cloned and sequenced and matched (87% sequence similarity) the previously published, putative *abcA* gene. Next, a quantitative RT-qPCR assay was developed for mRNA extracts (after conversion to cDNA) and applied to field samples taken during a controlled, hydrocarbon-release experiment at the Borden research field site.

Results/Lessons Learned. This presentation focuses on results obtained from 9 locations sampled in a hydrocarbon plume at a single time event at the Borden site. We found expressed *abcA* transcripts in more than half of the samples. Moreover, the patterns of gene expression were consistent with exposure to benzene and the anaerobic redox status of the sampling site (using groundwater methane as a redox indicator). Cloning and sequencing of the PCR-amplified DNA showed high sequence identity (96%) between the 287-bp gene fragment from the Borden groundwater microbial community and the sequence of the previously published *abcA* gene. Thus, future efforts aimed at assessing bioremediation progress can add this new RT-qPCR assay for anaerobic benzene biodegradation to the wide menu of existing geochemical, modeling, mass spectrometric, and other tools for assessing environmental cleanup.

Reference: Abu Laban N, Selesi D, Rattei T, Tischler P, Meckenstock RU.2010. Identification of enzymes involved in anaerobic benzene degradation by a strictly anaerobic iron-reducing enrichment culture. *Environ Microbiol* 12:2783-2396

Biodegradation of Anthracene by Paenibacillus sp. HD1PAH Supplemented with Biosurfactant of Pseudomonas aeruginosa H7h

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Background/Objectives. Polycyclic Aromatic Hydrocarbons (PAHs) pollution in the crude oil contaminated sites is not only the problem in India but also in other parts of the world. Anthracene is one of the chief pollutants among the PAHs species present in the crude oil. The soil bacteria which are present in the crude oil contaminated site may play an important role in the degradation of several PAHs species like anthracene. Further, application of bacterial metabolites such as biosurfactant along with the PAHs degrader bacteria may enhance the biodegradation process of PAHs.

Approach/Activities. Anthracene degrading bacterial isolate has been isolated through enrichment culture from the crude oil contaminated soil of Assam, India. Degradation efficacy of the different isolate was studied in flask culture using anthracene as sole carbon source. The optical density (OD) and bacterial biomass (B) was taken as the parameters to study the degradation efficacy of the different isolates. The most efficient isolate in terms of degradation was identified through 16S rRNA approach and it was identified as Paenibacillus sp. HD1PAH. The bacterial strain Paenibacillus sp. HD1PAH was further employed for degradation of anthracene in flask culture study supplementing with the crude biosurfactant of Pseudomonas aeruginosa H7h strain. For the study 100ml MSM with 2% anthracene solution along with 2% crude biosurfactant solution was taken in the 250ml conical flask and 5 ml of broth culture of the bacterial strain from the stock was poured to the flask. The flasks were incubated at 350C maintaining a speed of 200 rpm for 96 hours. Optical Density (OD) and Biomass (B) for the treatments were measured at 0h, 4h, 8h, 12h, 24h, 48h, 72h and 96h of incubation. Samples were also collected at different duration and were analyzed in Gas Chromatograph (FID) for quantification of anthracene degradation. Both positive and negative control was also setup for comparison of the results.

Results/Lessons Learned. The results of the study reveal that Paenibacillus sp. HD1PAH is an efficient degrader of anthracene. Further, anthracene degradation efficiency of Paenibacillus sp. HD1PAH is significantly enhanced as a result of application of crude biosurfactant of Pseudomonas aeruginosa H7h. Quantitative analysis of the degradation pattern will be highlighted at the time of presentation.

Solitary Extradiol Dioxygenase Gene Supports the Biodegradation of Aromatic Hydrocarbons

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Direct evidence that TPH removal is a primary effect of bioremediation processes occurring in the soil can be obtained by specifically targeting genes responsible for the functionality of the autochthonous microbial community. Majority of the culture-independent surveys of catabolic gene diversity in contaminated environments have used conserved nucleotide sequences to design primers for detecting the presence, abundance and diversity of catabolic genes that encode a defined group of enzymes thought to be critical in the target environment. Our previous study improved upon this by adopting a metagenomic approach in combination with functional selection and PCR screening with newly designed primers to identify key catabolic gene groups (Brennerova et al., 2009). Representative fosmid library was constructed from metagenomic DNA of soil sample coming from an area under bioventing treatment located in Czech Republic. The sample was collected from a saturated zone with total petroleum hydrocarbons (TPH) reaching 22 000 mg/kg dry soil weight. Function-based screening approach together with transposon insertion and PCR based assay identified a new catechol 2,3-dioxygenase gene, named *hrb*C. The *hrb*C gene represented the third main group of catabolic genes with catechol *meta*-cleavage activity in the locality. The novel gene encodes an enzyme with an exceptionally high affinity for various catecholic substrates.

Roche 454 GS FLX Titanium pyrosequencing platform was used for sequencing of the fosmid inserts carrying *hrb*C. Analysis of the fully assembled contigs (34.2 Kb to 42.3 Kb) showed that the library clones shared a conservative metagenomic fragment with minimal length of 22.8 Kb. The newly isolated extradiol dioxygenase gene resides within a cluster of housekeeping genes encoding enzymes for amino acid metabolism. The solitary localization and much lower GC content of *hrbC* (51.9%) when compared to the adjacent metagenomic DNA (56.6%) indicates its acquisition by horizontal transfer. The only successful experimental system for exploring the changes of *hrb*C, and other genes characteristic for the biodegradation potential were the outdoor mesocosm systems using soil from the contaminated environment. Absolute quantitative real time PCR detected a rapid increase in the *hrb*C gene copy numbers after increasing of the TPH concentration, thus, indicating a concomitant remedial response of the soil microbial community. Presence of the gene and its transcripts were detected for highly contaminated with aromatic hydrocarbon localities.

The ring-cleavage dioxygenase is considered to be the biotransformation rate-limiting enzyme leading to accumulation of toxic catechol intermediates. This is the first evidence for a functional solitary type of biodegradation gene, representing evolutionary short-circuit for a key enzyme needed to overcome the substrate range limitations. The *hrb*C gene is an example for the complex mechanisms shaping the catabolic potential of the soil microbial population.

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Forensic Evaluation of Historic Fuels Releases at the J3 Pumphouse Davis-Monthan Air Force Base, Arizona

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Background/Objectives. A release of JP-4 occurred in1985 from a break in a pipeline feeding the J3 pumphouse, the main pumphouse used for aircraft fueling operations. The 1985 release was investigated in 1989-1991 under the CERCLA basewide remedial investigation. Additional investigations effectively delineated the plume, and the site was being remediated when an apparent new release was encountered during installation of replacement groundwater monitoring wells in 2003. Free product was encountered at 245 feet below ground surface adjacent to the J3 pumphouse but in a location outside the previously delineated plume. Initial evidence pointed to a JP-8 release, which would date the release to sometime after 1993 when the conversion to JP-8 occurred. However, an active leak detection system had been installed at the J3 pumphouse, and tanks and piping received routine inspections and hydrostatic testing. The findings of a JP-8 release were thus disputed. Since a potential ongoing release would adversely affect performance of the remediation system, and evidence to this effect was already being observed, resolving this apparent dilemna was critical to both maintaining the aircraft fueling operations and the continued remediation of the site.

Approach/Activities. Samples of fuel-saturated soil were collected and analyzed by Transwest Geochem, Inc.; chromatograms were then compared to both JP-4 and JP-8 standards. Samples were also provided to both Friedman and Bruya, Inc. and to the aerospace fuels laboratory at Wright Patterson Air Force Base for additional analyses to support characterizing the type of fuel present and whether it represented a newer release. A physical inspection of the underground storage tanks and associated piping was also performed by removing most of the soil from above and to the sides of the tanks. Hydrostatic testing of the tanks and accessible piping was conducted along with a comparison of piping with as-builts to look for unknown segments or connections not being tested.

Results/Lessons Learned. The results of the chemical testing of the fuel-saturated soil supported the presence of JP-8. Benzene was identified at concentrations greater than typically found in JP-8, likely due to JP-8 comingling with residual JP-4 fuel in the subsurface. The JP-8 release appeared to have occurred in close proximity to the historic JP-4 release, which resulted in a comingled plume. At least one ongoing release point was identified at the pumphouse, a leaking flange at the end of a previously unknown pipe segment. However, this leak could not account for the apparent large volume of JP-8 released to the subsurface.

The lack of apparent or identifiable source(s) for the more recent JP-8 release, and the failure of the leak detection methodology to identify the release or its source(s) was a concern in trying to ascertain whether the pumphouse could continue to operate using operational and leak detection methodology in place at the time without resulting in the potential future loss of fuel and further degradation to the environment. Improved monitoring and leak detection systems were ultimately installed to help prevent any future releases from the pumphouse. The five tanks closest to the new suspected release point were also removed from service and abandoned without impacting fueling operations at the base.

Source Identification by Advanced and Tiered Analytical Tools

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Background/Objectives. A tiered analytical approach has been developed in which the level of analytical sophistication employed is determined by a project's data quality objectives. Cutting edged analytical tools are used in environmental forensics laboratory to obtain a better understanding of the mysteries surrounding oil spills. In environmental forensic community the use of multiple lines of evidence with sound science and legally defensible results for litigation purposes are currently in practice.

Approach/Activities. Hydrocarbon Fingerprinting is a classic tool to differentiate crude oils and refined petroleum products. Updated ASTM D3328 and D5729 fingerprinting methods with one dimensional Gas Chromatography for oil spills have been widely used and accepted in forensic community. They provide the first assessment on the type of hydrocarbons and bulk estimation on each category. Typically, ASTM D6729 will provide sufficient compositional information for gasoline range hydrocarbons. Some alkylate blending stock indices (e.g. an isooctane index), based on the detailed hydrocarbon analysis (DHA) are shown to be beneficial for use as a diagnostic tools to differentiate the origin of hydrocarbon contaminated matrices. Other equivalent analytical methods such as PIONA or EPA 8260C/EPA 8270C also can provide compositional information to satisfy the quest for source identification.

Results/Lessons Learned. Biomarkers are stable and resistant to biodegradation over geologic time. This technique has been widely used in upstream oil exploration. For heavily biodegraded hydrocarbons, the use of a double ratio plot of triterpanes and steranes can help to provide additional evidence for oil source determination. Middle distillate range material, low molecular weight biomarkers: such as diamondoids and sesquiterpanes have been used as the useful diagnostic biomarker to track back the origin of spills. Classical one dimensional fingerprinting technique falls far short of the resolving power for heavier oils and cannot result in unequivocal conclusions. Comprehensive two dimensional Gas Chromatography (GCxGC) techniques will enhance our knowledge toward the complexed petroleum composition. In this paper, the GCxGC technique has been applied to some challenging mixed heavy crude oils with quantitative measurements. The unique capabilities of GCXGC, e.g. biomarker ratio distribution plots, chromatogram mountain plots, and difference chromatograms, can provide unequivocal information.

The Use of Trace Evidence in Environmental Forensics in Determination of Source and Fate of Pollutants

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Background/Objectives. The purpose of this talk is to examine some of the basic concepts of what today is commonly called “environmental forensics”. I believe we can trace the beginnings of the topic back to the late 1800s with the development of crime scene forensics and the involvement, directly or indirectly of several well-known characters. While the techniques available at that time certainly did not have the power of analytical techniques used today, the basic concepts and observations made in those early criminal cases are still directly applicable to cases today. However it was really until the 1970s that environmental forensics as we know it today was really born. There are many reasons for this including, but not limited to such factors as: the publication of the Silent Spring by Rachel Carson which certainly stimulated people’s awareness of environmental issues-particularly issues associated with DDT; roughly in parallel with this was the commercial availability of various analytical equipment such as gas chromatographs (GC) and gas chromatography-mass spectrometry (GCMS).

Approach/Activities. In addition in the US the EPA was developing procedures for monitoring specific contaminants at various sites. Procedures which, by the way, are for the most part of very limited use in environmental forensics! Numerous regulations were developed for concentrations permitted for certain compounds in contaminated sites which if exceeded required expensive clean-up methods. However environmental forensics, whilst related has different goals. While monitoring is important, another important issue is determining responsibility for a spill or release of a contaminant into the environment-be it in the air, soil or water. The first examples of this application were probably in the North Sea with all the oil exploration that was underway in the 1970s. The Norwegian Coast Guard starting using crude oil fingerprinting techniques to determine the source or point of release for crude oils in the N. Sea. Many of these techniques were the same that had been developed a few years earlier and were starting to be used by the oil companies in their exploration efforts.

Results/Lessons Learned. As we move toward the present, many of the techniques being used are improved versions of the techniques being used in the 1970s, with the addition of the widespread use of stable isotopes. In addition a much wider range of compounds is now being investigated along with a far wider range of environments. New compounds continue to emerge as contaminants of concern along with new problems. One classic emerging problem being hydrofracking which has a number of issues related to it which will be discussed in this talk.

In summary this talk will examine the evolution of environmental forensics and also see how many of the older concepts and ideas are still be applied to new and evolving problems. It will also discuss some of the more recent areas where environmental forensics can again play a role in solving or attempt to solve some of these problems.

Determination of the Vertical and Horizontal Extent of Subsurface Hydrocarbon Fuel Releases using Environmental Forensic EPA Method TO-15/SW8260B and Mining Visualization Software

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Background/Objectives. Fueling areas at DOD facilities can often have a mixture of various hydrocarbon fuel types with releases occurring over various periods of time and may have varying degrees of weathering. This can make the determination of the vertical and horizontal extent of such fuel releases very difficult using conventional investigative techniques. Using Environmental Forensic (EF) Gas Chromatography/Mass Spectrometry (GC/MS) analysis by EPA Method TO-15 of soil gas and EPA SW8260B of co-located soil samples coupled with Mining Visualization Software (MVS), near real time decisions can be made to determine where the next location is advanced to pinpoint contamination source areas. EF TO-15/SW8260B and MVS are two different complementary approaches that can reduce investigation time and provide near real-time measurement systems combined with on-board real-time decision-making processes. Central to this initiative is collaboration among all stakeholders on project-based decisions.

Approach/Activities. The areas of concern are fueling and storage facilities which are potential sources for Volatile Organic Compounds (VOCs) released to the subsurface. Based on historic information and testing of monitoring wells, elevated VOC concentrations are observed in groundwater at the various sites. No single potential source areas have been identified at the sites. By using EF TO-15/SW8260B specific marker compounds were used to follow migration pathways back to source areas. The specific marker compounds along with traditional TO-15/SW8260B analyte list combined with MVS facilitated a better understanding of subsurface conditions by identifying specific fuel types. This information combined with historic fuel usages enabled investigators to determine when the releases potentially took place and their possible points of release. The complexities associated with the potential multiple VOC sources were addressed by application of EF and MVS methods.

EF and MVS methods were used to construct the underlying stratigraphic framework and identify potential VOC pathways in the vadose and saturated zones. EF combined with MVS evaluates the potential sources by integrating advanced analytical techniques and real-time modeling along with and other critical information such as hydrogeology, primary source vs. secondary source, contaminant temporal trends, spatial patterns, transport and fate of contaminant of concern.

Results/Lessons Learned. The complexities of the subsurface releases were not well understood or defined. Using EF coupled with MVS analyses improved the CSM providing information critical to the real-time decision making process to direct drilling locations such that the source/s could be better defined. This understanding assisted stakeholders in determining if potential Vapor Intrusion (VI) issues may be present and if site remediation is required.

Back to Contents

Source Characterization Using Environmental Forensics at Complex Petroleum Impacted Sites

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Background/Objective. In site investigations, a good understanding of contaminant sources is essential as these sources are the starting points of contaminant migration pathways which determine the extent of contaminants. The conventional approach for source characterization at petroleum impacted sites has relied on the general characteristics of petroleum hydrocarbons (e.g., total petroleum hydrocarbons, BTEX and oxygenates). While this approach is often appropriate and accepted by regulatory communities in general, at many complex sites, sources of the petroleum hydrocarbons cannot be resolved, because most source diagnostic compounds are not available in standard laboratory analyses. The objective of this paper is to demonstrate the effectiveness of applying environmental forensics to source characterization at petroleum impacted sites.

Approach/Activities. Environmental forensics is a discipline that focuses on characterization of contaminant sources such as petroleum and various products. It was originally developed for resolving liability issues among responsible parties. However, most techniques such as chromatogram pattern recognition, diagnostic compounds and ratio analysis, and biomarker fingerprinting can be equally applied in source characterization in conventional site investigations. Use of environmental forensics enhances characterization of petroleum sources, which in turn helps to better understand release migration pathways and the extent of contaminants so that more focused and cost effective remediation can be conducted.

Results/Lessons Learned. This paper presents three case studies to demonstrate the results of application of environmental forensics to source characterization. The first case study presented is associated with a release of petroleum product(s) at a site with documented historical releases. Application of chromatographic pattern recognition technique resulted in the differentiation of current from historical releases, which then assisted with expedited remediation by limiting cleanup to the area that was impacted only by current release(s). The second case study uses petroleum biomarkers to determine crude source(s) at sites where potentially multiple sources are present. The findings of this study identified release migration pathways, which lead to optimizing the site's remedial design. The third case study involves a site with a suspected on-going release of a fuel oxygenate, which was present in a comingled light, non-aqueous phase liquid (LNAPL) plume. Advanced chromatographic data processing resulted in resolution of the comingled LNAPL plumes and in the identification of association of the oxygenate with one particular type of LNAPL. Further, the study revealed that the fluctuation of oxygenate concentrations in the LNAPL was due to hydrodynamics caused by the site's LNAPL recovery wells. The findings of the study were used to avoid unnecessary and costly investigations to identify the source(s) of the previously suspected, ongoing oxygenate releases.

Development of Environmental Forensic Technique in Source Identification of Diesel Fuel Contaminated Sites in Taiwan

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Background/Objectives. Soil and groundwater contamination by petroleum products released from underground or aboveground storage tanks is a serious and widespread environmental problem in Taiwan. Diesel fuels are among the most frequently spilled petroleum products. The objective of this study is to develop proper chemical analysis methodologies to characterize and identify diesel contaminated sites from environmental forensics prospect.

Approach/Activities. Soils contaminated by diesel fuel produced in 2000, 2002, 2003, and 2005 were used for our weathering study. The slightly degraded oil is usually indicated by partial depletion of n-alkanes; a moderately degraded one is often indicated by heavy loss of n-alkanes and partial loss of lighter polynuclear aromatic hydrocarbons (PAHs); for highly degraded oil, the n-alkanes and branched alkanes could be completely lost, and PAHs and their alkyl homologues could be highly degraded. The compositional analyses of four aging contaminated soil samples include the following: (1) total petroleum hydrocarbons, (2) distribution of n-alkanes and some selected isoprenoids (pristine and phytane), (3) PAH, and (4) biomarker compounds (bicyclic sesquiterpanes).

Results/Lessons Learned. After the long term weathering processes of 8 and 10 years, compounds with molecular weight smaller than C9 alkanes were disappeared in soils contaminated by diesel fuel in 2003 and 2005, respectively. Also it was found that fuel constituents with molecular weight smaller than C10 alkanes were disappeared in aging contaminated soil of 2002. For soil sample through 13 years of weathering processes, compounds with molecular weight smaller than C11 alkanes were degraded, furthermore, after the long term weathering processes of 365 days, compounds with molecular weight smaller than C12 alkanes were disappeared in soils contaminated by diesel fuel in both oil companies. Isoprenoids, bicyclic sesquiterpanes and alkylated PAHs are less susceptible to the effects of biological indicators of biodegradation. The ratios of characteristic factors such as Pr/Ph, C15 sesquiterpane/8β(H)-drimane (BS3/BS5), C15 sesquiterpane/8β(H)-drimane (BS4/BS5), C15 sesquiterpane/C15 sesquiterpane (BS4/BS6), C15 sesquiterpane/8β(H)-homodrimane (BS3/BS10) and 8β(H)-drimane/8β(H)-homodrimane (BS5/BS10), methylphenanthrene Indices(MPI), methylnaphthalene ratio(MNR), methylphenanthrene ratio(MPR) can be utilized as forensic indicators in diesel contaminated sites. The results demonstrated that characteristic ratio of diesel fuel in 2005 with soils contaminated by diesel fuel in 2005 were similar. Apparently results of characteristic ratio match the information sources.

Finally, source identification was attempted for samples collected from different fuel contaminated sites by using the unique pattern of sesquiterpanes. Furthermore, it was demonstrated that diagnostic ratios of sesquiterpanes were not affected by evaporation. It is anticipated that the information generated from this study will be adopted by decision makers to evaluate the liability of cleanup in diesel contaminated sites in Taiwan. The database, forensic criterion, and parameters established in this study should be coupled with other information such as hydrogeological condition, environmental condition of contaminated sites for better results of environmental forensics.

Treatment Optimization through Refinement of a Conceptual Site Model Using Compound Specific Isotope Analysis

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Background/Objectives. Two adjacent automotive component manufacturers in Japan had experienced releases of trichloroethene (TCE) and tetrachloroethene (PCE) to soils and groundwater beneath their plants. One of the manufacturers extensively used these solvents in its processes, while the adjacent manufacturer had no documentation of solvent use. To design the remediation system, the site conceptual model (CSM) required refining. The CSM involved a monolithic source that migrated from one building to under the adjacent. Further, because only trace detections of daughter compounds were detected in groundwater, the CSM did not consider intrinsic degradation to be a significant fate mechanism. As a result, the initial remedial design involved both source treatment as well as perimeter groundwater control to prevent offsite migration of the solvents in groundwater. The perimeter control system represented a costly potentially redundant system if it could be determined that intrinsic degradation was occurring and could be quantified. Further, cost savings could also be realized with a more focused source treatment.

Approach/Activities. Three rounds of sampling and data interpretation using compound specific isotope analysis (CSIA) were applied. The first used 3D-CSIA (^{13}C, ^{2}H and ^{37}Cl), while the second two interpretations used ^{13}C only in a focused manner after the initial 3D-CSIA interpretation showed no significant difference in the δ^{2}H or δ^{37}Cl values.

Results/Lessons Learned. By tracking fractionation patterns the authors were able to trace detections of TCE from individual wells back to the source locations to better focus the locations for steam injection. Further, the quantification of fractionation (e.g., isotope enrichment factors and first order degradation rates) was used to define the degradation mechanism and from this establish source cleanup criteria for to incorporate intrinsic degradation processes into the remedial design eliminating the perimeter control system.

Forensic Analysis and Modeling of LNAPL Properties to Craft Robust LNAPL Conceptual Site Models

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Background/Objectives. Forensic analysis of LNAPL physical and chemical properties in support of legal activities is well-established, but routine forensic analysis of LNAPL data to craft robust LNAPL conceptual site models is less common. For the purpose of site characterization, risk evaluation, and remedy design, the LCSM forensic analysis focuses more on LNAPL properties as they exist, in addition to identifying and tracking probable migration pathways and source areas. Relevant data for such forensic analyses includes laser induced fluorescence (LIF) data and NAPL physical and chemical properties (e.g., PIANO analyses, density, viscosity, simulated distillation). Inherent to such analyses are a combination of data pre-processing and multivariate statistical analysis methods designed to augment and identify groups and gradients for a site. The objective is to better understand the data as they exist (including mixing and weathering gradients) rather than to attempt to reproduce the data conditions as they may have been at the time of the release(s). Of particular interest is the success such methods yield when reanalyzing routinely collected data for petroleum impacted sites, rather than insisting upon new litigation quality analyses.

Approach/Activities. The approach consisted of the collection and analysis of a range of LNAPL data for multiple facilities, and the forensic analysis of such data to enhance existing LNAPL conceptual site models and bolster risk-based remediation technology decisions. Data included NAPL types, physical NAPL properties (e.g., density, viscosity), chemical NAPL properties (e.g., simulated distillation, PIANO analyses), and other readily available and routinely collected data. A variety of data pre-processing techniques were utilized, and multivariate statistical analysis methods implemented included ordination via principal components analysis and non-metric multidimensional scaling as well as cluster analysis with bootstrapping techniques. Results of each method were compared to ensure consistency, and then transformed back from multidimensional space to real-world coordinate space in order to evaluate groupings and gradients in both 2D and 3D space as they related to NAPL distribution, characteristics critical to remedy selection, and potential source pathways.

Results/Lessons Learned. Results demonstrate that such analyses provide surprisingly robust results consistent with more comprehensive forensic analyses conducted. LNAPL characteristic groups and gradients critical to remedy technology selection were clearly identifiable, and weathering and mixing gradients could also be identified where present. The results of this work demonstrate that forensic analysis of LNAPL data should not be confined to the realm of litigation, but should also be incorporated into routine LNAPL conceptual site modeling. In addition, results indicate that for the purpose of LCSM development, litigation quality analyses are not necessary, and reliable results may be generated from routinely collected LNAPL physical and chemical properties common to petroleum impacted sites.

Using Environmental Forensic Compound Specific Isotope Analysis (CSIA) to Determine Potential Off-Site Releases of Chlorinated Solvents at a Former Manufacturing Facility

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Background/Objectives. A former manufacturing facility had historic release(s) of Tetrachloroethene (PCE) and Trichloroethene (TCE) to the subsurface with both on-site and off-site groundwater impacts. Site remediation has employed source area removal and groundwater extraction and treatment at the downgradient property boundary. The responsibilities for off-site subsurface impacts were disputed by adjacent property owners who also utilized PCE and TCE for multiple on-site activities.
To determine if the on-site PCE and TCE releases were contributing to off-site subslab concentrations that maybe contributing to possible Vapor Intrusion (VI) concentrations detected in adjacent properties, AECOM designed an investigation protocol which included Compound Specific Isotope Analysis (CSIA). Isotopic signatures from on-site releases were compared to adjacent property groundwater and soil gas. Because the raw materials used during the manufacturing process and the synthesis used impart a unique isotopic signature, CSIA can be used to determine if the released solvents are similar or different. AECOM's objectives were to: verify that an off-site source was contributing PCE and TCE to a co-mingled groundwater plume; determine to the extent practicable that the PCE and TCE in groundwater from the former manufacturing facility was different than the PCE and TCE in groundwater on the adjacent properties and; Confirm that soil gas impacts on adjacent properties were from on-site sources and not from off-site groundwater impacts.

Approach/Activities. AECOM developed a subsurface and soil gas investigation with an existing on-site environmental supplier during routine site monitoring. AECOM collected CSIA groundwater samples from 13 on and off-site monitoring wells and three soil gas locations consisting of 16 discreet depth intervals. These samples were analyzed for two isotope (2-D) CSIA analyses for PCE and three isotope (3-D) CSIA for TCE.

Results/Lessons Learned.

- Based upon a ¶-value analysis of the groundwater PCE and TCE concentrations adjacent property sources are contributing to the co-mingled plume.
- CSIA is a relatively new forensic technique requiring longer analytical analysis turn-around times beyond standard methodologies.
- Utilization of CSIA as a forensic tool requires additional levels of effort to describe and communicate results due to the complexity of the analytical results.

Petroleum Hydrocarbon Forensics Demonstrate Ongoing Releases at Legacy Upstream Site

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Background/Objectives. Ongoing releases of petroleum hydrocarbon liquids at upstream legacy asset sites operated by other entities may result in additional remediation costs and may delay site closure. Increases in the thickness of light non-aqueous phase liquids (LNAPL) with time in groundwater at a natural gas booster station, despite long-term operation of an LNAPL remediation system, suggested that ongoing releases of gas condensate and other petroleum hydrocarbon liquids was occurring. A forensic-level assessment of LNAPL in groundwater was conducted to better understand the source and distribution of petroleum hydrocarbon liquids in site groundwater.

Approach/Activities. Unrefined and refined petroleum hydrocarbon products, including gas condensate, are complex mixtures containing hundreds or thousands of individual hydrocarbon compounds. The exact composition of petroleum hydrocarbon products may vary due to several factors, including the original oil source and the subsequent refining process. Changes in the composition of petroleum hydrocarbons also occur due to weathering processes, including volatilization and biological degradation, that take place after a product has been released to the environment. Petroleum hydrocarbon forensics, or “fingerprinting,” is an important tool in evaluating the composition of petroleum hydrocarbons in LNAPL, soil, and water at environmental sites.

LNAPL samples were analyzed by high-resolution gas chromatography with a flame ionization detector (GC/FID). This analysis identifies more than 100 compounds in the C3 to C44 carbon range, which spans nearly the entire range of petroleum constituents from lighter products (e.g., gasoline) to heavier products (e.g., residual fuel oil). Sample chromatograms were used to identify the composition and extent of weathering of petroleum hydrocarbon liquids in site LNAPL samples.

Results/Lessons Learned. LNAPL primarily consisted of light gas condensate (C3 to C10) with varying proportions of heavy gas condensate (C11 to C40) or other hydrocarbon mixtures. The distribution of petroleum hydrocarbons in site LNAPL samples varied by location including; 1) primarily light gas condensate with small amount of heavier hydrocarbons (C14- to C18) in close proximity to the booster station, 2) primarily light gas condensate with some weathered heavy condensate in the distal portion of the LNAPL plume, and 3) mixed gas condensate and relatively fresh heavy condensate in the central portion of LNAPL plume. The presence of relatively fresh heavy condensate in samples in the middle portion of the LNAPL plume indicated that releases of heavy condensate not related to historical booster station activities likely had occurred. LNAPL composition results were consistent with known potential sources of heavy condensate produced by site third party drilling activities.

Back to Contents

Sustainable Bioremediation of Petroleum Hydrocarbon Impacts Using Hydrogen Peroxide as a Bio-stimulant

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Background/Objectives. The presence of Light Non-Aqueous Phase Liquid (LNAPL) was detected in close proximity to a sensitive aquatic receptor. Due to the presence of benzene and ethylbenzene concentrations above applicable groundwater standards and proximity to an aquatic habitat, remedial action was required to address the identified risk conditions. A solution was required that could remediate the identified contaminants while presenting minimal risk of releasing deleterious substances into the adjacent aquatic habitat. Physical constraints to remediation included a bulk fuel tank farm and concrete containment structure. The solution developed was to conduct a LNAPL recovery program followed by installation of an in-situ remediation system using 29% hydrogen peroxide (H_2O_2). This slow trickle system was implemented with the objective to remediate groundwater contaminant concentrations below high-risk trigger values while safeguarding the aquatic receptors. This research was conducted as part of Federated Co-operatives Limited's commitment to the Sustainable In-Situ Remediation Co-operative Alliance (SIRCA).

Approach/Activities. H_2O_2 addition was deemed best suited for use in proximity to an aquatic habitat. As a result, H_2O_2 was added into nine injection wells at a rate of 86 L/d (60 ml/hr). It was postulated that the presence of dissolved iron in groundwater would assist in the formation of radicals for direct destruction of hydrocarbon compounds. Additionally, the peroxide-dosing was adjusted to also favour the oxidation of Fe and Mn Terminal Electron Acceptors (TEA) thereby making them available to address one of the rate limiting steps for biodegradation of the hydrocarbons. Over the course of 18 months, 8000L of 29% H_2O_2 was injected while the groundwater contaminant concentrations and groundwater chemistry (hardness, pH, dissolved oxygen and oxidation reduction potential) were monitored. Recent monitoring events also included screening of nutrients and TEA (total nitrogen, dissolved nitrate/nitrite, orthophosphate, sulphate, and speciated Fe/Mn). Temperature loggers were installed in the injection wells to monitor temperature increase due to H_2O_2 decomposition and hydrocarbon degradation.

Results/Lessons Learned. In this unique setting, the remediation approach was successful in reducing BTEX and PAH constituents below high-risk levels within 18 months. The data suggested that under the prevailing site conditions and lack of an activator, H_2O_2 participated in oxidation / reduction reactions indirectly replenishing TEA rather than producing free radicals. Availability of oxygen and other TEA supported the microbial breakdown of short chain and mono- and polycyclic aromatic hydrocarbons. The presentation will focus on the chemical processes of bioremediation in groundwater using time trends of contaminant and nutrient concentrations, as well as measurements of TEA. Additionally, it was identified that the use of H_2O_2 to biologically stimulate reduction in contaminants had a significantly reduced environmental footprint compared to conventional remedial approaches.

Estimate and Evaluation of Biodegradation Rates in Biosparging, Air Sparging and Oxygen Sparging

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Background/Objectives. A bioventing system was implemented at a natural gas processing site. During the system start-up and optimization, a respiration test was conducted to determine the oxygen utilization rate (OUR) in the vadose zone, which was then used to estimate the hydrocarbon biodegradation rate to determine the total hydrocarbon mass removal rate of the system. This concept was applied to the saturated zone of sites with biosparging, air sparging, and oxygen sparging. A saturated zone respiration test was conducted to determine the dissolved oxygen utilization rate (DOUR) which was used to estimate the hydrocarbon biodegradation rate in the saturated zone. The DOUR and biodegradation rates were used to evaluate the system performance of biosparging, air sparging, and oxygen sparging.

Approach/Activities. For saturated zone respiration test, air or oxygen was sparged into the saturated zone for approximately 48 hours, or until dissolved oxygen (DO) concentrations stabilized. The sparging system was then shut off and DO was measured from nearby groundwater monitoring wells at approximately two, four, six, 24 and 48 hours, or until DO readings stabilized. Based the monitored data, soil parameters, and operation data, the DOUR and biodegradation rate were estimated in the saturated zone. The respiration test was conducted at three natural gas processing sites with biosparging, air sparging, and oxygen sparging systems, respectively, all impacted with TPH and BTEX in the soil and groundwater. At the biosparging site, the biodegradation rate was used to evaluate contaminant removal through biodegradation and volatilization mechanisms and optimize system operation. At the air sparging site, the biodegradation rate was used to evaluate the effectiveness of transitioning from air sparging/SVE to biosparging/bioventing for cost saving and sustainable operation. At the oxygen sparging site, the biodegradation rate was used to compare the performance of oxygen sparging with regular air sparging.

Results/Lessons Learned. Respiration tests can be conducted in the saturated zone to estimate DOUR and biodegradation rates of biosparging, air sparging, and oxygen sparging systems. For the biosparging site, 83% of the TPH removed during biosparging was attributed to biodegradation, and the remaining 17% was attributed to volatilization. However, seventy-five percent of TPH volatilization occurred within the first three months of biosparging when this mechanism was dominant over biodegradation. Since volatilization only initially dominates contaminant removal, systems can be optimized by reducing sparging flow rates after the first three months of operation, thus reducing energy consumption and stimulating biodegradation. For the air sparging site, the air sparging/SVE system was converted to a biosparging/bioventing system after four months of operation because biodegradation became the dominant mechanism. For oxygen sparging site, the DOUR was determined to be higher with oxygen than with regular air. This is likely to be because the bacteria population is oxygen limited and providing a sparge rich in oxygen created a larger population for biodegradation.

Major Natural and Technological factors Affecting Efficiency of Bioremediation of Jet-Fuel in Sedimentary Bedrock

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Background/Objectives. The remediation of large-scale petroleum impacts to soil and groundwater at the former Soviet Army air base at Hradcany was the most significant remedial action undertaken by the Czech Ministry of Environment to mitigate Soviet-era environmental damage in the former Czechoslovakia. The Hradcany facility served as an army air base from the World War II era until 1992. The presence of extensive soil and groundwater contamination by petroleum hydrocarbons (TPH, mainly jet fuel alkanes of C8-C15 range, and BTEX) limited the future use and redevelopment of the site and endangered groundwater resources.
In 1997, petroleum contamination was found to be present in soil and groundwater across an area of 28.2 hectares. The average TPH concentration was 11,000 mg/kg at the site and light non-aqueous phase liquid (LNAPL) was present in 50 percent of the area ranging in thickness from 1 cm to 80 cm. The total estimated quantity of TPH released to the environment was about 7,000 tons. The contamination migrated in the sandy-gravel fluvial sediments of Ploucnice River and in the underlying marine Cretaceous sandstones.

Approach/Activities. The clean-up goals set for the site were risk-based. The remediation effort featured a complex approach including both physical and biological methods. The remediation approach was primarily biostimulation of aerobic metabolic oxidation of petroleum hydrocarbons by indigenous bacterial strains. The focus of the technology was to aerate the contaminated media. Initially, recoverable LNAPL was removed by vacuum extraction to the maximum extent possible, coupled with stimulation of biodegradation and VOC extraction in the unsaturated zone by venting. Later, the remedial activities were enhanced by air sparging (AS, injection of ambient air under groundwater table) and addition of nutrients (N, P, K) in order to fully support bacterial activity in the most contaminated layer in the zone of groundwater table fluctuation.

Results/Lessons Learned. Clean-up operations were conducted at the site from 1997-2008. Initially, the estimated TPH soil mass was approximately 7.150 metric tons. Remedial activities removed, based on the balance of the technology operation, approximately 4,046 metric tons of TPH (-+15%) from the Hradcany site, 93% by biodegradation, 4% by oil phase extraction (aka slurping), 2% by venting and 1% by pump-and-treat. The LNAPL extent decreased from 13.8 ha in 1997 to 0.01 ha by the end 2007 based on observations from 1,893 monitoring points. The site closure monitoring (2009-2011) verified reaching of the risk-based clean-up goals. During the remedial phase, a great deal of data was collected providing evidence of extensive biodegradation activity over a large area of the site. Regular measurement of groundwater temperature allowed the evaluation of its influence on observed bioactivity and to facilitate better, more effective operation of aeration system. Also operation of the AS technology, which was a major innovation in the remediation technology at the time of project commencement, was challenging. Addressing these challenges brought about a wide range of findings, including the critical dependency between aeration input and the extent of biodegradation activity. As the plume impacted a variety of sedimentary bedrock – Quaternary sediments, Cretaceous weathered sandstones and hardened sandstones with layered structure, the influence of geological structures on operation of the technologies was faced. Influence of geological structures onto reachable remedial results was observed and evaluated.

LNAPL Removal by Bioventing

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Background/Objectives. An institution in Rhode Island was the site of a leaking underground storage tank (LUST) containing No. 2 fuel oil. Following the removal of the UST and fuel-impacted soil, a groundwater extraction system operated for ten years, removing a total of 4,700 gallons of light non-aqueous phase liquid (LNAPL) petroleum, in addition to the estimated 2,000 gallons removed in the excavated soil. After ten years, although LNAPL persisted across much of the plume length, the groundwater extraction system was removing less than 20 gallons per month. Bioventing was proposed as an efficient, low-cost remedial alternative to remove measurable (in observation wells) LNAPL fuel oil to the extent feasible. The process employed relies on seasonal water table changes to redistribute the residual fuel oil in and above the capillary zone, thus exposing the petroleum hydrocarbons to the aerated zone promoting its biodegradation. The monitoring that was performed demonstrated that bioventing, with some limited vacuum enhanced recovery, was able to remove LNAPL more cost-effectively while still limiting both dissolved phase petroleum and LNAPL migration.

Approach/Activities. In fall of 2010, we installed a bioventing system across the limits of the LNAPL plume (covers approximately 1 acre) and an enhanced vacuum recovery system at release and down gradient locations. The bioventing system, which incorporates multiple wells, extracts soil vapor continuously to maintain soil vapor oxygen levels close to atmospheric levels. Extracted soil vapor oxygen and carbon dioxide levels are used to estimate fuel oil consumption and equivalent gallons of LNAPL removal. Removal rates and soil vapor concentrations are compared to seasonal changes in groundwater elevations. Removal rates are within expected ranges (literature values). Monitoring of downgradient concentrations of dissolved petroleum hydrocarbons has been performed throughout both phases of remediation. Background oxygen consumption and carbon dioxide generation conditions are evaluated. Cost data was gathered on the operation of the pump and treat system for comparison to the bioventing system costs.

Results/Lessons Learned. We estimate that the bioventing system, which has operated nearly continuously over a four year period, continues to remove fuel oil at an annual rate of approximately 2,400 gallons per year (2014); ten times the removal rate of the pump and treat system. This on-going significant rate of biodegradation, in spite of significant mass removal, is attributed to the continued presence of measurable LNAPL and seasonal redistribution of LNAPL within the capillary zone due to fluctuations in the groundwater table. The associated rise and fall in total concentrations of volatile organics in the extracted soil vapor with seasonal changes in groundwater levels mirrors this behavior. LNAPL thickness, though variable over the course of both pump and treat operation and bioventing, has shown a declining trend consistent with the gradual reduction in the LNAPL mass. The rate of fuel oil removal by the bioventing system (as measured by oxygen consumption and carbon dioxide production) is highest during periods of low groundwater elevations. The majority (>97%) of this removal has been achieved via aerobic biodegradation, with less than 3% of removal attributed to the active product recovery system. Costs have been reduced by more than 70%. The rate of removal has remained high, though we have exceeded the original estimate of residual mass. We suspect this is due to the release of much more fuel oil than originally estimated. Indeed, after obtaining fuel oil delivery records between 1995 and 2013, the original estimate of a 12,000 gallon release was increased to over 28,000 gallons.

Measurement of CO_2 Flux for Quantification of Natural Source Zone Depletion and Evaluation of Air Sparging Influence on Source Zone Depletion

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Background/Objectives. The presence of light non-aqueous phase liquids (LNAPL) in soil and groundwater has frequently increased regulatory attention and requirements for remedial action. In-situ biodegradation of LNAPL through natural source zone depletion (NSZD) is known to contribute to significant reductions in petroleum hydrocarbon mass and can present a viable pathway for site closure. The rate of hydrocarbon mass reduction via NSZD can be estimated by vadose zone soil gas monitoring and measurement of dissolved biodegradation parameters (ITRC 2009) as well as the application of surficial CO2-efflux measurements using CO2 flux chambers (Shiota et al., 2011). However, evaluation of how in-situ remediation technologies such as air sparging can affect NSZD rates is not well understood. In the present study, CO2-efflux measurement is applied for the quantification of NSZD and evaluation of the influence of air sparging on in situ biodegradation.

Approach/Activities. Multiple techniques were used to evaluate and quantify NSZD at two petroleum hydrocarbon release sites in the western United States. The rate contaminant biodegradation was estimated by measurement of CO2 gas generation associated with contaminant degradation at petroleum hydrocarbon contaminated sites using CO2-efflux methodology (Shiota et al., 2011; Shiota and Mayer 2012). Measurements of CO2-efflux were made to assess the influence of both long-term and short-term air sparging on the rate of NSZD.

Results/Lessons Leaned. This case study demonstrates the application of CO2-efflux measurement for quantification of NSZD and evaluation of enhanced in situ biodegradation through air sparging at two petroleum hydrocarbon contaminated sites, but also provides valuable insights into how multiple lines of evidence can be used demonstrate NSZD. It also provides insights into the applicability and limitations of air sparging for enhanced in situ biodegradation.

Dynamic Chemical Responses to Active Treatment

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Background/Objectives. A technical evaluation of dynamic chemical responses to active environmental treatment beneath a former chemical manufacturing facility located in Victoria, Australia. Groundwater at the Huntsman Chemical Company Australia (HCCA) site in Melbourne, Australia, is 8–9 m below ground level in fractured rock. A groundwater contamination plume extends some 350 m off-site. The main contaminant of concern in the plume is benzene. Within the plume area, shallow aquifer light non-aqueous phase liquid (LNAPL) and vadose zone impacts were identified in the middle of the Site. The LNAPL covers an area of approximately 50 x 50 m; varying in apparent thickness from 5–63 cm. Dominant contaminants of concern in the LNAPL were isopropyl benzene, alpha methyl styrene, cyclohexane and benzene. Isopropyl benzene and alpha methyl styrene alone made up over 60% of total mass in the LNAPL. Benzene, the dominant contaminant of concern in the groundwater plume, represented only 5% of the total mass in the LNAPL. A range of other VOCs were also present in the LNAPL.

Benzene represented a significant proportion of the mass in the groundwater under the LNAPL along with MIBK, phenol and chlorinated phenols. Together these accounted for over 95% of the dissolved mass in groundwater. The difference in composition between the LNAPL and groundwater reflects the varying solubilities of the contaminants, and indicates the LNAPL is no longer a major contributor to groundwater impact. A similar difference in chemical composition was evident in the vadose zone which was characterised by cyclohexane and benzene.

Approach/Activities. HCCA commenced active treatment using limited air sparge (AS) and soil vapour extraction (SVE) wells screened across the water table to recover contaminants from the sub-surface. The treatment system recovered over 7,500 L of chemicals over a 12-month period until asymptote and diminishing returns were evident. It successfully treated the LNAPL, and VOCs in the vadose zone, in the treatment area. The main recovered (condensed) VOCs were isopropyl benzene, benzene, alpha methyl styrene, ethyl benzene and cyclohexane.

Results/Lessons Learned. The treatment system recovered over 7,500 L of chemicals over a 12-month period until asymptote and diminishing returns were evident. However the composition of recovered compounds after the first month did not match the ratio of compounds in either the LNAPL or the underlying groundwater.

In the first month of operation significant quantities of “light end” compounds (e.g. cyclohexane) were recovered, after which the proportion of heavier compounds increased steadily. Even here, however, benzene concentrations were much lower than expected from groundwater data, and concentrations of alpha methyl styrene and isopropyl benzene were both much higher. It was considered that this could only be explained by volatilisation of a distributed secondary source in the vadose zone. The ratio of these compounds continued through to project completion suggesting ongoing depletion vadose zone impacts.

The results presented here for active treatment at the HCCA site highlight the need to consider changes in chemical mix over time in achieving a complete treatment solution.

Passive Gas Delivery and Ozone Injections to Treat TPH and LNAPL Adjacent to a Tidally-Influenced Estuary

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Background/Objectives. Historical releases of petroleum compounds occurred at three locations adjacent to a tidally-influenced estuary at a 100+ acre federal facility located in Connecticut. Releases of petroleum products to the environment may have occurred due to leaks in underground storage tanks (USTs) and fuel distribution lines, vehicle and locomotive maintenance operations, associated waste disposal practices, and marine fueling activities. The three locations are all within 100 feet of the tidally-influenced estuary and concentrations of total petroleum hydrocarbons (TPH) in groundwater exceed Connecticut Department of Energy and Environmental Protection (CTDEEP) Remediation Standard Regulations (RSRs). At one location, the data suggest groundwater concentrations consistent with the presence of light non-aqueous phase liquid (LNAPL). Several remedial challenges exist in these areas due to the configuration of an adjacent pier structure, location of nearby building structures, and the presence of multiple critical utilities. Excavation of the highly impacted TPH soils as a means to treat groundwater or aggressive *in situ* chemical oxidation is therefore not an option. The proposed remedial solutions for these areas include passive gas delivery, ozone injections, and monitored natural attenuation (MNA) with land use controls (LUCs) as a means to reach groundwater RSRs and minimize the remedial footprint and disturbance to above-ground operations.

Approach/Activities. At two of the three locations, passive gas delivery utilizing iSOC™ units is the proposed remedial option; at the final location, *in situ* ozone injection is currently proposed. At all three locations, MNA and LUCs will be implemented post active treatment until RSRs are reached. During late 2014/early 2015, additional groundwater monitoring wells will be installed to more clearly define the horizontal and vertical extent of TPH exceedances in groundwater and to more clearly define LNAPL limits. Concurrently, soil and groundwater will be collected from the area slated for ozone treatment for bench-scale treatability testing. The treatability testing will be performed in early 2015 to (i) yield design parameters; (ii) to assess the potential for secondary impacts (mobilization of metals) due to oxidation; and (iii) evaluate the potential for MNA. It is anticipated that the additional delineation and bench-scale testing data will be incorporated into the final remedial design to be completed in mid-2015.

Results/Lessons Learned. This poster/presentation will focus on the evaluation, design, and implementation of the above described remedial actions to treat TPH in a challenging subsurface environment adjacent to a tidally-influenced estuary. The supplemental delineation data and bench-scale treatability study results will be presented and the poster/presentation will discuss how the resulting data affects iSOC™ and ozone injection layout and delivery methodologies.

Application of Physical Removal and Aerobic Bioremediation of Petroleum Hydrocarbons Using Innovative Well Designs

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Jay Grosskleg and Trevor Carlson (Federated Co-operatives Ltd., Saskatoon, Canada)

Background/Objectives. In-situ remediation was selected to manage Petroleum Hydrocarbon Contamination (PHC) that was present beneath a residential apartment building. Our research and remediation work was initiated to eliminate vapour inhalation risks associated with PHC impacts present beneath the building and to reduce the mass of contaminant present. The in-situ remediation approach combined physical PHC removal (multiphase extraction (MPE)) and air sparging to facilitate aerobic bioremediation. A combination of vertical and horizontal wells were installed as components of the remediation system, with horizontal wells being the primary component of the design. Limited access beneath the building and surrounding properties (i.e., roadways) required the installation of single entry horizontally drilled soil vapour extraction (SVE), air sparging and MPE dewatering line concepts as major components of this remediation system. Vertical recovery wells (RWs) and bioventing (BV) wells were also installed in PHC impacted source zones to enhance remedial efforts and reduce the remediation timelines. The objective was to remediate PHC mass from beneath the apartment building property, while providing vapour intrusion protection to the occupants of the apartment building.

This research was conducted as part of Federated Co-operatives Limited's commitment to the Sustainable In-Situ Remediation Co-operative Alliance (SIRCA).

Approach/Activities. Multiple SVE and air sparge wells were installed beneath the building property using a directional drill rig in October 2013. The lines were comprised of perforated steel for air sparge, PVC for SVE and MPE dewatering lines of varying designs and materials. The air sparge lines were installed within the PHC impacted soil beneath the apartment building property. Air was pumped into the air sparge lines to create an aerobic environment conducive to PHC biodegradation. The SVE lines were installed above the air sparge lines to provide soil vapour transport control and reduce the potential for volatized PHCs from entering the apartment building. Dewatering lines were installed between the air sparge and SVE lines.

Transducers were used to evaluate the hydraulic and pneumatic radius of influence of the air sparge, SVE and dewatering lines, and in 2014, advanced drilling and soil geochemical analysis were used to evaluate the remediation of soil PHC impacts following initial operations on the horizontal wells. Drilling identified additional impacts in the front of the apartment building, in an area where the horizontal wells were not designed to target. Alternating vertical SVE and BV were installed in areas identified with recalcitrant PHC impacts. The SVE and BV wells consisted of PVC well screen connected to dedicated recovery and injection lines. Air was applied through the BV wells to facilitate aerobic biodegradation of soil PHC impacts and the SVE wells were used to physically remove PHC soil vapour.

Results/Lessons Learned. The MPE system has operated for approximately 7,600 hrs, recovered over 1.5 M L of impacted groundwater and remediated approximately 12,200 Kg of PHC mass from beneath the apartment building property. The remediation activities are ongoing and are being completed in a staged approach. Future activities planned may include further soil geochemical analysis, surfactant and nutrient injections and carbon isotope analysis of the recovered soil vapour to evaluate PHC mass removal.

Multi-Faceted Approach to the Remediation of a Petroleum Hydrocarbon Plume at an Active Retail Service Station

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Background/Objectives. In 2012, the detection of benzene in the potable water supply for a kiosk at a retail service station led to a subsoil and groundwater investigation, which identified the presence of a hydrocarbon plume beneath the kiosk and fuel service infrastructure and surrounding area. Twenty-eight boreholes/monitoring wells were completed to delineate the extent of impacts both on and off-site. Several petroleum hydrocarbon parameters within the fine grained, clay soil were reported to exceed the regulatory guidelines at an average depth of 2.25 metres below grade (mbg), which was at the approximate groundwater interface. Groundwater modelling indicated that groundwater was flowing from east to west across the site, with an average hydraulic gradient of 0.02 m/m. A multi-faceted remedial approach was required that would provide timely in-situ remediation, while allowing the retail service station to remain operational. Our objective for this site was to install infrastructure that would allow for several in-situ methods to be utilized independently or simultaneously towards the overall remediation of the site, while allowing for the retail service station to remain 100% operational. The remediation system was designed to allow for several options including mechanical extraction of hydrocarbons through groundwater recovery and treatment, air sparging, nutrient amendment to promote in-situ bioremediation and oxidant amendment to promote chemical decomposition.

Approach. Prior to installation of the remediation infrastructure, the potable water line servicing the kiosk was replaced and an in-line carbon filtration system was installed. Two 0.4 m wide by 30 m long trenches were excavated to a depth of 0.4 mbg, downgraident and perpendicular to groundwater flow direction. Within these trenches, 18 boreholes were completed using a hydro-excavator, with 14 extraction wells and 4 injection wells installed to a depth of 3.4 mbg. Each well was constructed with 50.8-mm, 0.010-mm slotted PVC screen and Tiger-Flex hose, which was placed in the trench and connected to either a dual phase vacuum extraction (DPVE) system or an air sparge (AS) system. The DPVE system consisted of a 59 HP vacuum which worked to enhance the natural groundwater gradient by pulling groundwater across the site to the west, and mechanically removing the contaminated groundwater for on-site treatment and discharge to the local sewer system. The AS system consisted of a 26.7 HP blower, which introduced oxygen into the groundwater to promote aerobic degradation of the petroleum hydrocarbons. The AS system was also designed to allow for nutrient and oxidant amendment to be delivered to the sub-surface. The amendments would be injected directly through the injection wells and then pulled across the site, beneath the retail service station by the DPVE system.

Results. The installation of the remedial system infrastructure was completed by the end of October 2014. The effectiveness of the remediation system installation will be evaluated over the next several months through regular site monitoring, including the collection of groundwater samples to document trends in groundwater petroleum hydrocarbon concentrations and other key indicator parameters including dissolved oxygen, oxygen reduction potential, headspace carbon dioxide, oxygen and organic vapour concentrations. We anticipate several monitoring events worth of data will be available at the time of the presentation.

Risk Evaluation and Mitigation of Corrosion on Underground Utilities for Ozone Sparging

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Background/Objectives. When in-situ chemical oxidation (ISCO) ozone sparging is applied to a petroleum hydrocarbon-impacted site, a soil vapor extraction (SVE) system is usually installed to mitigate the potential risk of ozone off-gassing due to health and safety concerns to site personnel and/or corrosion concerns to active underground utilities such as pipelines. An evaluation of off-gassing ozone was conducted to: 1) estimate off-gassing ozone concentrations in the vadose zone; 2) evaluate off-gassing ozone impacts to underground utility corrosion; and 3) recommend a lower cost more green/sustainable solution than current ISCO ozone design and practices.

Approach/Activities. A bench-scale ozone soil column test was conducted to estimate the potential ozone off-gas concentrations in the vadose-zone soil. The column test results were verified with a field test to evaluate the impacts of ozone off-gassing to underground utilities. Two soil columns were packed with soil from a petroleum hydrocarbon-impacted site. One column was injected from the bottom with humidified nitrogen as a control, and the other with humidified ozone (3.8% by weight) for seven days. Ozone concentrations of the influent and effluent of the column were measured to understand the ozone consumption rate in the soil column and thereby estimate ozone reduction within the vadose zone. Accordingly, the expected ozone concentration was calculated at the underground utilities.

The field corrosion test was conducted by installing eight steel coupons in four different wells – two ozone sparge wells (sparged at 3.8% ozone by weight), one oxygen sparge well (sparged at 53-63% oxygen by weight), and one groundwater monitoring well (exposed to soil vapor). Each well was outfitted with one steel sample with protective coating and another without protective coating. The oxygen and ozone sparge wells were injected sequentially for 60 minutes per cycle for 72 cycles over 25 days. The coupons were exposed in this way for approximately one month, then removed and transported to a laboratory to measure the mass change as an estimate of the corrosion rate.

Results/Lessons Learned. The ozone consumption rate in the bench-scale soil column test was measured to be approximately 70% ozone reduction through 1 foot of vadose-zone soil. If ozone is sparged at a 3.8% by weight concentration from 30 to 32 feet bgs under such ozone consumption rate, the expected ozone concentration at an underground pipe at a depth of 8 feet bgs is 0.01 parts per billion, three orders of magnitude less than the surface ozone background concentration. The field corrosion test indicated that uncoated steel coupons placed in the groundwater monitoring well without any sparge had the highest corrosion rate of 0.783 mils per year, followed by coupons with ozone and oxygen exposure which had a corrosion rate of 0.191 and 0.028 mils per year, respectively. One theory is that moisture is the main contributor to corrosion, and ozone and oxygen sparging help dry the soil vapor and slow corrosion.

Ozone off-gassing from ozone sparging exhibited no concerns to health and safety and underground utility corrosion. Thus an SVE system for the purpose of collecting residual ozone is not necessary. The elimination of an SVE system would substantially reduce capital and O&M costs and decrease the carbon footprint as a more green/sustainable remediation.

Remediation and Restoration of the Lac-Mégantic, Québec Crude Oil Train Disaster

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On July 6, 2013 an unattended train derailed in the centre of the Town of Lac-Mégantic, Québec, approximately 3 hours east of Montréal. The train's cargo, Bakken North Dakota formation crude oil contained in 74 rail cars, spilled and resulted in multiple explosions with the fire destroying a portion of the downtown killing 47 residents and creating a major environmental disaster. The spill and resultant explosions and fire destroyed over 30 buildings and municipal infrastructure, impacted soils and groundwater in the immediate spill area as well as surface water and sediments in Mégantic Lake and Chaudière River. Following five months of emergency response activities the site has been stabilized, major urban restoration planning has been completed and a soil, sediment, and groundwater remedy is being implemented. AECOM was contracted by the Town of Lac-Mégantic and the Québec Ministry of Sustainable Development, Environment and Climate Change to design and oversee construction of all remediation and restoration activities. AECOM's objectives were to: develop and administer a site-wide Health and Safety Plan, Remediation Plan, impacted building Assessment and Rehabilitation Plan, and oversee and report on all spill site restoration and ancillary commercial renovation activities.

Site remediation consisted of utilizing existing emergency response soil, groundwater and sediment data to develop a remedial strategy, integrate the strategy into infrastructure and building restoration and demolition activities as well as numerous off-site activities all related to the revitalization of Lac-Mégantic. Impacted soil volumes requiring removal and treatment are anticipated to be 400,000 tonnes and all treated soils are required to meet Québec Level A soil standards. Soils from impacted areas within the "zone incendiée" (area destroyed by fire), around remaining building foundations, storm sewer replacement and miscellaneous other related construction activities will be removed and transported off-site to a treatment area. Several treatment technologies were evaluated including ex-situ biological treatment, soil washing and thermal treatment. Enhanced biological treatment and select off-site thermal treatment were selected. Remediated materials will be reused where appropriate in the site-wide restoration. In addition, a groundwater cut-off trench and strategically located recovery wells situated throughout the site collect and transfer impacted groundwater to a stationary carbon-based treatment system. Additionally, Chaudière River and some Mégantic Lake sediments impacted by the spill will be further delineated and removed.

The schedule for the remediation is aggressive with some building demolition, infrastructure replacement, soil and groundwater remediation and restoration extending into 2015. As a result, a strategically staged and sequenced plan has been developed with construction beginning in May 2014. The various components of the plan will ensure clean-up of the downtown area to performance objectives, re-design and installation of required municipal infrastructure, successful treatment of removed soil, groundwater recovery, treatment and monitoring, and flexibility to enable future site development in concert with on-going discussions and consultations with the residents of Lac-Mégantic.

This presentation will provide an update on restorative construction activities, overview of the application of innovative and sustainable remedial technologies and approaches, and provide the basis for the vision of the future of Lac-Mégantic.

Back to Contents

State of the Practice: Remediation of Crude Oil Impacted Soils

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Remediation of soils impacted with crude oil is a challenge for oil companies at industrial sites worldwide. Clean-up goals can range from > 3% to < 0.1% Total Petroleum Hydrocarbons (TPH) based on local regulatory climate and final use of the remediated soil. Many technologies for *in-situ* and *ex-situ* soil remediation are available, primarily based on physical removal, biological degradation, reuse, chemical oxidation, physical separation, and thermal destruction. The choice of technology can depend on various factors, including desired cleanup goal, soil type, composition of petroleum compounds, availability of resources, and costs. The most commonly used technologies are physical removal and biotreatment. This presentation will cover the development of various cleanup goals, barriers to implementation of existing technologies, and development of novel technologies.

Use of Ligninolytic Enzymes in Encapsulated Formulation for Degradation of Heavily Weathered Crude Oil Contaminated Soils

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Background/Objectives. Hydrocarbon contamination resulting from drilling and extraction of oil has become a major environmental problem due to the extensive soil contamination and other environmental damage. Microbially-mediated breakdown of heavy weathered total petroleum hydrocarbons (TPH) typically is limited to aromatic compounds up to 4-rings and saturated compounds up to 25 carbons. Our research focuses on the ability of ligninolytic enzymes to degrade larger molecular compounds through the use of radical reactions, with the potential to enhance crude oil degradation.

Approach/Activities. Here, we propose a novel approach of combining the activities of encapsulated fungal oxidoreductases (manganese peroxidase, lignin peroxidase and laccase) with naturally occurring microbial populations to enhance degradation potential.

Results/Lessons Learned. The primary data indicate that addition of encapsulated fungal oxidoreductases may break down heavy TPHs (>C38), resulting in 45% enrichment of the medium size (C12-C35) hydrocarbon pool. Degradation of the C12-C28 and C28-C35 fractions during a 14 day incubation resulted in 12 and 15% decreases, respectively, in comparison to control (untreated) soil. Future analyses will help understanding chemical basis of the TPH degradation with the formulation and efficiency of encapsulated enzyme.

Methanogenic Degradation of Branched Hydrocarbons (*iso*-alkanes) in Oil Sands Tailings

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Background/Objectives. In northern Alberta, Canada, shallow oil sands ores are surface mined and the bitumen is extracted using modified Clark hot water extraction processes. The process produces huge volumes of tailings which are deposited into tailings ponds that currently hold >920 million m^3 of fine tailings with a total surface area of ~186 km^2. The established tailings ponds emit greenhouse gases (methane; CH_4 and carbon dioxide; CO_2) that are generated during the process known as methanogenesis. The unrecovered hydrocarbons in oil sands tailings sustain methanogenesis in tailings ponds. Our previous studies revealed that only *n*-alkanes (straight-chain hydrocarbons) and BTEX compounds (benzene, toluene, ethylbenzene and xylenes; monoaromatics) in tailings were methanogenically biodegraded by indigenous microorganisms during a year-long incubations. The current long-term studies were conducted to investigate biodegradation of recalcitrant hydrocarbons such as *iso*- and *cyclo*-alkanes in oil sands tailings under methanogenic conditions.

Approach/Activities. Laboratory experiments were conducted using mature fine tailings (MFT) collected from two tailings ponds operated by two different companies in 160-mL microcosms (serum bottles) under anaerobic headspace (30% O_2-free CO_2, balance N_2). MFT-S was amended with a mixture of 5 major *iso*-alkanes (3-methylhexane [3-MC_6]; 3-ethylhexane [3-EC_6]; 2-methylheptane [2-MC_7]; 4-methylheptane [4-MC_7]; 2-methyloctane [2-MC_8]) and 3 major *cyclo*-alkanes (ethylcyclopentane [$EcyC_5$]; methylcyclohexane [$McyC_6$]; ethylcyclohexane [$EcyC_6$]) whereas MFT-A received a mixture of 3 *iso*-alkanes (2-methylbutane [2-MC_4]; 2-methylpentane [2-MC_5]; 3-methylpetane [3-MC_5]). These respective *iso*-alkanes are abundant in the respective tailings ponds. In a parallel experiment, MFT-S was also inoculated with hydrocarbon-degrading enrichment cultures. Gas chromatographic analyses were performed to monitor hydrocarbon degradation and CH_4 production in the microcosms during incubation. MFT samples were retrieved from the microcosms periodically to perform pyrosequencing of 16S rRNA genes for microbial characterization.

Results/Lessons Learned. In MFT-S during ~1700 d incubation, complete degradation of 3-MC_6, 2-MC_7, 4-MC_7 and 2-MC_8 and partial of degradation 3-EC_6 and $EcyC_5$ were observed while $McyC_6$ and $EcyC_6$ remained undegraded. *Iso*-alkanes were biodegraded preferentially in the order: 3-MC_6 > 4-MC_7 > 2-MC_8 > 2-MC_7. In MFT-A incubated for ~2400 d, complete degradation of 2-MC_5 and partial degradation of 2-MC_4 and 3-MC_5 was observed. In both MFT-S and MFT-A, pyrosequencing of 16S rRNA genes revealed overwhelming dominance of *Peptococcaea* (*Desulfotomaculum*) and in some cases *Smithella* working in syntrophic relationship with both acetoclastic (*Methanosaeta*) and hydrogenotrophic (*Methanoregula* and *Methanoculleus*) methogens to metabolize *iso*-and *cyclo*alkanes to CH_4. The results advance our knowledge about the nature of hydrocarbons degradable under methanogenic conditions and provide scientific information for the effective management of oil sands tailings.

In Situ Extracellular Electron Transfer in Tar Oil Contaminated Aquifers: Elucidating the Role of Mn(IV) as Terminal Sink for Electrons From Anaerobic PAH Oxidation

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Background/Objectives. Tar oil is a complex mixture of groundwater pollutants that is frequently encountered at industrial sites, including municipal gas plants and wood impregnation facilities. Several hundred tar oil-derived organic compounds may be present at these sites, including hetero- and homocyclic polyaromatic hydrocarbons (PAH) that may additionally carry alkyl chains. Biodegradation of hydrophobic aromatic tar oil pollutants is known to occur under aerobic and a variety of anaerobic terminal electron accepting (TEA) conditions. The application of extracellular electron shuttles (EES), i.e. small, reversibly oxidizable and reducible organic compounds, to increase the rates of extracellular electron transfer from PAH oxidation to solid-phase aquifer TEA , including Fe(III) and Mn(IV) minerals, is explored in the present study.

Approach/Activities. In the present study, the effect of a variety of EES on the anaerobic degradation of PAH is explored under laboratory-scale conditions using historically contaminated soils and aquifer material. EES investigated include different quinone moieties, natural dyes (all 100 µM) and humic acids. PAH degradation was studied anaerobic bioreactors using the soils' naturally present TEA and artificially added sources of Fe(III), including uncoated nano-scale Fe_2O_3-particles and iron(III)citrate. In addition EES were used as reagents – to our knowledge, for the first time – in a small-scale field test at a tar-oil contaminated wood impregnation site.

Results/Lessons Learned. Biodegradation of several dozen PAH significantly increased with the addition of most EES in laboratory tests. A small amount of abiotic chemical PAH oxidation was detected in the killed controls. Among the tested quinone moieties, the magnitude of the stimulating effect was related to the number of sulfonate groups.
In the field test, the addition of small concentrations of quinones to PAH-contaminated groundwater was associated with an increase in concentrations of aqueous Mn species, while this was not observed for water-soluble Fe species. Changes in PAH profiles were monitored using GCxGC-TOF-MS. The results indicate that the addition of EES to anaerobic, historically PAH-contaminated aquifers can increase the availability of poorly soluble minerals with the abililty to accept electrons from PAH oxidation via a coupled microbial - extracellular electron transport route. The role of Mn-species in biogeochemical pollutant transformation processes needs to be elucidated in greater detail.

Pyrolytic Remediation of Soil Contaminated with Heavy Hydrocarbons

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Background/Objectives. Biochar, a charcoal formed from the pyrolysis of biomass, has attracted significant research interest due to the appeal of reaping agricultural and climate benefits from biomass waste. Key areas of interest include the effects of biochar amendments on soil fertility and plant growth, as well as the potential for long-term carbon sequestration in soils. Our research expands the application of pyrolysis in inert atmospheres to remediate soil contaminated with heavy-hydrocarbons (HHC) and add agricultural value to it by creating a char similar to biochar, albeit with a non-biomass feedstock. In addition to total petroleum hydrocarbon (TPH) reduction, the benefits of the new process may include (like traditional biochar) improved soil fertility, plant growth, and carbon sequestration. We report here results from the pyrolysis of several HHC-contaminated soils from various locations with TPH concentrations ranging from 5,000 -150,000 mg/kg, to examine the broad efficacy of this treatment method in varying climates and onsite cleanup conditions.

Approach/Activities. We designed a 400-mL fixed bed reactor (FBR) to conduct pyrolysis experiments on HHC soils under flowing nitrogen. The soils are heated to pyrolysis temperatures (i.e. 300°C-600°C) by a tube furnace and the resulting char is analyzed for residual TPH using analytical GC-FID methods. Soil fertility studies are conducted in a greenhouse using Simpson black-seeded lettuce planted in uncontaminated soils with a range of treated-soil amendments. Variations in plant germination, size, and robustness will be examined to shed light on the potential value of this remediation technique to treat heavy hydrocarbons in soil and provide agricultural benefits.

Results/Lessons Learned. Our pyrolysis experiments have shown consistent reductions of TPH in contaminated soils to below detection limits (< 4 mg TPH/kg soil), and thus the prospects are good that regulatory cleanup standards can be met. Moreover, we have produced hydrocarbon-rich off-gas and condensates as by-products of the pyrolysis process that have the potential for reuse as combustion fuel, leading to higher process efficiencies and smaller environmental and economic footprints for this technology. We are currently optimizing operating parameters such as pyrolysis temperature and time to gain a better understanding of the most efficient operating conditions for desired TPH levels. Soil fertility experiments are also currently underway. We postulate that, unlike soil incineration and thermal desorption approaches that destroy soil fertility, the biochar-like residue generated by pyrolysis will enhance fertility relative to both the original HHC soil and untreated uncontaminated background soil.

Enhancement of Bioremediation of Soils Contaminated with Organic Hydrocarbons Using an Electron Beam

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Background/Objectives. Electron beam irradiation is being investigated as a method to reduce hydrocarbon content and enhance the bioavailability of soils contaminated with heavy crude oil.

Approach/Activities. During treatment, a 50g-100g soil sample in a sealed batch reactor is exposed to a 10 MeV electron beam at a dose rate of 8 kGy/s. The reactor is aluminum to allow for beam penetration while still capturing all gases, liquids, and solids. The volume of the reactor is such that pressure remains near ambient during experiments. Various temperature control schemes were tested. The efficacy of contamination removal was screened for treatment dosages up to 2000 kGy using ultraviolet visible absorbance spectroscopy. Hydrocarbon distributions were analyzed by MS-MALDI, and TPH and carbon distributions were also determined through commercial analysis. Manufactured spiked soils and weathered field impacted soils were tested with TPH ranging from ~1% to 10% (w/w). The manufactured samples were mixture of a field attained clay soil with 10% of 18 API crude oil.

Results/Lessons Learned. The field attained weathered samples were heavier hydrocarbons. Hydrocarbon reduction and changes in carbon distributions were evident and dependent on dose and water content. For example, the hydrocarbon content of a dry soil (<1% water) was reduced from 9% to <2% with a 960 kGy dose, while a wet soil (~20% water) experienced significantly less reduction for the same dose. A noticeable fraction of the oil separates from the soil as liquid. The oil remaining in the soil undergoes chemical changes due to the electron beam energy. One portion is polymerized, immobilizing it in the soil, and another portion is cracked, reducing its viscosity and molecular size and making it more bioavailable.

Back to Contents

Thermal Treatment for Solubilization and Biodegradation of Weathered Heavy Hydrocarbon Contaminated Soils

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Background/Objective. Long-term weathering of spilled crude oil in the vadose zone of surface soils is known to result in the accumulation of heavy hydrocarbons (HHs) that are recalcitrant to biodegradation and present a significant remediation challenge. One potential approach to *in situ* remediation is the introduction of heat in conjunction with the addition of surfactants and/or HH-transforming microbial cultures. Soil heating at 20, 30, 45 and 60°C was hypothesized to be beneficial for remediation of HHs, since thermal energy may decrease adsorption of HHs, lower their viscosity, as well as increase their aqueous phase solubility and diffusivity. The addition of surfactant may further enhance HH bioavailability, with the amphiphiles serving as a primary substrate suitable for promoting (co-)metabolism of HHs.

Approach/Activities. Thermal treatment at 60°C was investigated to enhance both surfactant-assisted HH solubilization and biodegradation using microcosms of real-world contaminated soils (at 3% THP). A surfactant investigated for HH solubilization was Tween 80. In parallel, thermophilic microbial enrichment cultures, which may ultimately be used to bioaugment contaminated soil microcosms, were set up using a minimal media amended with crude oil depleted in light hydrocarbons, incubated in the presence and absence of the investigated surfactants.

Results/Lessons Learned. Current literature and preliminary lab results suggest that a combination of thermal treatment at 45°C combined with *in situ* surfactant solubilization using Tween 80 may be a promising and potentially cost-effective approach for remediating weathered heavy hydrocarbons in some *in situ* soils, as this technology appears initially to be soil dependent. Encouraging results obtained in the above laboratory experiments will be reported. Currently available data suggest a notable benefit of both thermal treatment and surfactant amendments when attempting to remediate HH-contaminated soils.

Thermally Enhanced Solubilization and Oxidation of Weathered Heavy Hydrocarbons in Soils

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Background/Objectives. Weathered long chain (C_{15}-C_{40}) heavy hydrocarbons (HHs) are generally complex and recalcitrant to biological and chemical degradation. In addition, their physiochemical characteristics, e.g., high viscosity and hydrophobicity, and low volatility pose a significant remediation challenge for the contaminated soils. Various treatment options are available for hydrocarbon remediation in soil; however, previous studies indicated that a single treatment option may not degrade the HHs in soil to the desired level. Thermal treatments have the potential to change the physical and chemical characteristics of HHs, such as reducing soil sorption coefficients, increasing aqueous phase solubilities and diffusivities, and increasing reaction rates. These changes may increase the HH degradation, promote bioavailability, and accelerate biological attenuation. While a combination of treatments may offer a greater degree of HH degradation, there has been no study with a sequence of thermally-enhanced processes. The objective of this study is to determine the effectiveness for HH degradation in soil of two thermally-enhanced treatment options, solubilization and oxidation. Each of these options could be a suitable pre-treatment for bioremediation by making HHs more bioavailable.

Approach/Activities. Laboratory-scale batch solubilization and oxidation experiments were conducted with HH contaminated soils. The solubilization experiments were performed on two soils using three solubilizing agents, Tween 80, beta-cyclodextrin, and rhamnolipids, at doses of 0.225, 2.25 and 22.5% $w_{surfactant}/w_{soil\ dw}$. Soil washing was performed with an excess amount of solution, and under static condition with the solution amount equal to 60% water holding capacity (WHC) of the soil. In different experiment batches, the test vials or flasks were incubated at 20, 30, 37, and 60°C for 3, 4, and 15 days. In oxidation experiments, three soils were treated with two oxidizing agents, thermally activated sodium persulfate and manganese dioxide catalyzed hydrogen peroxide, by varying the oxidant dose. Sodium persulfate solution was added to the test vials in excess of soil saturation and at 60% WHC of the soils to achieve the oxidant dose of 1, 5, and 11% $w_{oxidant}/w_{soil\ dw}$. In different batches, the test vials were incubated at 30, 60, and 80°C for 1, 2, 4, and 7 days. The solubilization and oxidation of HH were evaluated by tracking the chemical oxygen demand (COD) and the total petroleum hydrocarbon (TPH) content of the soils.

Results/Lessons Learned. The solubilization experiments under soil washing conditions showed a favorable performance of the surfactant Tween 80 that increased with dose. Higher temperature and longer incubation period also resulted in better solubilization compared to the control. Experiments conducted at 60% WHC did not show significant removal of HH from the soils, as indicated by soil COD, which could be due to insufficient surfactant dose. In this case, the biodegradable surfactant could aid in the subsequent HH bioremediation processes. The heat activated persulfate oxidation resulted in lower soil COD, which decreased with both increasing persulfate concentration and increased temperature. In this ongoing study, both surfactant-mediated solubilization and chemical oxidation of soils were identified as promising treatments whose efficiency showed strong dependence on the type of soil treated.

Efficacy of Pyrolyzed Biomass as a Sustainable Remediation Strategy for Heavy Hydrocarbon Contaminated Shallow Soils

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Background/Objectives. Low-tech, sustainable and eco-friendly methods for reducing measurable total petroleum hydrocarbons (TPH) in shallow soils contaminated with heavy hydrocarbons (HH) continue to present a challenge to the petroleum industry. Amending HH-contaminated soils with locally obtained pyrolyzed agricultural waste biomass (biochar) is proposed as a strategy for both stabilizing and increasing biodegradation of the components of HH contamination. Biochar is proposed as a potential strategy for soil remediation due to its high surface area, high porosity, aromaticity, high absorption capacity, and amenability to colonization by microorganisms.

Approach/Activities. The global hypothesis is that biochar will serve as sink for HH and stimulate biodegradation of lighter hydrocarbons in the bulk soil. Additionally, biochar will serve as a favorable surface for microbial colonization to enhance HH biodegradation. Three HH contaminated soil and biochar made from two feedstocks (walnut nutshells, pine wood) at similar pyrolysis temperature (900 °C) were characterized for physical and chemical properties. Batch incubations (25 °C) were used to investigate sorption of contaminants to biochar and evaluate extractability of total petroleum hydrocarbon (TPH) from biochar-amended soils. Soil (50 g) was amended with biochar at three application rates (2, 5 and 10% w/w). Mineral solution (for essential nutrients) and ethanol (for mobilization of TPH) were added to each treatment. The treatments were set-up in triplicate using a randomized block design and maintained at water holding capacity (WHC) of 65-75%. Appropriate incubations were conducted for 60 days after which soils were destructively sampled. Controls eliminating one or more components (soil, biochar, fertilizer, solvent, microorganisms) were also set up. Similar incubations were also performed on one of the soils contaminated with light crude incorporating co-amendments of orange peels, soybean oil, molasses, synthetic surfactants, tryptic soy and biosolids.

Results/Lessons Learned. Some key soil characteristics were TPH, 24,000 mg L^{-1}; pH, 7.1; organic matter content, 3.7%; moisture content, 38%. The biochar exhibited differences in surface area; ash content; pH; porosity and absorption capacity that were attributed to feedstock. Results show addition of mineral fertilizer alone can reduce TPH in all the contaminated soils. Pine wood biochar addition (at 5%) can further enhance this reduction to below regulatory limits, particularly in soils with light crude, achieving this within 60 days. The walnut shell was not as effective in reducing TPH. Addition of co-amendments did not appear to result in significant improvements in the overall TPH reduction. These results suggest biochar does impact biodegradation of HH contaminated soils and if well understood, this work will provide a low-tech and relatively low-cost method for dealing with extensive shallow HH contamination.

Advanced Oxidative Pre-Treatment of Heavy-Hydrocarbon-Contaminated Soil to Enhance TPH Removal and Bioremediation

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Background/Objectives. Heavy hydrocarbon contaminated (HHC) soils are recalcitrant to natural attenuation, because these relatively large and complex contaminants tend to be hydrophobic, poorly soluble, and unavailable to microbiological attack. A potential method to alter the chemical structure of a wide range of organic molecules is advanced oxidation, in which reactive oxygen species (mainly hydroxyl free radicals) attack organic molecules at ring structures, double bonds, and certain non-C components. This study evaluated the potential of TiO_2 photocatalysis and hydrogen peroxide (H_2O_2) as a pretreatment approach to enhance bioremediation of HHC soil by oxidizing the organic compounds and increasing their solubility and bioavailability to the microbial community.

Approach/Activities. Initial tests were performed with TiO_2 slurries using UVA light to demonstrate the potential for photocatalysis to transform simple model hydrocarbons (alkanes or polyaromatic hydrocarbon (PAHs)). Identical tests were performed with H_2O_2 with/without UVA light to understand the transformation contribution of generated hydroxyl radicals under UVA light and of direct oxidation by H_2O_2. We first used a commercially available TPH standard (consisting of C10 to C28 alkanes) to determine if there are preferential photocatalytic/H_2O_2 degradation patterns corresponding to specific hydrocarbon structure. Further testing were accomplished using small amounts of model polycyclic or polyaromatic compounds (androstane, Benzo(*a*)pyrene, triacontane, and phytane). Spiked soils were exposed to sunlight to determine the potential for direct photolysis, or to H_2O_2 (as a positive control) to oxidize target compounds in the soil matrix. HHC soil was also treated with TiO_2 photocatalyst. BOD5 and TCOD were measured after the pre-oxidation treatment to evaluate changes in biodegradation activity.

Results/Lessons Learned. We observed faster photo-oxidation of shorter alkanes, but this size-dependent effect was not observed when the alkanes were treated H_2O_2 and UVA. In the initial test, H_2O_2 was more effective for removing hydrocarbons than photocatalysis, possibly due in part to the shadowing effect of TiO_2. Degradation of these alkanes by H_2O_2 under UVA light was due to not only the generated hydroxyl radicals but also the direct oxidation by H_2O_2. In degradation tests with polycyclic and polyaromatic compounds, over 50% of all the four model compounds were degraded after 1 day of photocatalytic or H_2O_2 treatment under sunlight, demonstrating effective oxidation by both methods. In separate tests with HHC soil, both TiO_2 photocatalytic and H_2O_2 treatment preferentially removed the smaller hydrocarbons. H_2O_2 was more effective than photocatalysis due to its ability to reach hydrocarbons below soil surfaces, where sunlight was unable to fully penetrate. After both TiO_2 photocatalysis and H_2O_2 treatment, the BOD_5/TCOD ratio for treated soil increased, indicating enhanced bioavailability and biodegradation potential of TPH compounds. Therefore, amending HHC soils with photocatalytic TiO_2 or H_2O_2 may entrance the efficiency of land farming and bioremediation operations.

Enzymatic Pretreatment of Heavy Hydrocarbon Contaminated Soil for Enhanced Bioremediation

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Background/Objectives. Bioremediation and natural attenuation, when applicable, are often the most cost effective approaches to manage soil contamination by hydrocarbons. However, the low bioavailability of heavy hydrocarbons (HHCs) (which are often too large and/or too hydrophobic for bacterial uptake) and their relative inability to induce appropriate catabolic enzymes in indigenous bacteria limits their biodegradability. We therefore sought to develop novel approaches to enzymatically activate HHCs through oxidation, or immobilize them to reduce mobility and their contribution to total petroleum hydrocarbons (TPH).

Approach/Activities. We postulated that (extracellular) enzymatic pretreatment to partially oxidize or break down heavy hydrocarbons would increase their bioavailability and susceptibility to biodegradation, and thus decrease remediation costs while increasing the degradation rate. Furthermore, many of the enzymes associated with extracellular hydrocarbon biodegradation are also capable of initiating oxidative polymerization reactions that would stabilize certain heavy hydrocarbon fractions, thereby reducing TPH levels. In order to assess the feasibility of this approach, we assayed the ability of commercially available enzymes (i.e., laccase and peroxidase) to transform several model (recalcitrant) hydrocarbon compounds (i.e., anthracene, perylene, androstane, and friedelin). Furthermore, we analyzed the effect of enzymatic pretreatment on both TPH and oxygen consumption by the indigenous microbial communities of HHC-contaminated soil from several sites.

Results/Lessons Learned. We successfully utilized a laccase-mediator system to demonstrate significant transformation of all model compounds tested. A one-hour contact time was sufficient to achieve greater than 90% transformation of perylene (5-ring polycyclic aromatic hydrocarbon), and greater than 50% transformation of androstane (4-ring polycyclic alkane). Preliminary respirometry data also demonstrated a significant increase in oxygen consumption by laccase-treated soil versus untreated or surfactant-amended soil. TPH analysis of laccase-treated soil will also be reported. Overall, the use of a mediator system greatly extends the laccase substrate range, and holds promise for increasing HHC bioremediation rates and efficiency.

Evaluation of a Novel Extractant for Remediation of Heavy Hydrocarbon-Impacted Soils

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Background/Objectives. Over the past 20 years, a number of surfactants and cosolvent formulations have been tested for their ability to recover petroleum hydrocarbons and other organic compounds from impacted soils and sediments. In these applications, the active ingredient was designed to (a) increase the aqueous solubility of the target compound(s) and/or (b) reduce the interfacial tension (IFT) between the aqueous and oil phases to induce mobilization of free product. Despite the demonstrated ability of selected surfactants and cosolvents to recover substantial quantities of mass at both laboratory and field scales, surfactant enhanced remediation is often considerably more expensive than traditional bioremediation approaches (e.g., biopiles) and performance can be substantially reduced for high molecular weight hydrocarbons. Recently, a water-soluble, non-toxic, non-volatile, non-flammable, biodegradable plant protein, GreenStract©, has shown promise for recovering heavy hydrocarbons from soil. When the protein solution is contacted with impacted soils, petroleum hydrocarbons are released from the solid phase, coalesce, and can then be recovered as a separate phase. The objective of this research was to evaluate the ability of GreenStract© to treat heavy hydrocarbon-impacted soils and sediments.

Approach/Activities. Nine impacted field soils were tested in this study. Batch reactor experiments were conducted in glass jars that were filled with 20 g soil and 20 mL of a 0.5% (as active ingredient) aqueous GreenStract© solution and mixed on a rotary tumbler. Results were compared to control treatment with water alone under the same conditions. Additionally, column experiments were carried out for two soils to investigate hydrocarbon removal in an *in-situ* system. Three soils were also treated in a completely mixed reactor (50 g soil with 200 mL treatment solution) to evaluate the effect of increased mixing on treatment performance. Pre- and post-treatment soils were analyzed for total petroleum hydrocarbons (TPH) following EPA Method 8015B.

Results/Lessons Learned. Greater than 80% TPH removal was obtained for five of the impacted soils treated with GreenStract©, corresponding to TPH concentrations <1500 mg/kg in the treated soil. Although water alone was able to remove >80% TPH in four soils, GreenStract© performed better than water in three of the nine impacted soils. The lower TPH removal observed in the other soils may be due to their higher clay content (e.g. two of these soils contained >50% clay). Comparisons between batch and column results indicate that *ex-situ* mixing yields substantially greater recoveries than *in-situ* flushing. An improved batch mixing scheme increased TPH removal by 45% for two soils treated with GreenStract. Based on these preliminary results, the GreenStract© solution is a promising candidate for ex-situ treatment of heavy hydrocarbon-impacted soils. Further research is being conducted to compare the performance and cost of GreenStract© to conventional surfactants (e.g., Aerosol®-MA, Tween®-80), evaluate combined remedies (e.g., chemical oxidation or bioremediation) for harder to treat soils, and assess the relationship between soil/TPH properties and hydrocarbon removal efficiency.

Biodegradation of High-Saline, High-Temperature Groundwater Impacted with Hydrocarbons

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Background/Objectives. Laboratory experiments were carried out to evaluate the potential for natural, aerobic biodegradation to degrade aromatic hydrocarbons, including benzene, toluene, ethylbenzene, xylenes, trimethylbenzenes and naphthalene. Aquifer sand and groundwater from two sites were incubated for 106 days. Borden (Canada) samples were incubated at 100C, whereas samples from a Saudi Arabian site (Jeddah) were incubated at 300C, close to the natural in situ conditions. The changes in hydrocarbon concentration, microbial community structure, and stable C isotopic ratio of these samples versus the change in controls samples in which biodegradation was inhibited were monitored during the duration of these tests.

Borden samples showed no significant biodegradation, while almost complete biodegradation of the target hydrocarbons was reached in the Saudi Arabian samples. Denaturing gradient gel electrophoresis analyses found that, while Borden microorganisms were the most diverse, they showed little response during incubation. Saudi Arabian samples were initially less diverse, likely as they were somewhat adapted to hydrocarbon contamination, but a positive respond was noted as the hydrocarbons were biodegraded. Microbial communities for the Saudi Arabian samples contained significant numbers of samples capable of hydrocarbon degradation and these increased during incubation.

Approach/Activities. A pilot-scale test at the Saudi Arabian field site was carried out to evaluate the effectiveness of enhanced aerobic biodegradation on a high temperature, saline petroleum hydrocarbon plume. A series of oxygen emitters installed perpendicular to the flow direction was used deliver oxygen to the subsurface media to create an aerobic reactive zone. The pilot test was run for seven months and the results indicated that all the target compounds decreased with removal percentages varying between 33 percent for the trimethylbenzenes to greater than 80 percent for the BTEX compounds. MtBE decreased 40 percent on average whereas naphthalene was reduced 85 percent on average. Microbial population examination, up- and down-gradient of the emitter reactive zone, suggested that the bacteria population went from an anaerobic, sulfate-reducing dominated population to one dominated by a heterotrophic aerobic bacteria dominant population.

Results/Lessons Learned. In general, given the conditions stated above, field aerobic biodegradation may exceed expectations and the high salinity and elevated groundwater temperature do not appear to inhibit in situ aerobic biorestoration.

Anaerobic and Aerobic Biodegradation of the Oil Dispersant Components 1,2-Propanediol and 2-Butoxyethanol in Seawater

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Background. The largest accidental oil spill in the history of the petroleum industry was the *Deepwater Horizon* explosion and seafloor well blowout, which released an estimated 206 million gallons of oil. Oil dispersants (COREXIT) were used in unprecedented quantities during the response. The main goal of this research was to evaluate biodegradation of the oil dispersant components 1,2-propanediol (1,2-PD) and 2-butoxyethanol (2-BE) in seawater and under anaerobic conditions, such as those found in near-shore estuarine environments.

Relatively little is known about the biodegradability of these two compounds in seawater. These compounds are also present in unconventional natural gas development hydraulic fracturing wastewater brine which is injected deep underground for disposal.

Approach. Microcosms were prepared with sediment from Bay Jimmy, which was impacted by the *Deepwater Horizon* oil spill. A synthetic seawater was added, along with approximately 12 mg/L of 1,2-PD or 2-BE. Treatments included addition of nitrate, Fe(III), anaerobic unamended, and aerobic. Enrichment cultures were prepared by volumetric transfer of well-mixed material from the sediment microcosms into seawater and lower ionic strength media. 1,2-PD and 2-BE were quantified by gas chromatographic analysis, following solid phase extraction and elution with dichloromethane and methanol.

Results. This study showed that: 1) 1,2-PD biodegraded in seawater under aerobic and anaerobic conditions in microcosms; this appears to be the first report of 1,2-PD biodegradation in a high salt environment; 2) Biodegradation of 1,2-PD was sustained in aerobic and anaerobic enrichment cultures through two transfers (1% v/v). Nitrate, Fe(III) and sulfate were not used as the electron acceptors, and rates of biodegradation were similar across all amendments. Based on this, fermentation to pyruvate is a possible pathway. Pyruvate was not detectable in the high ionic strength seawater via HPLC, so transfers of 1,2-PD were sustained in lower ionic strength media so that fermentation products could be better quantified; thus far, none have been detected; 3) 2-BE biodegraded in seawater under aerobic and anaerobic conditions in microcosms; this too appears to be the first report of 2-BE biodegradation in a high salt environment; and 4) Biodegradation of 2-BE was sustained in aerobic and anaerobic enrichment cultures, through two transfers (1% v/v). Nitrate, Fe(III) and sulfate were not used as electron acceptors. Molybdate (a specific inhibitor of sulfate reduction) slowed but did not stop consumption of 2-BE. Sulfide was detected, but at levels well below the amount expected if complete mineralization occurred with sulfate as the terminal electron acceptor. Based on these results, the presumptive pathway for anaerobic biodegradation of 2-BE in this study was via fermentation. Products were not measured, although 2-butoxy acetic acid and hydrogen are likely intermediates.

Biodegradation of Alkylated PAHs in Marsh and Mangrove Systems in Coastal Louisiana

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Background/Objectives. In May of 2010, MC252 oil from the blown out Macondo well began to reach the coastal wetlands of southern Louisiana. Of the 1773 km of oiled shoreline, ~45% were classified as marshes, yet cleanup activities were only authorized on 68 km or 4% of the total oiled shoreline. As a result, a disproportionate importance was placed on the natural recovery of oiled marshes and associated habitats over sand beaches. This study was performed at three sites in coastal Louisiana; a marsh site on the southern border of Bay Jimmy in Plaquemines Parish, LA, a marsh site just inland of Fourchon Beach in Lafourche Parish, LA dominated by *Spartina alterniflora*, and an adjacent mangrove site also inland of Fourchon beach dominated by *Avicennia germinans*. Both sites were contaminated by MC252 oil from the Macondo well blowout located approximately 105 miles and 111 miles away, respectively. The objectives of this study are; (i) characterize the weathering of polycyclic aromatic hydrocarbons from MC 252 oil in Bay Jimmy and Fourchon beach wetland systems, and (ii) evaluate biodegradation mechanisms of contaminated oil in the wetland system.

Approach/Activities. Weathering of alkylated PAHs from the Fourchon beach site was quantified using 4 sets of grab samples from the site collected from August 2011 through November 2013. The grab samples were collected from the surface from 23 locations at 3.5 m intervals and were stored at 4 °C prior to analysis. Marsh and mangrove soil samples were extracted with hexane/acetone (50/50) and analyzed using gas chromatography with a mass selective detector. In addition, the mineralization of hydrocarbons from MC252 oil in these soils was evaluated using measurement of CO_2 flux and $\delta^{13}C$ signature in both Bay Jimmy and Fourchon beach sites. High resolution porewater nutrient profiles were obtained at each location using dialysis samplers made of 50 cm long plexiglass at 1.5 cm intervals, covered with HT-200, 0.2 µm pore size membranes. Finally, laboratory microcosm studies were used to confirm the rate and nature of biodegradation processes for alkylated PAHs in these environments.

Results/Lessons Learned. Significant weathering of MC252 oil in Fourchon beach and Bay Jimmy samples were observed with loss of lower molecular weight PAHs (naphthalenes, phenanthrenes and dibenzothiophenes). Alkylated phenanthrenes and dibenzothiophenes were the dominant PAHs measured at these sites. Weathering rates of approximately 5% per year relative to alkylated chrysenes were observed at the Fourchon sites 3 years after initial oiling. Flux chambers in marsh locations trapped CO_2 that exhibited $\delta^{13}C$ signatures lower than indigenous organic matter. The lower $\delta^{13}C$ signatures observed were similar to the levels expected from MC252 oil and therefore suggest the potential for mineralization of PAHs in MC252 oil in marsh sites at Bay Jimmy and Fourchon Beach. High-resolution nutrient profiles obtained at these locations during the winter and summer indicate the presence of adequate amount of nitrogen and phosphorous in the marsh and mangrove locations to support biodegradation. High levels of sulfate (> 1000 mg/L) were measured and zones of sulfate depletion coincident with oiled soil layers. Biodegradation of alkylated PAHs in laboratory microcosms with contaminated sediments were observed only under aerobic conditions with first order rates of 0.88-18 /year and no losses was observed under anaerobic conditions. Taken together, results indicate that biodegradation of 3-ring alkylated PAHs is occurring, although slowly (~5% per year), and only in the presence of oxygen.

Approaches to Monitor and Characterize Surface Water Sheens

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Background/Objectives. Understanding the source of persistent sheens in surface water bodies is important for assigning liability at petroleum hydrocarbon liquid spill sites. Sheens are often of natural biogenic origin associated with microbial activity. However, sheens can also be derived from petrogenic sources (e.g., petroleum hydrocarbons such as crude oil, gasoline, diesel fuel, and asphalt), pyrogenic sources (e.g., combustion-related materials such as coal tar and creosote) or mixed petrogenic/pyrogenic sources (e.g., used lubricating oils). This presentation will review the sheen monitoring and characterization approaches used at a site where crude oil spilled into a marsh.

Approach/Activities. A sheen monitoring program was implemented at the site for visual assessment of sheen properties, characteristics, and physical characterization. The 2007 National Oceanographic and Atmospheric Administration (NOAA) guidance provides the standard for sheen descriptions and characterizations for visual assessment. These sheen descriptors were modified for site-specific application. Because physical characterization does not provide conclusive information related to the sheen source(s) and chemical composition, a sheen sampling and analysis program was implemented to supplement visual inspection. Surface water sheen samples were collected and analyzed for polycyclic aromatic hydrocarbons (PAHs; including alkylated PAHs), and total petroleum hydrocarbons (TPH) to provide appropriate information for source determination using environmental forensic techniques. The evaluation of hydrocarbon compositions was based primarily on the comparative composition distributions (chromatograms) generated for PAHs and aliphatic hydrocarbons. In addition to the project example, other forensic analysis tools will be discussed.

Results/Lessons Learned. Sheen monitoring and characterization is crucial for sites with multiple potential sources of sheen. Using data obtained from this project, methods for sheen monitoring and characterization will be described along with examples of how fundamental understanding of potential sheen sources supports setting up site-specific sheen monitoring and characterization programs as well as defining appropriate delineation for remediation. Additionally, key tips for photographing sheens, methods for sheen sampling and analysis (including which analytical methods are most important), and tips for enabling the best determination of sheen source(s) will be presented.

Back to Contents

Anaerobic-aerobic Method of Bioremediation of a Fenny Bog with Old Oil Pollution in Western Siberia: A Pilot Scale

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Overview. In Western Siberia, Russia, big territories polluted by accidental crude oil are already have restored mainly by technologies of “on site” bioremediation. However, there are more a lot of fenny impassable bogs polluted by oil more than 20 years ago. On a surface of such old pollution an asphalt-like crust is formed and it remains without any change, and no plants grow there. These bogs need a remediation. Earlier in laboratory conditions we developed an anaerobic-aerobic method of bioremediation for fenny bogs polluted with fresh crude oil. And this method would allow us to carry out the bioremediation of such bogs without using heavy equipment and without breaking integrity of their landscape and their biogeocenoses which has been developing there for ages.

Background. In 2013, near Megyon-town, Western Siberia, Russia, it was provided to us a site for field trial of the anaerobic-aerobic method of bioremediation with application of the oil-degrading preparation “Rhoder” and an acceptor of electrons. However, this site of the fenny bog was covered by an asphalt-like 20-year-old oil crust, which maintained a weight of a man about 60 kg without breaking. Oil was appeared after the break of the crust and accumulated in falls. The thickness of the crust was 1.2-1.5 cm. The moss of black color impregnated with oil was under this crust. The layer of the moss strongly polluted with oil didn't exceed 15-25 cm. The concentration of the material extracted by chloroform was 848.2-946.3g/kg of absolutely dry matter (DM). Hexane fractions of hydrocarbons (HC) at a depth of 0-10 cm were 446.7-526.8g/kg DM, and hexane fractions of HC at the depth of 10-25 cm were from 468.7g/kg to 890.8g/kg DM.

Approach. The allocated site was divided into three allotments (of each 25*30 sq.m). On the first allotment the “Rhoder” with fertilizers was applied on a surface of the crust and the acceptor of electrons with the “Rhoder” was introduced into thickness of the moss polluted with oil. On the second allotment indigenous microorganisms, which had developed within 20-year-old pollution of the bog with oil, were activated by application of fertilizers. The third allotment was served as a negative control without any treatment. On the first allotment the asphalt-like crust was hacked with feet after the first introduction of working solution of the “Rhoder” with the acceptor of electrons into the thickness of the moss. Before the second treatment an easy garden cultivator was used to try hacking the crust. Treatments of two experimental allotments were carried out three times.

Results. As a result, on the first allotment, where the anaerobic-aerobic method of bioremediation was performed, the concentration of saturated HC in the moss layer of 0-10 cm was decreased by 23.0%, the concentration of aromatic HC – by 28.0%, and the concentration of resins-asphaltenes substances was decreased by 34.4%. In the moss layer of 10-25 cm on the same allotment the concentration of saturated HC was decreased by 72.6% (from 405g/kg to 111g/kg DM), the concentration of aromatic HC - by 66.5% (from 148.7g/kg to 49.9g/kg DM) and the concentration of resins-asphaltenes substances was decreased by 57.2% (from 106.9g/kg to 45.7g/kg DM). Indigenous microorganisms in the peat layer of 0-10 cm and 10-25 cm on the second allotment practically didn't show the decrease of the oil pollution. The same results were observed in the negative control (the third allotment).

Washover Tidal Events as a Source of Oil Persistence on Coastal Headland Beaches

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Background/Objectives. MC252 crude oil on coastal headland beaches and barrier islands are remobilized and redistributed by storm-driven washover events from the beach subtidal and intertidal zones to the beach supratidal and marsh zones. Washover events on coastal headland beaches occur when storm surge from cold fronts, high tides, tropical storms, and hurricanes move across the beach eroding the beach surface, reworking and depositing sand in the back marshes and shallow mudflat areas. Connections between the beach and these marsh and mudflat areas occur through washover channels, eroded by the action of these storm events. These marshes and mudflat areas have different biodegradation potential due to differences in the biogeochemical conditions in these zones. The objective of this study is to understand the role of washover events in transporting and distributing alkylated polycyclic aromatic hydrocarbons (PAHs) ultimately resulting in different biodegradation profiles on the beach environment.

Approach/Activities. Three sets of field measurements were conducted to understand the impact of washover events on Fourchon Beach, Louisiana, a coastal headland beach heavily impacted by the spill,; (i) measurements of relative weathering of 2 oil types: submerged oil mats (SOMs) and surface residue balls (SRBs) sampled immediately after washover events in 2011-2013, (ii) a systematic survey of core samples from washover channels and (iii) evaluation of depth and distribution of PAHs within contaminated washover channels. SOMs, SRBs and soil cores collected from the beach were extracted with hexane/acetone (50/50) and analyzed for PAHs using gas chromatography with a mass selective detector. Losses in alkylated PAHs were estimated based on weathering ratio of alkylated phenanthrenes and dibenzothiophenes to chrysenes and as a ratio of total PAHs to C30-hopanes. The role of biodegradation was confirmed in microcosm studies using site materials in the laboratory.

Results/Lessons Learned. A survey of 59 washover channels across 3 miles of beach found measurable oil in ~10% of the samples indicating the importance of this previously hypothesized transport process across the beach surface. Weathering ratios of alkylated phenanthrenes and dibenzothiophenes in SOM and SRB oil forms mobilized during washover events from subtidal areas showed minimal weathering of these compounds relative to poorly degradable C30-hopanes or alkylated chrysenes. As a result, washover events appear to mobilize oil similar in PAH characteristics to the original oil, which reached the shoreline in 2010. SRBs from washovers trapped on the supratidal surface demonstrated significant weathering once deposited (10-90% removal). This weathering occurs over the time frame of months to a year, presumably due to biodegradation driven by enhanced oxygen status on the beach surface. In the core samples from the washover channels, PAHs were detected in the top 25 cm. Weathering ratios of PAHs in these tidally-flooded, anoxic washover channels indicated reduced weathering processes relative to supratidal zones but more than subtidal SOM samples. Microcosm studies confirmed the absence of any measurable change in alkylated PAHs under anaerobic conditions. Additional studies on microbiological characterization using next generation sequencing to evaluate biodegradation are in progress. Taken together results suggest that washover events that rapidly move oil into the mudflats and marsh areas

Bioremediation of Deepwater Horizon Crude Oil in Louisiana Salt Marshes Amended with Clay Minerals

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Background/Objectives. The Deepwater Horizon oil spill that occurred in 2010 discharged nearly 5 million barrels of crude oil from approximately 1,500 m below the ocean surface. This uncontrolled release lasted 84 days and had catastrophic impact to ecosystems along the coast of the Gulf of Mexico. Thousands of these marshlands were adversely affected following the oil spill, especially in Bay Jimmy, Louisiana. Salt marshes are one of the most difficult environments to remediate due to their sensitive and important ecosystems. Traditional oil removal methods can do more harm to the marsh than the oil itself. Bioremediation is the preferred cleanup approach for these delicate environments. Typically bioremediation has been carried out by the addition of nitrogen and/or phosphorus compounds but the results have been inconsistent. It has been shown that oxygen is the limiting factor. Previous laboratory studies conducted in oiled seawater demonstrated that clay minerals enhanced microbial growth resulting in oil degradation. However, this had not been tested at field sites or on oiled marine sediments where oil is known to persist. The main objective of this research was to test clay minerals as a bioremediation alternative for enhancing degradation of oiled salt marsh sediments.

Approach/Activities. Laboratory microcosm experiments were conducted to evaluate the application of clay minerals on oiled salt marsh sediments. Microcosms contained oiled salt marsh sediments and seawater from Bay Jimmy and selected microcosms were amended with montmorillonite or kaolinite clay minerals. Field experiments were carried out at two locations, vegetated and non-vegetated, in Bay Jimmy salt marshes impacted by the Deepwater Horizon oil spill. The non-vegetated marsh suffered die-off from oil impact. Each location had a control and a treatment plot amended with montmorillonite clay minerals. For microcosm and field experiments, concentrations of *n*-alkanes and PAHs were compared between control and clay amended sediments to evaluate oil degradation enhancement.

Results/Lessons Learned. Results from the laboratory microcosms showed that clay minerals did not enhance oil degradation. In fact, oil concentrations in the controls were significantly less. Clay minerals may have caused an increase in pH which inhibited enzyme-catalyzed processes required for metabolism. For future laboratory studies it may be necessary to pretreat the sediment prior to commencement to provide an acclimation phase for the indigenous microorganisms. The results from the field studies demonstrated for the first time that degradation of *n*-alkanes and PAHs was significantly enhanced by the addition of montmorillonite compared to controls. Vegetated treatment plots were more effective than non-vegetated treatment areas. It is suggested that bivalent cations adsorbed to montmroillonite's surface suppressed the diffuse double layer. This allowed the oil along the clay's surface to be accessible to the bacteria where oil could be readily consumed. Additionally, oil-mineral aggregation may have played a significant role during the initial stages. Clay minerals may serve as a new and unique bioremediation strategy for oiled salt marsh sediments.

Back to Contents

Biodegradation of Oil by Arctic Marine Microorganisms

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Background/Objectives. As oil exploration and shipping routes expand in Arctic regions, the potential for oil to enter the Arctic Ocean increases. The biodegradation of oil by indigenous microorganisms is thought to be the main process contributing to the removal of oil from the environment. In near shore environments of the Arctic Ocean, we recently found the chemical loss of oil to range from 46-58% after 60 days. Combining degradation rates with molecular microbial analyses can provide further insight into the identity of oil-degrading microbes and how the Arctic marine microbial community responds to oil, both in near shore and offshore environments.

Approach/Activities. Seawater was collected August-September from the Hanna Shoal Study Area, located approximately 80 km offshore from Wainwright, AK. Seawater samples were collected from the surface, pycnocline and just above the seafloor from 18 different locations in order to determine the baseline microbial community structure and the presence of genes for oil biodegradation and nutrient cycling throughout the water column. Surface seawater was also incubated with Alaskan North Slope (ANS) crude oil to determine oil biodegradation rates in offshore environments and to assess how oil affects the microbial community structure and the presence of genes associated with key metabolic pathways. Mesocosms containing surface seawater and unweathered ANS crude oil (15 mg/L) were incubated at 2°C with minimal nutrient addition (16 mg/L Bushnell Haas). Mesocosms were sampled at 5, 10 and 28 days for chemical loss and molecular microbial analyses. Petroleum losses were quantified using GC-MS analysis. Next-generation sequencing of 16S rRNA genes allowed the identification of bacteria present throughout the water column in the Hanna Shoal Study Area and the identification of bacteria that grew in response to oil. The GeoChip microarray was used to detect and quantify genes for oil biodegradation and nutrient cycling in baseline water column samples and in mesocosm incubations over time.

Results/Lessons Learned. The microbial community in surface, pycnocline, and benthic samples differed in structure, but oil-degrading bacteria and oil-degrading genes were present throughout the water column and were not stratified with depth. GeoChip microarray analyses also revealed a strong stratification in the abundance of individual functional genes between surface and benthic samples. When Arctic seawater was incubated with oil, some bacterial taxa and oil biodegradation genes increased in their relative abundance, suggesting a potential role in biodegradation. *Oleispira* and *Colwellia* species increased in relative abundance over the course of the incubations. Members of these genera were also active in the biodegradation of the Deepwater Horizon oil spill. Within 28 days, 36% of the total measurable hydrocarbons in ANS crude oil had biodegraded. Future studies are needed to better understand the seasonal and spatial variability of oil biodegradation potential in Arctic seawater as well as in ice-covered waters.

Bioremediation of Weathered Crude Oil in Complex Soils: A Southern Minnesota Field Study

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Background/Objectives. A winter-time crude oil leak onto a rail line saturated an adjacent complex mixture of railroad ballast and sandy heterogeneous soil in southern Minnesota, providing an opportunity to examine the effectiveness of several bioremediation products (with and without inorganic fertilizer application) on various components of the Bakken crude oil in the field. The spill occurred in frozen soil conditions, with significant subsurface transport over the first five weeks. The crude oil had undergone some degree of weathering through the spring thaw, with the data collection spanning from May – August.

Approach/Activities. The 99-day field study employed GC-MS to evaluate and quantify the presence/degree of weathering of crude oil within each sample plot and analyze the final contamination composition after biodegradation. Biodegradation of BTEX, TPH-GRO, TPH-DRO, and TPH-MOR compounds was tracked in the shallow soil subsurface (2-4" bgs), with respect to an untreated control. Data was collected on natural attenuation, fertilized (high and low dosages), and unfertilized rates for each selected Oppenheimer Biotechnology remediation product. Oppenheimer Biotechnology products utilize highly concentrated, naturally occurring communities of selective hydrocarbon degrading archaea within a mineral matrix.

Results/Lessons Learned. Total hydrocarbon reductions observed in the highly heterogeneous matrix were 95.6% of BTEX compounds and 61.5% in the heavier TPH-DRO and TPH-MOR compounds, as compared to natural attenuation reductions of 72.6% (BTEX) and only 7% (DRO, MOR). Soil temperatures and % moisture ranged between 63 °F – 114 °F and 8.1% - 14.7%, respectively. Greater hydrocarbon losses were not observed in the higher fertilizer dose plots compared to low dosage plots, but fertilizer application in general resulted in a 17.7% average reduction in BTEX-GRO compounds and a 31.5% average reduction in DRO, MOR compounds, demonstrating a successful use of bioremediation under complex field conditions.

Diurnal and Seasonal Temperature Changes Affects Biodegradation of Petroleum Hydrocarbons in sub-Arctic Soils by Altering Microbial Community

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Background/Objectives. Cold temperatures affect microorganisms involved in biodegradation of petroleum hydrocarbons by altering inter-cellular biochemical reaction rates, membrane fluidity or bacterial substrate affinity. Because different bacteria respond differently to temperature changes in the environment, temperature changes could results in a shift in microbial community structure, which in turn may indirectly alter the overall rates and extents of biodegradation activity. This study investigated changes in microbial populations and degradation activity in soils subjected to (i) diurnal temperature changes over the duration of a summer season at a sub-Arctic site; and (ii) seasonal temperature changes representative of freezing and thawing during fall and spring.

Approach/Activities. Microcosms containing crude-oil contaminated soils from a sub-Arctic site in Canada, were incubated at three different temperature regimes as; constant 5°C (CST5), constant 15°C (CST15), and diurnal variable temperature between 5°C and 15°C (VART5-15). VART 5-15 represents the typical diurnal air temperature profile of the site in the summer. Pilot-scale experiments were conducted with a contaminated soil from another sub-Arctic site, in Canada. The soil was incubated at two different temperature regimes as freezing phase (2°C to -5°C over 60 days) and thawing phase (-5°C to 14°C over 100 days). The concentration of petroleum hydrocarbons, soil respiration as well as soil general microbial community and community of alkane hydrocarbon degraders were characterized during the experiments.

Results/Lessons Learned. Significant biodegradation of semi-volatile (>C10-C16) hydrocarbons was observed in all microcosms, however, the extent of biodegradation was comparable in CST15 and VART5-15 (41-48%) and was significantly higher than CST5 at 11%. Comparable biodegradation extents in CST15 and VART5-15 were associated with similar microbial communities in these systems, which were different than CST5 system.
While *Actinobacteia* phylum were relatively abundant at all temperature regimes, the members of γ-*proteobacteria* were evolved in CST15 and VART5-15 systems. On the other hand, soil respiration rate as indicator of microbial metabolic activity, was significantly higher in CST15 than VART5-15 systems. Temperature based shift in microbial community and biodegradation pattern was also observed in pilot scale experiments, where during the freezing phase, 21% biodegradation of semi-volatile hydrocarbons was associated with appearance of members of *Actinobacteia (Corynebacterineae)*. Significantly higher biodegradation as 31% was occurred during the thawing period where an *Alkanindiges*-related strain, member of γ-*proteobacteria* phylum, was evolved. Overall these results suggest that (i) in case of variable temperatures, the higher temperature regulates the soil microbial community composition, as well as the extent of biodegradation (ii) microbial community shifts and metabolic activity of petroleum degraders can be detected at sub-zero temperatures.

Influence of Bioaugmentation on Canadian Oilsands and Tailings Processing

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Background/Objectives. Canadian oilsands are a major source of oil but their processing results in tailings ponds and associated runoff water that contain contaminants of concern (COCs) including polyaromatic hydrocarbons (PAHs). The main concerns are mature fine tailings (MFT) composed of residual hydrocarbons, water and fine clay. Tailings contain COCs including heavy metals, naphthenics, and PAHs. Solvents are also used in processing that end up in the tailings ponds as well. Naphthenic acids and PAHs degrade very slowly and pose a long-term threat to surface and groundwater as they can be transported as suspended solids in the MFT. The objective here is to improve processing of oilsands and resultant tailings ponds and associated COCs through bioaugmentation. Increasing biodegradation and separation of hydrocarbons from clay, sand, and other particles would enhance settling of the MFT, improving water quality in the pond effluent, and potential recover hydrocarbons.

Approach/Activities. Canadian Athabasca oilsands and tailings were used in bioaugmentation evaluations. For laboratory tests, BioTiger™, a patented microbial consortium that can metabolize PAHs, was applied in bioaugmentation tests. Untreated oilsands, tailings, and *Eschericia coli* were used as controls. BioTiger™ is made up of 12 aerobic bacteria selected based on their enzymatic and/or biosurfactant production. Of the 12 cultures tested five were shown to completely degrade phenanthrene, a PAH, as a sole carbon and energy source in 24 h. Bioaugmentation of Canadian Athabasca oilsands tailings resulted in increased (5X) microbial densities but active metabolism as measured by respirometry was not observed without the addition of yeast extract (1g/L). Microscopic techniques were combined with Mass Spectrometry-Gas Chromatography (GC-MS) to evaluate BioTiger™ interactions with the tailings and oilsands. The individual BioTiger™ strains were tested in microbial media as well as with the tailings to examine relative growth rates.

Results/Lessons Learned. Results demonstrated bioaugmentation of BioTiger™ increased separation of organic carbon from particles in oil sands and enhanced settling with reduced MFT for improved water quality. It was demonstrated that increasing the ratio of oil sands tailings to BioTiger™ decreased microbial viability up to 50%. Oil sands tailings can have inhibitory effects so concentrations and turnover rates must be taken into consideration for remediation efforts. There were natural bacteria observed in the oilsands and tailings, but were not very active nor did they respond to any of the treatments applied here. The tailings and oilsands bioaugmentation testing described here has the potential to ameliorate the environmental impact of oil sands processing and improving overlaying water quality.

Amorphous and Crystalline Phosphorus Interactions with Organic Acids during In Situ Hydrocarbon Degradation in Cold Soils

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Background/Objectives. In the clay rich, calcareous soils of Western Canada, managing phosphorus in the parent material, capillary fringe and saturated zones is critical to insuring the long-term successful remediation of residual hydrocarbons smeared across these three soil zones. As a consequence, naïve application of phosphorus can result in immediate immobilization onto the soil with a coinciding stall in hydrocarbon remediation. As part of the Sustainabile In Situ Remediation Cooperative Alliance (SIRCA), a large scale field experiment has begun to address novel phosphorus fertilizers and/or organic acid adjunctants in cold soils to decrease the immobilization of phosphorus onto soil. This experiment will assess how the crystallinity of soil phosphorus influences soil hydrocarbon degrading activity with differing phosphorus fertilizers and organic acids.

Approach/Activities. Two large (1 m diameter) injectors were installed to 5m and backfilled with quartz sand at a high (ca. 125 L solution/day) or low (25 L solution/day) permeability location at a site. The large bore injectors are instrumented with a two-inch monitoring well, three six-inch incubation wells, as well as a float injection system designed to maintain a constant head of a specific injection solution within the large bore injectors. Ground water wells were installed up and down gradient of these injectors at the site. Soil amendment solutions initially consisted of 1 uM H_3PO_4, 11 uM SO_4 and 0.08 uM HNO_3 at circumneutral pH, which is similar to background concentrations of sulphate and nitrate at this site.
In addition to these injectors, soils from eight similar sites were dried, homogenized and then their phosphorus mineralogy altered by either increasing (saturating with calcium) or decreasing (acid wash followed by magnesium) the crystallinity of soil phosphorus. Soils were then spiked with diesel, and duplicates placed in each injector inside one of the incubation wells for a total of four replicates per site. Hematite and hydroxyapatite were also used to act as end member controls of phosphorus precipitation. Soil mineralogy, microbiology and chemistry are all being assessed every three months with sacrificial bags of treated soil removed from the site. The initial soil amendment solution will be followed by a low concentration citric and malic acid solution to evaluate how organic acids influence soils with adsorbed phosphorus.

Results/Lessons Learned. Initially, treated soils retained their potential to degrade hydrocarbons but had radically altered phosphorus crystallinity. The influence of initial phosphorus crystallinity on soil interactions with orthophosphate will be reported as well as results from the first year of field monitoring. Initial results from altering the amendment solution from orthophosphate to low concentrations of organic acids will also be discussed.

Petroleum Hydrocarbon Degradation in Frozen Soils Using Bonemeal Biochar

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Background/Objectives. Bioremediation in cold regions is a slow process which is limited by extreme environmental conditions and short growing seasons. Conventional methods of ex-situ petroleum hydrocarbon remediation rely on fertilizer additions and soil turning to stimulate the microbial community to catabolize organic contaminants; however this approach has yielded inconsistent results in regions dominated by frozen conditions. Biochar is a soil amendment that results from heating organic biomass under oxygen limited conditions, which has received interest because of ability to enhance plant growth and improve fertility in agricultural soils. Few studies have been conducted on petroleum hydrocarbon contaminated soils in cold regions, but there have been some successful reports of increased petroleum hydrocarbon degradation rates in biochar amended soils as compared to the control. However, the physical, chemical, and biological mechanisms driving petroleum hydrocarbon degradation in frozen, biochar-amended soils are not well understood. The objective of this study is to determine if bonemeal biochar enhances petroleum hydrocarbon degradation in frozen soils, and to link this degradation to changes in chemical processes and its subsequent effect on the soil microbial community.

Approach/Activities. Sandy, aged-diesel contaminated soil from Iqaluit, Nunavut, Canada was used in a bench-scale laboratory trial which investigated the use of bonemeal biochar as a soil amendment to enhance petroleum hydrocarbon degradation in frozen soils. Petroleum hydrocarbon degradation under thawed conditions was assessed using a fertilizer control and amended treatments; 3% (w/w) bonemeal biochar plus fertilizer, 6% (w/w) bonemeal biochar plus fertilizer, 5% (w/w) compost plus fertilizer and 10% (w/w) compost plus fertilizer. Thawed vials were incubated at 10°C and destructively sampled over 0, 30, 60 and 90 days. Petroleum hydrocarbon degradation under frozen conditions was also evaluated using a fertilizer control and an amended treatment; 3% (w/w) bonemeal biochar plus fertilizer. Frozen vials were incubated at -5°C and destructively sampled over 0, 30, 60 and 90 days. Destructive sampling also occurred at 0 and 90 days in every treatment in order to determine the temporal extent of the chemical and biological effects of amendment application.

Results/Lessons Learned. Under frozen conditions, 3% (w/w) bonemeal biochar significantly reduced the F3 fraction by 22%, as compared to fertilizer which only increased degradation by 3%. Total hydrocarbon-degrading populations were higher in biochar amended soils incubated under frozen conditions than in populations incubated under thawed conditions. Stimulation of the microbial community was apparent during functional gene analysis which indicated that over time, genes coded for key steps in the hydrocarbon degradation pathway significantly increases in both frozen and unfrozen soils. There was no significant difference detected in liquid water content or nutrient supply rates between frozen soils amended with bonemeal biochar as compared to the control treatment. Our results suggest that with bonemeal biochar, remediation may be active under frozen conditions due to biotic influences which extends remediation periods and provides new cost-effective remediation strategies for cold regions.

Back to Contents

Development of the Method for Softening of an Asphalt-like Crust on a Surface of a Bog with Old Oil Pollution

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Overview. In summer, 2013, one site of a bog covered with an 20-year-old asphalt-like oil crust was provided to us as a trial field for our anaerobic-aerobic method of bioremediation with the application of the oil-degrading preparation “Rhoder” and an acceptor of electrons in spite of the fact that this method was developed for bioremediation of raised bogs polluted with fresh crude oil. After the first treatment of the crust with the "Rhoder" and fertilizers, it became clear that without destruction or softening of a crust it was impossible to receive significant reduction of this pollution. It was confirmed with the results obtained on the allotment where the anaerobic-aerobic method of bioremediation was performed. The use of machinery on such bogs was unacceptable for the destruction of the crust and there was a question to choose some reactants for softening this asphalt-like crust and then carry out the anaerobic-aerobic method of bioremediation of the bog.

Background. The moss and the asphalt-like crust were used as models in laboratory experiments. This moss and asphalt-like crust were selected from the raised bog polluted with oil more than 20 years ago (town Megyon, Western Siberia, Russia). The chemical analyses of the crust and the moss had showed a high level of pollution with hydrocarbons (HC).

Approach. The moss, polluted with oil, with the weight of 500 g was placed in capacities (diameter of 110 mm and height of 120 mm) and the asphalt-like crusts with the thickness of 15 mm were placed above. In these capacities, except a negative control, a reactant "A" in various concentrations was applied on surfaces of crusts several times and the reactant "B" was applied only once in other capacities. Eight options of processing of the crust were executed to choose the softening reactant. The asphalt-like crusts didn't mix up. Fertilizers and the "Rhoder" (3 times after the last additives of reactants) were applied on the surfaces of crusts for moss bioremediation in several options of the experiment. The same amount of distilled water was added in the capacity with negative control. Samples of the moss and crusts for analyses were selected before, during and after the crust softening and the "Rhoder" with fertilizers application on the moss and crusts.

Results. Preliminary researches showed that solutions of reactants with concentrations of active components of 20% and 10% sharply lifted pH of the moss, and thus the total amount of microorganisms was very much decreased. Therefore the reactant "A" in the experiment on the moss with the asphalt-like crust was taken in lower concentrations and applied several times. The reactant "B" was taken in concentration of 3.5% and used only once. As a result of the conducted researches the concentration of HC (Hexane fraction) was decreased by 46-47% with the optimized concentration of the softening reactants "A" or "B" instead of the former 23% without application of any reactant, and we could choose the best of two reactants.

The Role of Organic Acids in Increasing Phosphate Availability for Hydrocarbon Remediation in Cold Soils

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Background/Objectives. *Ex-situ* urban remediation is a costly and disruptive process, whereas, *in-situ* bioremediation is an attractive and viable alternative at this site due to its location in a city center. To stimulate hydrocarbon degrading bacteria, optimum levels of oxygen (O), phosphorus (P), and nitrogen (N) are required. Oxygen and N are easily supplemented, but P can become limiting and has been known to stall *in-situ* remediation. The reason for this is because P can be rapidly consumed by non-degraders, sorb strongly to soil minerals, and react with other cations (Ca, Fe, and Al) to forum insoluble phases. One cost effective and simple solution of increasing P availability is to add organic acids to the soil. Organic acids are known to increase the availability of P by competing for soil surface sites and by preventing the formation of minerals that P would normally adsorb to. As part of the Sustainable In Situ Remediation Cooperative Alliance (SIRCA), the objectives of this study are to understand the ternary interaction between P, organic acids, and site mineralogy.

Approach/Activities. To understand the basic mechanisms of P adsorption, laboratory experiments that use basic laboratory analyses and spectroscopic methods were executed. Among them, Fourier Transform Infrared (FTIR) spectroscopy is a powerful method to study P sorption mechanisms, and can evaluate the competitive nature of organic acids to mineral surfaces. Likewise, synchrotron spectroscopy can reveal accurate P speciation data. All of the laboratory methods will give a basic knowledge of P interactions; however, simulating subsurface and groundwater conditions in the laboratory is challenging. Therefore, a novel experiment was designed for the field site in which samples would be submerged into the site groundwater and the existing infrastructure (namely underground storage tanks) will be utilized to provide a continuous flow of treatment to the samples.

Results/Lessons Learned. Organic acids can increase phosphate solution concentration in two ways: (1) both organic acids and phosphate bond to mineral surfaces via oxygen atoms, so compete for the same sites, and (2) organic acids chelate ions such as Ca and Fe preventing the formation of minerals or phosphate precipitates. Increasing the phosphate solution concentration increases the bioavailability, but also the mobility leading to a loss of phosphate from the system. For an efficient and cost effective bioremediation treatment solution, this interaction between phosphate, organic acids, and mineralogy is studied, and results from the spectroscopic experiments will be discussed.

Speciation and Movement of a Polyphosphate Amendment: The Remediation of a Hydrocarbon Contaminated Cold Soil Aquifer

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Background/Objectives. Petroleum hydrocarbon (PHC) contamination of soils and groundwater is a significant environmental problem for urban, rural, and industrial pumping stations. The use of in situ bioremediation is a less invasive and expensive technique of reclaiming PHC soils. This is particularly effective in urban settings where removing the contaminated soil may not be feasible. The in situ bioremediation of PHC aquifer soils is most often limited by nutrient (N and P) requirements of the microbial communities. This cold soil study site is an urban pumping station located in Northern Saskatchewan, with phosphorus bioavailability identified as the major limitation to PHC bioremediation. Phosphorus is highly reactive and bioavailable in its hydrolyzed species (PO_4^{3-}) allowing for microbial uptake and hydrocarbon degradation to occur. However, in calcareous soils this species will often adsorb and precipitate with a wide range of minerals limiting its mobility and bioavailability. Polyphosphates are sometimes used as a phosphorus source as they are thought to have increased mobility while slowly hydrolyzing to a bioavailable species. However the mechanisms of polyphosphate interaction with soil minerals before hydrolysis is not well understood. As part of the Sustainable In situ Remediation Cooperative Alliance (SIRCA), the objective of this study is to determine P speciation, chemical fate, and movement of polyphosphate in cold climate aquifer soils.

Approach/Activities. This research studies the chemical speciation and movement of a polyphosphate amendment application to PHC contaminated aquifer cold soil site. Underground horizontal perforated injection lines have been installed on-site as an amendment delivery system. These lines were used to apply the polyphosphate amendment at a depth of 1.5m while the targeted zone of PHC extends to a depth of 4.5m. Soil samples were collected at vertical and horizontal gradient of the site to determine the speciation of P as it moves through the soil to determine potential P bioavailability. Phosphorus speciation will be measured using X-ray absorption spectroscopy (XAS) and sequential chemical extractions to determine the fate and potential bioavailability of P.

Results/Lessons Learned. The polyphosphate amendment has shown to effectively infiltrate through the soil profile to the desired depth of 4.5m, as indicated by total P concentrations along the vertical gradient. Phosphorus speciation throughout the site is dominated by calcium phosphate mineral species. The mineralogy of the site is rich in both calcite and dolomite minerals indicating that as the polyphosphate slowly infiltrates and hydrolyzes it is forming surface precipitates on these minerals. This would initially act to reduce P bioavailability and thus limit bioremediation although in the long-term P soil loadings are increasing and this phase may provide continued low levels of phosphate to the soil solution.

Phosphate Reactive Transport in Hydrocarbon Contaminated Cold Soils

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Background/Objectives. In many subsurface systems contaminated with petroleum hydrocarbons (PHC), microbial degradation is limited by availability of phosphorus (P). Effective delivery of phosphorus to hydrocarbon-contaminated soils is challenging due to the high affinity of phosphate with mineral surfaces and low solubility of calcium phosphate minerals. Research is needed to improve efficient transport of phosphate to contaminated subsurface areas and accurately model the geochemical processes that limit nutrient availability in flow-through systems.

Approach/Activities. This laboratory-scale project involved the design and construction of soil columns to assess the phosphorus transport kinetics in saturated flow conditions. Fifty cubic cm columns were chosen to ensure saturated flow over the column's entire cross sectional area, and saturated conditions were maintained via pumping reactants from the bottom of the column. The specific soils studied are calcareous subsurface soils from Saskatchewan, Canada that are hydrocarbon contaminated sites. These soils are generally very low in organic matter with neutral to slightly alkaline pH and high calcium concentrations. Changing the geochemical properties with soil pretreatments (Ca depletion, low molecular weight organic acids (LMOA) and Ca saturation) is expected to change phosphorus transport rates compared to unaltered (control) soils from the site. Effluent from the columns is collected at regular intervals using automated fraction collectors, and a colorimetric method (molybdenum blue) is used to determine concentration of P in the effluent samples. Data collected is used to create breakthrough curves (BTC). Using these BTCs we can determine characteristics of the adsorption-desorption non-equilibrium and soil-solvent-solute interactions of the P on the soil characteristics.

Results/Lessons Learned. Since the soils being used will be high in calcium, it is to be expected that low solubility calcium phosphate minerals will precipitate and be the dominant initial P species in the system after P addition. Pre-treatments applied, such as low molecular weight organic acids (LMOA), aid in phosphate mobility, as the organic acids and phosphorus compete for the same binding sites, and Ca-LMOA aqueous complexes may also prevent the formation of phosphate precipitates.

Geochemical Approaches to Enhance Phosphorous Availability and Stimulate Hydrocarbon Degradation in Cold Soils

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Background/Objectives. In the clay rich, calcareous soils of Western Canada, phosphate availability is one of the major limitations to microbial degradation of PHC. Phosphate availability is quite limited in subsurface environments due to a combination of adsorption on iron oxide and carbonate minerals and calcium phosphate precipitation reactions. Phosphorous availability issues have been encountered in not only aerobic remediation sites, but also at several other test sites where alternative electron acceptors (e.g., nitrate and sulfate) have been used to promote PHC degradation, suggesting this is a general limitation to hydrocarbon remediation for cold soils. Accordingly, our research group is investigating the effectiveness of increasing phosphate solubility via (a) changing the form of phosphorus added, (b) adjusting the site's geochemical conditions with $MgSO_4$, (c) adding low molecular weight organic acids to both compete with phosphate adsorption and chelate calcium.

Approach/Activities. Our research combines laboratory-based research into rates and mechanisms of adsorption/desorption with field-scale sampling of contaminated sites where different phosphate management strategies are being tested. In both cases, we characterize the availability of phosphate with sequential chemical extractions and the mechanisms of phosphorus retention with molecular-scale spectroscopic measurements of soil solids. The methods used for solid-state speciation include synchrotron-based X-ray Absorption Near Edge Structure, X-ray Microprobe, and X-ray Diffraction spectroscopies, as well as laboratory-based Fourier Transform Infrared spectroscopy.

Results/Lessons Learned. Our results indicate that the best methods to increase phosphorus transport are to work with rather than against current geochemical conditions on the site. We achieve this by directly measuring what the major sinks are for phosphate in cold soils, and then developing site-specific nutrient management strategies for remediation. Our overall strategies involve (a) Providing continuous low concentration phosphate flow rather than large spikes (b) Addition of Mg in this source can result in Mg saturation of surface sites that inhibits calcium phosphate mineral precipitation (c) Providing a more mobile polyphosphate species that eventually hydrolyzes after transport and (d) Adding organic ligands that can compete for phosphate adsorption sites on mineral surfaces.

Evaluating Biochar Amendments and Phosphate Polymers for In Situ Hydrocarbon Remediation in Cold Soils

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Background/Objectives. The historical release of petroleum hydrocarbons contaminants into soil and groundwater systems has been a common environmental problem at numerous urban, industrial, and rural settings over the past century. In-situ remediation of these soil and groundwater impacts is greatly preferred over ex-situ remedial methods due to the significant land development and infrastructure issues at play. Additionally, from a cost and environmental sustainability perspective, our research has shown that in-situ methods have the advantage.

Our research has shown that the use of natural microbial communities to degrade hydrocarbons is a less invasive way of using nature to facilitate the reclamation of hydrocarbon contaminated soils and aquifers, but such systems are often phosphorus limited. One potential phosphorus source for remediation in these systems is bonemeal-based biochar made from fish, cattle, or other meat sources. Biochars have been shown to be a cost-effective way to supply nutrients and reactive surfaces and have the potential to greatly enhance bioremediation in hydrocarbon contaminated sites.

This research was conducted as part of Federated Co-operatives Limited’s commitment to the Sustainable In-Situ Remediation Co-operative Alliance (SIRCA).

Approach/Activities. The research site for our studies is a bulk petroleum and gasoline station located in Meadow Lake SK. Our research program was designed to evaluate the performance of phosphorus sources in situations where there are no transport limitations; the soil contaminant and phosphorus addition are in close proximity at all times. For our research program, we used two discrete monitoring wells. One monitoring well was installed in a contaminated location of the site and one in an uncontaminated control area. Segregated soils, obtained from the well installation were each amended with one of a variety of phosphorus sources (both adsorbed phosphorus forms and several different bonemeal biochars). Each amended soil was also spiked with fresh diesel fuel (in the case of the contaminated well), and then reintroduced into the well in permeable soil bags. After 5 and 10 months, soil bags were removed from the wells to evaluate the transformations of phosphorus and their effectiveness as an amendment.

Results/Lessons Learned. Previous studies have demonstrated biochars offer enhanced degradation in laboratory and biopile systems relative to ortho-phosphate additions for Northern soils. This project will determine whether biochars have any significant advantages in subsurface *in-situ* bioremediation. This real world evaluation is an important step that should be undertaken prior to investing in engineering approaches (slurries/emulsions/hydraulic fracturing) that may be required to introduce biochars into subsoil contaminant plumes.

Back to Contents

Evaluating Key Sources of Variability in Pre-Drill Sampling Results at Residential Water Wells

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Background. The media and general public have expressed significant concerns regarding the potential impact of shale gas extraction on surrounding drinking water resources, particularly residential water supply wells. Determining whether changes in groundwater chemistry (methane, salts, etc.) are natural in origin or caused by drilling operations can be difficult, particularly when i) inconsistent sampling and analytical methodologies are employed and ii) water quality can vary naturally over time due to various factors (e.g., intensity of residential water use, well construction, aquifer geochemistry, precipitation events, changes in temperature). Understanding the sources of variability in concentrations of dissolved gases and other water quality parameters and the isotopic signature of dissolved gases in residential water wells is critical to discerning natural changes in water quality from those associated with oil and gas extraction activities.

Objectives. The overall goal of this three-year DOE-NETL-funded research study is to form a better understanding of the inherent variability in pre-drill and post-drill analytical results and develop practical recommendations for improved sample collection methods, sample analysis, and data interpretation for pre- and post-drill sampling programs in areas of active shale gas extraction. Specific aims under Phase I (Year 1) of the project were to i) investigate the effects of common sampling methodologies on resulting pre-drill water well quality and ii) to quantify the degree of variability in methane concentration, isotopic signature, and general water quality parameters over an 18-month period.

Approach/Activities. Two field studies were completed at a series of residential water supply wells in northeast Pennsylvania, to evaluate the significance of sample methodology and temporal effects on observed water quality variability. The selected wells were located greater than 2,500 ft from existing and proposed gas production well locations. The sampling variability study evaluated several potential sources of variability in groundwater quality including different purge volumes (i.e., no purge, purge to parameter stability, and 0.5, 1, and 3 casing volumes), sample collection methods (i.e., direct fill, inverted bottle method), and sampling containers (i.e., 40 ml VOA vials, IsoFlask™). For the temporal variability study, monthly water quality results and real-time weather station, downhole transducer, and water use data were evaluated to quantify the degree of variability in dissolved methane concentrations and identify relationships with general water quality parameters (e.g., redox, temperature, pH), aquifer characteristics, and water use.

Results. Evaluation of various sampling protocols revealed that the selected sample container has a predictable, and in some cases significant, effect on dissolved methane concentrations, while the volume of water purged prior to sample collection does not exhibit an obvious relationship with dissolved gas concentrations. In addition, our data show that, over time, dissolved methane concentrations correlate with redox indicator parameters as well as concentrations of total dissolved solids and associated dissolved ions. These findings improve our understanding of the inherent variability in pre- and post-drill results and offer insight into methods for improving sample collection protocols and data interpretation.

Preservation of Dissolved Gas Samples Collected via Displacement Methods

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Background/Objectives. Previous work has identified large sampling event to sampling event variability in methane concentrations. It was realized that one source of this variability was the dissolution of methane into the air. Methods of sample collection based on displacement of water were developed to help reduce this variability. However, this also resulted in the displacement of any preservatives.
Teflon™ lined septa are permeable to oxygen, and in displacement filled samples the oxygen introduced via diffusion through the septa along with the lack of a preservative can introduce substantial bioactivity. This causes a lack in accuracy, but what's more the population of active bacteria can vary extensively among vials from a single sample, so there can be a large variation in the actual concentrations that appears to be poor precision.

Approach/Activities. A procedure was developed for adhering a solid preservative to the walls of the sample vial, such that the preservative is not lost during displacement sampling. This procedure can be used for a variety of sampling methods, and insures that an effective quantity of preservative is added to each sample. This allows for a separation of the effects of preservation and sampling, enabling a careful evaluation of sampling methods that are less time consuming.

Results/Lessons Learned. A basic preservative was coated onto the bottom of three 40 ml vials. The three vials, as well as a fourth, untreated 40 ml vial, were filled via a displacement method known as the "bucket method". After several volumes were displaced from the vials, a pH strip was placed into the vials immediately before they were capped. Time series photography showed that within 35 minutes the pH in the treated vials was an inhibitive 10 while it was neutral in the untreated vial.

Organically-Modified Silica Hydrogels with Encapsulated Bacteria for Bioremediation of PAH from Hydraulic Fracturing Waters

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Background/Objectives. Hydraulic fracturing is a nonconventional method for extraction of oil and gas which pollutes extensive amounts of fresh water. This process involves pumping water, sand, and chemicals into deep shale wells at high pressures to create fractures, releasing oil, natural gas, and other organic compounds. The water used during these operations, highly polluted with the added chemicals and the hydrocarbons from the well, is then recovered prior to oil and gas extraction (produced water). Many of the chemicals found in the produced waters, including polycyclic aromatic hydrocarbons (PAH), are known toxins, mutagens, and carcinogens and pose an enormous hazard to the environment and human health. Bioremediation is a promising technique for removal and destruction of the pollutants, rather than concentration for landfill disposal as in conventional technologies. Natural microorganisms which can biodegrade PAH are ubiquitous in the environment and can be harnessed for the treatment of produced waters through bioencapsulation, where the cells are confined within a 3D structure. In this study, an organically-modified silica encapsulation system was developed to maximize the removal of PAH bioremediation by the encapsulated bacteria while maintaining the structural integrity of the gel.

Approach/Activities. Silica gels with encapsulated Pseudomonas putida NCIB 9816-4 were prepared sol-gel synthesis with MTMS (methyltrimethoxysilane) and TMOS (tetramethoxysilane). A range of gel hydrophobicities were generated by varying the silicon alkoxide precursor ratio R (MTMS/Total). The gels were characterized to determine their hydrophobicity, microstructure, mechanical properties, adsorption, and biodegradation activity. The hydrophobicity of each gel was determined by measuring the water contact angle and fluorescence intensity of Nile Red, a lipophilic probe. The microstructure of the gels were evaluated by scanning electron microscopy (SEM). The mechanical properties were determined by testing cylindrical samples in axial compression. Equilibrium adsorption experiments were performed to measure the adsorption of fluorene. Finally, the degradation and total removal of hydrocarbons from a synthetic fracking produced water solution containing phenol, p-cresol, indole, p-methoxyphenyl methyl sulfide, azulene, naphthalene, and phenanthrene was measured by GC-MS after 48 hrs.

Results/Lessons Learned. Incubation of the gels with a hydrocarbon solution showed enhanced removal of the hydrocarbons with increasing gel hydrophobicity. Equilibrium adsorption studies showed that the more hydrophobic gels adsorbed fluorene more than 150 times higher than the most hydrophilic gel. The water contact angle results indicated that the gels became more hydrophobic with increased methyl groups. Investigation of the gel microstructure by SEM revealed two distinct regimes: at $R \leq 0.6$, the microstructure was homogeneous, with pores ~ 5 nm in size, whereas for $R \geq 0.8$, aggregates of particles ranging from 1-10 µm were observed. Maximum stress at fracture was $\sigma f = 1.1 \pm 0.1$ MPa ($R=0$) for gels aged in PBS and a minimum value of 16.43 ± 3.45 kPa ($R=1$).

This study showed that the removal of PAH can be enhanced by increasing the hydrophobicity of the gel. While the mechanical properties decreased with increasing MTMS content, the gel with the highest removal was still mechanically stable.

Algae-based Treatment of Hydraulic Fracturing Flowback Water: Metal Removal and Lipid Accumulation by Green Microalgae *Dunaliella salina*

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Background/Objectives. Hydraulic fracturing of a horizontal well requires large amount of water: Two to seven million gallons of water mixed with different additives are required, of which about 9% to 53% returns (Pennsylvania numbers) to the surface. The resulting wastewater, referred to as flowback water, carries naturally-occurring underground contaminants (e.g., salts, heavy metals, radionuclides, and gases) and chemicals added to enhance natural gas recovery (e.g., biocides, corrosion inhibitors, polymers, and solvents). Increasing use of hydraulic fracturing technology is calling for the development of new, cheaper and environmental-friendly flowback water treatment solutions. Some microalgae have high salinity tolerance and are promising candidates for bioremediation of fracturing flowback water. Microalgae have been shown to tolerate and efficiently remove inorganic contaminants, including heavy metals. In addition, certain algal strains accumulate high level of lipid when cultivated in hypersaline media and they are therefore attractive for biodiesel production. However the capability of microalgae to grow in hydraulic fracturing flowback water and the effects of flowback contaminants on the algal lipid accumulation has not been investigated.

Approach/Activities. In this study, we explored the possibility of using hyperhalophilic (salt tolerant) microalga, *Dunaliella Salina,* for the removal of toxic metals from flowback water and biodiesel production. The effect of selected metals on lipid accumulation and composition was also investigated. We cultivated *D. salina* to grow on two samples of flowback water from natural gas extraction. Different dilutions of flowback water samples were introduced into 125-mL conical flasks, supplemented with essential algal nutrients, and sterilized. The flasks were then inoculated with pure culture of *D. salina* and incubated on an orbital shaking under constant lighting. Similar experiments were conducted with the same water samples but without supplemental salts and without sterilization. The algal biomass growth was monitored by the optical density (680 nm) and triacylglyceride (TAG) content of cells was measured by GC-MS after conversion into fatty acid methyl esters (FAME). In order to determine the potential of *D. salina* for the treatment of flowback water, a selection of metals of environmental concern was analyzed in the medium before and after the growth of algal biomass using ICP-MS.

Results/Lessons Learned. The highest algal growth was recorded in flasks containing flowback water without dilution. Dilution of the samples resulted in lower growth and no growth was recorded in samples diluted 64 times. Experiments conducted without supplemental salts resulted in growth inhibition in one of the two samples. The absence of sterilization also resulted in absence of growth in the same sample, presumably because of the presence of inhibiting microorganisms or loss of volatile contaminants. No significant difference was observed in TAG profile of *D. salina* in different treatments but the results support the hypothesis that exposure to toxic contaminants may increase cellular lipid accumulation. A significant removal of seven metals (out of the ten metals analyzed) was observed in at least one of the samples. Some metals (i.e., aluminum, barium, manganese, and strontium) were significantly removed in both samples. These results provide a proof-of-concept that raw fracturing flowback water can sustain the growth of the halophilic microalga, *Dunaliella Salina.*

Does Wastewater from Energy Resource Development Select for Antimicrobial Resistant Bacteria?

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Background/Objectives. Biocides are added to hydraulic fracturing fluids to inhibit corrosion and prevent downhole clogging. Well operators report using up to 1000 gallons of chemicals for biocidal purposes per fracturing event. Biocides with a variety of chemical structures are used including brominated (e.g., bronopol), chlorinated (e.g., quaternary ammonium chlorides), and azine (e.g., methylisothiazolinone) compounds. Large volumes of produced water are generated during development and operation of fractured oil and gas wells. This wastewater is often reused, treated and released to surface water, or disposed of in deep underground injection wells. The objective of this study was to determine if streams (water and bed sediment) impacted by this wastewater disposal contained elevated levels of antimicrobial and antibiotic resistance genes compared to unimpacted locations.

Approach/Activities. Stream water and bed sediment were sampled downgradient from a suspected leaking wastewater holding pond at a disposal facility in West Virginia. Background samples collected upgradient and off site were collected for comparison. Several water chemistry parameters were analyzed including pH, conductivity, and iron speciation.

Quantitative PCR (qPCR) was performed on DNA extracts for genes related to antimicrobial and antibiotic resistance. Several genes related to antibiotic resistance were analyzed because resistance mechanisms may provide protection from antimicrobial agents or other toxic compounds. The analysis suite included genes related to sulfonamide (*sul*1, *sul*2), tetracycline (*tet*(O), *tet*(W), *tet*(G)), and macrolide (*erm*F) resistance. Gene copy numbers were normalized to 16S rRNA gene copy numbers as a surrogate for total bacterial population and to correct for differences in DNA extraction efficiency. Whole genome shotgun sequencing was performed on bed sediment extracts using Illumina MiSeq. Sequences were analyzed with MG-RAST and compared to the Antibiotic Resistance Gene Database using a custom code. Cluster analysis with a Simprof test for significance was performed on the suite of log transformed, normalized gene copy numbers across sampling sites. Analysis focused on genes specifically related to biocides used in hydraulic fracturing (e.g., *qac*B for quaternary ammonium chloride biocides).

Results/Lessons Learned. Potential wastewater impacts were indicated by elevated conductivity and evidence of reducing conditions at downgradient sites. Resistance gene profiles from impacted sediments were more similar to one another than to those from background or moderately impacted sites. However, significant differences in the overall gene profiles between sites were not observed. Certain antibiotic resistance genes (e.g., *mex*B in bed sediment) were at higher relative abundance in moderately impacted areas compared to background. The change in resistance profiles may be related to shifts in the bacterial community following exposure to wastewater. Preliminary results indicate that complex selection processes may exist for and against different resistance genes in environments impacted by oil and gas wastewater. Ultimately results from the resistome will be incorporated with chemical species to begin to understand the complex interactions between the unconventional oil and gas wastewater chemistry and the microbiome.

Back to Contents

Lessons Learned from Deployment of CO_2 Efflux Monitoring Methods

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Background/Objectives. Quantifying rates of natural source zone depletion (NSZD) of petroleum hydrocarbons is important for receiving regulatory approval of NSZD as a remedy. After nearly a decade of research, two new methods are available to monitor and assess NSZD utilizing carbon dioxide (CO_2) efflux measurements collected at the ground surface. These methods were deployed on multiple sites across North America and Hawaii and the results indicate that NSZD can be effectively estimated via stoichiometric conversion of CO_2 efflux measurements at ground surface with a soil flux system and CO_2 traps. Measurements were collected from eight sites and field technicians and data analysts have observed various anomalies that have led to better understanding of the methods. This presentation will discuss the lessons learned for the two CO_2 efflux monitoring methods and provide the attendees with honest, practical guidance including information on use of the methods, costs, and their advantages and disadvantages.

Approach/Activities. The LICOR 8100A automated soil flux system (LI-COR BioSciences, Inc., Lincoln, Nebraska) uses an infrared analyzer and pump unit to measure CO_2 collected from the headspace of a hood that is set on a shallow soil collar embedded into the ground surface. The soil CO_2 efflux is calculated using a theoretical curve fit of the CO_2 concentration versus time data series. In contrast, the E-Flux CO_2 trap (E-Flux, LLC, Fort Collins, Colorado) is a patented sorbent unit consisting of three components, an open ended polyvinyl chloride (PVC) receiver pipe, a short PVC trap equipped with a moisture resistant media that adsorbs CO_2, and a protective cover. The trap assembly is set into a shallow hole, securely backfilled, and left in-place for a typical two to three week deployment period. During this time the CO_2 emitted from the subsurface is captured on the sorbent. At the end of the deployment period, the trap is retrieved and sent to the E-Flux laboratory for analysis. These methods were deployed at eight different sites to measure the amount of CO_2 resulting from natural degradation of petroleum hydrocarbons.

Results/Lessons Learned. While the methods were effectively able to measure CO_2 and estimate NSZD, there were specific lessons learned associated with each method. Examples of general lessons learned from CO_2 efflux monitoring included:

- Install duplicates in close proximity to each other using carefully controlled consistent installation methods to assess heterogeneity of CO_2 efflux,
- Institute standard procedures for installing the instruments, such as removal of vegetation and use of a standard weight for consistent re-compaction, and

Specific lessons learned from deployment of the LI-COR soil flux system included:

- Perform collar installation and measurements during clear weather conditions to avoid short-term bias/effects of rainfall
- Perform background measurements in multiple areas according to ground cover type

Specific lessons learned from deployment of the E-Flux CO_2 traps included:

- Pre-screen the CO_2 concentration or flux at the site to optimize the locations and number of traps deployed
- Utilize ^{14}C isotopic analysis to more accurately correct for background

Combined Use of Isotope Analysis and Passive CO_2 Flux Traps to Estimate Field Rates of Hydrocarbon Degradation

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Background/Objectives. As a result of a petroleum-driven economy, light non-aqueous liquid (LNAPL) contaminated sites in the US still make up a large portion of the environmental liabilities. While a large number of remedial technologies are available to deal with these sites, biodegradation-mediated natural source zone depletion (NSZD) is gaining widespread use as both as a candidate remedy and as a reference to evaluate the efficiency of active remedies. Previous work by our group and others has documented the importance of field-measured estimates of NSZD. Groundwater measurements can provide qualitative lines of evidence of the processes associated with NSZD (such as the depletion of electron acceptors). Since the end products of NSZD (CO_2 and methane, which in turn easily biodegrades as in encounters atmospheric O_2) are gases, estimates based on CO_2 gas transport in the vadose zone often exceed those based on groundwater measurements.

Approach/Activities. Our group has developed a novel CO_2 trap that provides average time-integrated flux measurements at ground level (grade). This design allows for free gas flow through the trap, allowing for the direct measurement of time integrated soil CO_2 effluxes (rather than single time measurements as in other approaches). The CO_2 traps have been tested in the laboratory and used at multiple field sites. After laboratory tests, we have multiple years of field experience using these CO_2 traps and using these data towards the refinement of site conceptual models.

This approach relies of being able to differentiate between background CO_2 fluxes (CO_2 generation from natural soil processes related to non-petroleum related microbial and plant activity) from those resulting from petroleum NSZD. This work will review isotopic data for two sites in different geographic locations, comparing ^{14}C and ^{13}C data with other lines of evidence of microbial activity. Additionally, the ^{13}C ratio has been correlated to ^{14}C data at additional sites, to illustrate the usefulness of both isotopes for two source model allocation of modern vs. ancient contributions to the CO_2 flux.

Results/Lessons Learned.
The data suggest that the measured natural attenuation rates are often significant. These rates can be incorporated into management plans by providing benchmarks for active remedies and also as means to estimate long-term longevity.

Carbon isotopic data indicates that modern carbon CO_2 fluxes are highly variable (both spatially and temporally). Thus, it is very important to only account for petroleum-derived CO_2 fluxes while estimating NSZD rates. In combination with carbon isotope data, available two source models offer a simple solution for this need. ^{14}C particularly offers an unambiguous differentiation of such sources.

Comparisons of the measured NSZD rates with other lines of evidence of microbial petroleum degradation (i.e., soil temperatures and microbial activity) at multiple sites consistently provide improved, self-consistent conceptual site models that lead to more efficient LNAPL management decisions.

Multi-Element CSIA in the Assessment of Attenuation at a Chlorinated Ethenes Plume: An Application at a Complex Contaminant Plume

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Background/Objectives. In the recent years, CSIA has gained widespread acceptance as a tool in contaminant attenuation assessment for several key groundwater contaminants, such as chlorinated ethenes (CEs) and MtBE. However, interpretation of CSIA data from contaminated sites is often challenging. In comparison to case studies presented in peer-reviewed literature, actual industrial CSIA applications are often conducted at sites that are not as well characterized (e.g., fewer CSIA sampling points, complex hydrogeology, unknown contaminant sources, uncertain site lithology). The main goal of this presentation is to illustrate the potential of CSIA in characterization contaminant attenuation in a relatively complex and challenging environment and to illustrate the significance of adequate sample coverage at such sites.

Approach/Activities. The study was conducted at the CE plume at Hill AFB, Utah (Operable Unit (OU) 10). The plume consisted of a shallow subunit (primary shallow TCE source) and a deep subunit formed by leakage of the shallow source TCE into a deeper aquifer. The site was extensively studied in the past and historical logs of contaminant concentrations, geochemical parameters and detailed lithology were available. The igh density monitoring well network allowed greater spatial CSIA sampling density than that practical at the majority of contaminated sites. The samples were analyzed for CE concentrations and the C, Cl and H isotope ratios. The data obtained were interpreted following the standard CSIA methodology, to identify the prevalent attenuation processes and to estimate the attenuation yields. Finally, the interpretation process was repeated using a restricted CSIA database to simulate the “typical” data sets that would be collected in routine site assessment projects.

Results/Lessons Learned. CSIA data showed localized zones of reductive dechlorination of TCE in the peripheries of the shallow (aerobic) subunit, in the vicinity of fine grained sediment, but no evidence of aerobic degradation. More widespread evidence of degradation was apparent in the deep (anaerobic) subunit. Contrary to the idealized CE attenuation paradigm, the degradation was localized rather than showing a gradual progress along the plume gradient, even in the anaerobic deep plume. The maximum of TCE degradation occurred in the “source” area of the deep plume subunit. The results highlighted the significance of aquifer geology in controlling CEs attenuation and the attendant isotope fractionation. Interbedded clay layers and the clay aquitard likely provided conditions conducive to reductive dechlorination, and also controlled physical processes, such as transport, sorption, and diffusion. It is likely that the dechlorination occurred in the interbedded clay layers, where reductive conditions might be stronger, followed by back-diffusion of the CEs in the aquifer. The conclusions obtained from the full data set were then compared to the conclusions based on restricted data sets (representing the typical scope of sampling in routine site assessment). While the overall identification of the predominant degradation mechanisms would be generally unaffected, it is apparent that spatially localized features can be easily missed in low resolution sampling. One conclusion from the present work is that samples collected at lithology transitions zones may be particularly informative.

To What Extent Can C Isotopic Analysis Help Substantiate Natural Attenuation of Chlorinated Ethenes in Groundwater?

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Background and objectives: PCE DNAPL contamination at the former central dry cleaning facility in Rødekro, Denmark, was subject to thermal (steam) source zone remediation in late 2006. A > 2 km long plume of chlorinated ethenes (PCE and chlorinated degradation products) which has migrated downgradient from the source zone has not undergone active remediation. A study of the natural degradation within the plume prior to source treatment including stable isotope monitoring was conducted in 2006(-2007) by Hunkeler et al. (2011). This investigation documented complete degradation of PCE via TCE to DCE by reductive dechlorination 1-1.5 km downstream the source area, where the plume descends into more reduced groundwater. It further proved that cDCE was further degraded by reductive dechlorination to VC, and that VC was not accumulated but further degraded. Detection (< quantification limit) of specific degraders (Dehalococcoides) enforced that cDCE degradation was biotic reductive dechlorination. The understanding of the degradation within the plume, not least the documentation of VC degradation, was essential in the risk evaluation of the plume.

The objective of the new (2014) study is to evaluate how the source remediation has impacted the plume and in particular the natural attenuation within the plume. C isotopic analysis is expected to play an important role to substantiate the natural attenuation of the plume.

Approach: The evolution in plume composition and attenuation has been monitored by the Region of Southern Denmark on an annual basis since the remediation, and in 2014 a large monitoring campaign including redox, chlorinated ethenes, non-chlorinated degradation products, carbon and chlorine stable isotope composition, as well as specific degraders and their activity was conducted.

Results/Lessons learned: The source remediation has, in addition to direct reduction of the concentration level in and flux from the source area, resulted in the release of dissolved organic matter and some geochemical changes. This has had an effect on redox conditions and biodegradation by reductive dechlorination particularly in the near source area. However, also in the further downstream area of the plume redox and contaminant levels have changed, suggesting an evolution in natural attenuation at significant distance (>1 km down-gradient) from the treated source area. Stable carbon isotopic fractionation revealed significant changes (increase) in the degree of degradation of cDCE in particular both near the source area and > 1 km down-gradient which co-inside with the reduction in redox conditions. The findings document a significant increase in cDCE degradation without accumulation of VC. This reduces the risk posed by the contaminant plume to the drinking water resource. Stable chlorine isotope analysis is currently being conducted for cDCE. Dual isotope and microbial data will be processed for further interpretation of the changes in redox and degradation processes within the plume.

This project is unique in the integrated characterization approach for line of evidence evaluation of the natural attenuation of cDCE and VC in the cDCE dominated plume and the monitoring of the effects of source remediation on plume natural attenuation.

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Reference: Hunkeler, D.; Abe, Y.; Broholm, M. M.; Jeannottat, S.; Westergaard, C.; Jacobsen, C. S.; Aravena, R.; Bjerg, P. L., Assessing chlorinated ethene degradation in a large scale contaminant plume by dual carbon-chlorine isotope analysis and quantitative PCR. *Journal of Contaminant Hydrology* **2011,** *119*, (1-4), 69-79.

Demonstration of Natural Attenuation of Chlorinated Ethenes through the use of an Improved Conceptual Site Model, Compound Specific Isotope Analysis, and Magnetic Susceptibility

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Background/Objectives. This case study demonstrates how reinterpretation of existing hydrogeologic information and use of specialized analytical techniques can be used to demonstrate natural attenuation as an appropriate corrective measures alternative at a RCRA Corrective Action Site located in San Diego, California. Previous remedial efforts had mitigated the soil impacts; however, residual groundwater impacts remained (predominantly tetrachloroethene [PCE], trichloroethene [TCE], and 1,1-dichloroethene [1,1-DCE]). The project was at a key milestone when it was assumed by the current team. Classical lines of evidence suggested that natural attenuation through biologic processes was not occurring; however, an explanation through abiotic transformation had not been explored.

Approach/Activities. The Conceptual Site Model (CSM) was reinterpreted to include hydraulic head data that were previously considered anomalous. The inclusion of these data suggested a vertically downward hydraulic connection between the upper and lower water bearing zones that was documented to be occurring in an area of limited cementation and caliche veins compared to elsewhere on the site. Additional monitoring wells were installed to confirm the hypothesis. Monitoring wells were then identified along reinterpreted groundwater flow paths and sampled for compound specific isotope analysis (CSIA) of PCE, TCE, and 1,1-DCE. CSIA data derived from sampling of multiple wells along flow paths within areas of groundwater impact were used to demonstrate that degradation has occurred. Geochemical indicator parameters were obtained to confirm previously documented natural attenuation conditions. Samples of the aquifer matrix were obtained and analyzed for mass magnetic susceptibility. Magnetite has the ability to degrade chlorinated ethenes on the mineral surface through either a reaction with the Fe^{2+} within the mineral structure or with Fe^{2+} species sorbed to the surface of the mineral.

Results/Lessons Learned. Findings from the investigation activities confirmed the hydraulic connection between the upper and lower water bearing zones. The CSM was updated to reflect the reinterpreted groundwater flow paths. Decreasing concentrations of chlorinated ethenes along these groundwater flow paths were documented. Geochemical indicator parameters show that groundwater within the two water bearing zones was similar and characterized by aerobic conditions. The results of the CSIA provide strong evidence that 1,1-DCE is degrading along groundwater flow paths and reasonable evidence that this is also occurring with TCE. Although not explicit in the CSIA findings, concentration data provide evidence that PCE is also degrading. The magnetic susceptibility values are within the range shown to be responsible for the abiotic transformation of chlorinated ethenes as documented by the U.S. EPA. The findings demonstrate that natural attenuation is occurring and that impacted groundwater is confined to the site, based upon a reinterpretation of the CSM and collection of specialized data.

What has 180,000 qPCR Analyses Taught Us?
Database of Concentrations of Key Microorganisms and Functional Genes

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Background/Objectives. Quantitative polymerase chain reaction (qPCR) assays targeting aromatic oxygenase and benzylsuccinate synthase (*bss*A) genes have long been utilized to assess biodegradation at petroleum impacted sites especially when evaluating monitored natural attenuation (MNA). Likewise, *Dehalococcoides mccartyi* quantification is an indispensable component of assessment, remedy selection, and performance monitoring at chlorinated ethene sites. With extensive, widespread and long-term use of qPCR, the data are now available to determine the range of field concentrations of key microorganisms and functional genes and attempt to answer the question "What do these numbers mean?". This presentation describes observations extracted from a database of over 20 years of qPCR results performed on more than 27,000 unique environmental samples.

Approach/Activities. The database is an internally designed and maintained laboratory information management system containing qPCR results for more than 27,000 unique groundwater, soil, and sediment samples from all 50 states and 33 countries. Driven by field samples, the dataset is a reflection of common contaminants and site management practices including MNA. While containing approximately 100 unique gene targets, the most expansive datasets are the more frequently performed qPCR assays: (1) halorespiring bacteria (e.g. *Dehalococcoides mccartyi*), (2) reductive dehalogenase genes (e.g. vinyl chloride reducases), (3) functional genes involved in the aerobic (e.g. toluene monooxygenase) and anaerobic (e.g. benzylsuccinate synthase) biodegradation of petroleum hydrocarbons, (4) methane monooxygenase genes, and (5) functional genes for electron accepting processes. An external portal allows retrieval of percentile rankings of specific qPCR results and uploading of chemical and geochemical data to directly investigate the correlations between subsurface microbiology, contaminant biodegradation, and site management activities.

Results/Lessons Learned. Overall, the results clearly demonstrate the power of analyzing an extensive database in establishing rules of thumb or threshold concentrations of key microbial groups. For example, ethene production was observed in 80% of the samples in which the *Dehalococcoides* population was greater than or equal to 10^4 cells/mL. However, median concentrations of *Dehalococcoides* (n>15,000) and reductive dehalogenase genes (n>9,000) on the order of 10^2 copies/mL suggest that MNA may not always lead to generally effective rates of dechlorination and that careful implementation and routine performance monitoring are essential for successful biostimulation or bioaugmentation at chlorinated ethene sites. The database also can dispel preconceived notions regarding the environmental prevalence of specific functional genes. Detection frequency and median concentrations of *bvcA* and *vcrA* in water samples for example are comparable meaning that analysis of both is needed for thorough assessment. Similarly, BTEX utilizing bacteria are considered nearly ubiquitous. However, detection frequencies near or below 50% for known gene targets involved in anaerobic BTEX metabolism would seem to suggest that anaerobic biodegradation of even the alkyl substituted aromatics (TEX) cannot be universally assumed when assessing MNA as a site management approach.

BioPIC—A Spreadsheet-Based Decision Tool for Deducing Degradation Pathways and Selecting the Most Efficacious Bioremediation Approach for Chlorinated Ethylenes in the Subsurface

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Background/Objectives. Bioremediation, both natural and engineered, has emerged as the preferred remediation approach at many sites contaminated with chlorinated solvents. A number of prognostic and diagnostic tools are available, yet guidance documents to assist site owners in selecting the most efficacious remedy are limited. This paper presents an Excel®-based tool, BioPIC, that guides the user through selection of the most efficacious bioremediation approach at sites contaminated with chlorinated ethylenes. Further, if monitored natural attenuation (MNA) is the selected remedial approach, BioPIC allows the user to deduce the most important degradation pathway(s).

Approach/Activities. Protocols exist for the evaluation and implementation of MNA and biostimulation, yet, there is no clear guidance on how to choose between MNA, biostimulation, and bioaugmentation; a shortcoming that causes unnecessary expenses and potentially detrimental environmental impacts. In addition, the existing protocols are dated and do not consider the state-of-the-art prognostic and diagnostic tools that assist in decision-making. A systematic framework that effectively aids site owners in selecting the best bioremediation approach was developed under a project sponsored by ESTCP. This framework represents an extension of the 1998 USEPA Technical Protocol for Evaluating the Natural Attenuation of Chlorinated Solvents and (i) incorporates quantitative information of *Dehalococcoides mccartyi* biomarker genes, (ii) uses compound-specific isotope analyses (CSIA), (iii) considers the contribution of abiotic transformation of contaminants, and (iv) recognizes that MNA is an important component of integrated remediation strategies. Based on this framework, an Excel®-based tool, BioPIC, was developed to guide users through a decision tree to determine the most efficacious action to meet site-specific remediation goals. The new framework takes into consideration a site's biogeochemical profile in addition to site management requirements such as time constraints for regulatory compliance, cost, and risk tolerance. If bioremediation is required, BioPIC allows the user to determine if biostimulation alone is sufficient to effect site remediation, or if biostimulation in conjunction with bioaugmentation is required. If instead, it appears that MNA is the preferred remedial alternative, then BioPIC aids the user in determining site-specific degradation pathways. Successful selection and implementation of MNA often requires evidence of degradation and specification of degradation pathways.

Results/Lessons learned. BioPIC is a user-friendly Excel® tool based on the new ESTCP framework that integrates groundwater geochemical and contaminant data with quantitative real-time PCR (qPCR) and CSIA information, along with the current understanding of biological and abiotic degradation mechanisms. The integrated approach presented in BioPIC is a robust tool useful to identify the relevant degradation mechanism(s) at a site and to guide users in determining whether MNA, biostimulation, or bioaugmentation combined with biostimulation is the efficacious remedial approach to meet specific cleanup goals.

Back to Contents

Lessons Learned from NSZD Evaluation – CO_2 Flux and Temperature Measurements at an Active Refinery

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Background/Objectives. NSZD can be used as a remediation option for final treatment at a site, or as an economical alternative when active remediation is not cost effective. The main process involved in NSZD at most sites is aerobic biodegradation due to oxygen diffusion through the soil from the atmosphere. Since biodegradation releases heat, temperature measurements can provide an independent method for evaluation of NSZD at sites and the results can be compared to CO_2 flux measurement. In this study, an integrated CO_2 flux/temperature study was carried out at a cold weather refinery with the primary objective being to compare seasonal changes in temperature of the soil and CO_2 flux measurements made at the surface. This study was conducted at two large Tank Fields spanning 111 acres at a refinery site in north-central USA.

Approach/Activities. A CO_2 flux study was carried out to determine the rate of NSZD across the two tank fields. In the study, CO_2 flux was measured 3 times during the year at 40 locations. Over 1000 measurements were collected for this part of the study. An additional 170 CO_2 flux measurements were made hourly at seven locations to document diurnal fluctuations. The CO_2 absorber method was used at 4 locations to collect CO_2 for C^{14} analysis to separate CO_2 derived from vegetative and fossil carbon sources. Temperature measurements were made at different depths down 16 existing monitoring wells within the area of the CO_2 flux study. The CO_2 flux and temperature data were compared to vapor transport/biodegradation modeling estimates of the rate of CO_2 and heat generation based on NSZD of LNAPL at a depth of about 5 feet-bgs.

Results/Lessons Learned. For individual locations in this study, a direct relationship existed between CO_2 flux and temperature. Based on this correlation, it would be concluded that the rate of biodegradation is limited by temperature rather than O_2 supply. However, field measurements also showed a direct relationship between CO_2 flux and moisture content of the soil. This relationship is consistent with the vapor transport/biodegradation model with the rate of CO_2 flux is limited by the diffusivity of the soil. Perhaps due to unique site conditions responsible for the moisture/temperature relationship, the CO_2 flux method was not successful for determining the rate of NSZD at the site. It is recommended that sub-surface methods be used to develop a framework for interpretation of the CO_2 flux results.

A New Way of Looking at Plumes Using Tools Derived from the Ricker Method® Plume Stability Analysis

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Background/Objectives. Evaluation of the relative stability of a groundwater contaminant plume is generating increasing attention as many state regulatory agencies, EPA, and private stakeholders are realizing the applicability of plume stability as part of the environmental evaluation and/or remedial planning process of a site. Specifically, a plume stability evaluation allows the stakeholder to assess whether a contaminant plume is stable, decreasing, or increasing in size, which will allow better evaluation of whether additional remedial action is necessary, or if risk-based closure of a site is applicable, or whether natural attenuation processes may be occurring at a site. The recently published Ricker Plume Stability Method® is a unique method of evaluating plume stability that overcomes limitations posed by conventional well-by-well an-alysis techniques. Outputs from the Ricker Method® can be used to further dissect and evaluate chlorinated plumes allowing the Ricker Method® to be a powerful tool in plume diagnostics.

Approach/Activities. This session presents the Ricker Plume Stability Method®, which entails the use of innovative techniques to calculate and assess historical trends in ground water contaminant plume area, average concentration, mass indicator, and center of mass. We will also present how selected plume diagnostic tools derived from the Ricker Method® can be used for dissecting the characteristics of a ground water plume. Diagnostic tools to be discussed include transect analysis; plume difference evaluation; chlorinated compound molar analysis; commingled plume identification; and secondary compound plume overlays including LNAPL/ DNAPL, carbon source, dissolved oxygen/ORP, and dissolved gases.

A transect analysis allows a specific cross-section of the plume to be sliced and evaluated for that particular section of the plume's unique attributes, which can be tracked at various stages of remediation. A plume difference evaluation allows grid-based plumes to be subtracted to show a quantitative concentration change in any time span. Chlorinated compound ground water plumes can be further evaluated on a molar ratio basis that gives unique signatures to portions of the plume, which can be used to identify the plume's relative age, identify commingling, and evaluate relative progression of dechlorination. Using secondary compound plume overlays on top of the main contaminant plume, we will present examples of how one can evaluate specific areas of carbon sourcing and dissolved oxygen exhaustion to identify areas for future remedial treatment. Lastly, we will provide an example of evaluating bio-remedial indicator parameters that can be used as lines of evidence to identify the progress of MNA.

Results/Lessons Learned. The Ricker Plume Stability Method® has been successfully used to help stakeholders analyze unique groundwater plume characteristics including area, average concentration, and mass indicator, and describe the behavior of that plume as decreasing, increasing, or stable. Further, using the supporting plume diagnostic tools, we have been able to distinguish commingled plumes, demonstrate MNA progression, identify unknown source areas, define specific molar based signatures for chlorinated compounds, reduce monitoring requirements, and close sites.

Geolectrical Characterization and Monitoring of Hydrocarbon Degradation

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Background/Objectives. Hydrocarbon contamination of the subsurface is one of the most common environmental problems in the US and worldwide. Hydrocarbon plumes are not easily treated either due to their size (e.g. Deepwater Horizon (DWH) oil spill) or due to their high recurrence rate. Monitored natural attenuation tends to become the remediation method of choice in cases where there is no direct threat to humans, or other more invasive methods cannot be implemented. For natural attenuation, or even enhanced attenuation, to succeed, rigorous long-term monitoring of hydrocarbon degradation is needed. Methods that can provide continuous data collection at high spatial and temporal densities to permit continuous monitoring of the bio-geochemical processes controlling the contaminant remediation are required. Geophysical methods, frequently utilized to help characterize subsurface contamination, have the potential to be adopted for long term monitoring of contaminant degradation. We have recently monitored oil degradation processes in the aftermath of the DWH oil spill using an autonomous resistivity system. The next step is to develop quantitative links with specific bioremediation processes, so geophysical monitoring can be utilized at other sites.

Approach/Activities. We use the spectral induced polarization method (SIP), an extension to the resistivity method, to collect information not only on the ohmic electrical properties of the subsurface but also the low-frequency capacitive properties. SIP essentially provides us with proxy information on the changes in both fluids and the soil/fluid interface chemistry, making it one of the most promising geophysical methods to monitor oil degradation.

We performed a series of laboratory oil biodegradation experiments whilst continuously monitoring geophysical signals. We have focused our efforts on understudied hydrocarbon impacted saline environments. Sediments from the DWH spill area containing native microorganisms that will degrade oil have been tested under three different salinities, ranging from fresh water to brackish water. All experimental columns, including two abiotic controls, were ran in duplicate.

In a parallel experiment, we focused on alkane degradation only. We utilized a similar approach where biodegradation is promoted while continuously monitoring geophysical signals in addition to conventional geochemical parameters. For this experiment we used well characterized clean Ottawa contaminated with 5% bw heavy oil and inoculated them with *Rhodococcus ruber*. Active and control columns were ran in triplicate.

Results/Lessons Learned. Preliminary results show a dependence of the SIP parameters (both electrolytic and interfacial) on biodegradation processes. As oil degradation progresses, change induced in the pore fluid, mineral grain interface and microbial communities are reflected in the geophysical signals recorded. The fresh resistivity hydrocarbon gradually becomes more conductive as mineral weathering occurs, microbial communities change, and new minerals are formed. Our results suggest that we can link SIP parameters to geochemical and microbial changes occurring during biodegradation.

Utilization of QuantArray-Chlor® and QuantArray-Petro® Analyses to Evaluate Natural Attenuation at a Superfund Site

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Background/Objectives. The Solvents Recovery Service of New England, Inc. (SRSNE) Superfund Site is located in Southington, Connecticut. Between approximately 1955 and 1991, spent solvents were received, recycled and redistributed by this facility. As a result of facility operations, soil and groundwater at the site are affected by chlorinated volatile organic compounds (CVOCs), ketones, furans, and petroleum hydrocarbons. Monitored natural attenuation (MNA) of affected groundwater and dense non-aqueous phase liquid (DNAPL) is a component of the approved site remedy. A microbial survey was performed to support ongoing performance monitoring and evaluation of MNA remedy progress, and in support of an evaluation of the MNA remedy component within the context of other remedial activities at the site, including in-situ thermal remediation.

Approach/Activities. For this survey, Microbial Insights' Bio-Trap® and QuantArray® technologies were employed. Bio-Trap® samplers provide a representative sample of the subsurface microbial community, and QuantArray® is a quantitative polymerase chain reaction (qPCR)-based analysis that allows for assessment of key microbial groups and functional genes that mediate various degradation pathways for specific contaminant classes. Bio-Trap® samplers were deployed at 12 monitoring wells at the SRSNE site. Sampling locations were selected based on historical site data, encompass the variable geochemical conditions and range of constituent combinations observed at the site, and include wells within and outside of the vicinity of DNAPL. QuantArray-Chlor® is a tool to assess the potential for anaerobic reductive dechlorination and aerobic cometabolism of a range of CVOCs. QuantArray-Petro® analysis assesses the potential for aerobic and anaerobic degradation of a range of petroleum hydrocarbon constituents. In addition to enumerating gene copy numbers for microorganisms and enzymes relevant to the degradation of CVOCs and petroleum hydrocarbons, QuantArray® analyses enumerate methanogenic organisms, sulfate-reducing bacteria, and total bacteria to provide additional context for results.

Results/Lessons Learned. QuantArray-Chlor® results indicate robust microbial communities capable of full reductive dechlorination to innocuous end products and cometabolism of chlorinated compounds. QuantArray-Petro® results indicate robust microbial communities capable of aerobic and anaerobic degradation of petroleum hydrocarbons. Together these results support selection of MNA as a remedy for affected groundwater at the site. QuantArray techniques may be useful for other long-term MNA remedy sites where additional lines of evidence for the efficacy of MNA are desired.

Integrating Microbial and Geophysical Methods for Determining Biodegradation Pathways

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Background/Objectives. Traditionally, the bioremediation of hydrocarbon spills has been monitored by geochemical and microbiological methods. These methods require extensive sampling across a contaminated site or along a retrieved sediment core, because usually the locations of the zones of high microbial degradation activities are not known. Here, we are exploring the integration of geophysical techniques, in particular magnetic susceptibility logging, to guide the microbiological sampling of hydrocarbon-contaminated soils and sediment cores. Magnetic susceptibility values have been found to be elevated around the water table at hydrocarbon contaminated sites, probably due to the action of hydrocarbon-degrading and iron-reducing bacteria that precipitate magnetic minerals. Thus, magnetic susceptibility measurements could be used as a guide for targeted microbial sampling and determining the major microbial degradation pathways leading to enhanced bioremediation strategies.

Approach/Activities. Sediment cores were retrieved from the crude oil contaminated site in Bemidji, MN. Total DNA was isolated from core sediment samples and high-throughput DNA sequencing with the Illumina Miseq platform was used to characterize the members of the microbial community. The microbial populations associated with the elevated magnetic susceptibility values were analyzed using the statistical method of nonmetric multidimensional scaling.

Results/Lessons Learned. The magnetic susceptibility showed increased values at the free-phase petroleum contaminated site and in the cores retrieved from this location. The enhanced magnetic susceptibility occurred within the water table fluctuation zone. This was in contrast to the lower magnetic susceptibility values measured at the dissolved phase and the uncontaminated site and in the cores retrieved from these locations. The increase in magnetic susceptibility in the contaminated cores was associated with a methanogenic microbial community, which consisted of methane-producing Archaea, hydrocarbon fermenters and syntrophic Bacteria. Some of the identified Archaea may also be able to reduce iron. Based on our targeted sampling approach, we were able to zoom into the zones of highest microbial degradation activities during field campaigns stretching over several years. The targeted sampling enabled us to identify the dominant microbial populations and to model the dominant hydrocarbon degradation pathways, leading potentially to optimized biodegradation strategies.

Modeling Thermal Anomalies to Estimate the Biodegradation Rates of Hydrocarbon Degradation

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Background/Objectives. Vadose zone contamination is a common problem associated with LNAPL (light non-aqueous phase liquid) spill sites, generating potential risks of groundwater and vadose gas pollution. Natural source zone depletion (NSZD) can be used to evaluate the fate of released contaminants and estimate vadose zone LNAPL biodegradation rates by native soil microbes. Based on thermodynamic considerations and the magnitude of the measured rates, recent work indicates that NSZD might generate anomalous soil temperatures. Such thermal anomalies can be used as an additional line of evidence of contaminant biodegradation and also to estimate heat fluxes that could be used to indirectly estimate NSZD rates, as direct methods based on the mass discharge of contaminant biodegration products such as CO_2 are subject to gas transport limitations at sites that when soil gas transport is impeded (i.e. temporarily by rain events that water-saturate the soil, or by permanent concrete caps). Additional motivation to understand the relationship between temperature and contaminant biodegradation rates at the field sites resides in i) the facility to measure temperature in soils and ii) the potential to use temperature as a control to enhance in situ biodegradation.

Approach/Activities. A transient, one-dimensional soil heat transport model to study processes related to heat generation and transfer in the vadose zone upon petroleum biodegradation was developed. The model developed for this study assumes a simplified three-step biodegradation process consisting of i) anaerobic biodegradation of petroleum hydrocarbon compounds via methanogenesis, ii) subsequent methane oxidation occurring at a narrow zone where methane encounters counter diffusing atmospheric oxygen, and iii) aerobic degradation of contaminant in upper soil layers. The model was calibrated with data from two field sites where methanogenesis has been identified as a dominant anaerobic petroleum biodegradation process: the Bemidji spill site in Minnesota and a former refinery in the Western US. Simulated temperature profiles at different times of the year were compared with field measured data. Biodegradation rates were estimated from simulated thermal gradients, and compared to independent previous reports of NSZD rates. The interfering effects of fluctuating atmospheric and groundwater temperatures on the thermal gradient measurement were analyzed. Additional applications of the model are also explored to include the effects of warmer weather and localized heating at different soil zones (i.e., groundwater vs. surface).

Results/Lessons Learned. Simulated thermal profiles associated with fluctuating seasonal conditions reasonably match the measured seasonal data at both sites for both LNAPL impacted and unimpacted locations. Fluctuating ambient and groundwater temperatures strongly control thermal fluxes through the soil column and make it very difficult to distinguish heat generated from biodegradation (and quantitate contaminant biodegration-based heat fluxes) when looking at soil temperatures alone. However, background correction and averaging methods are promising as they cancel out noise associated with fluctuating boundary conditions and reveal thermal gradients caused by biodegradation of petroleum. Model results indicate that the locations to measure thermal gradients are key to measuring heat generated from biodegradation and that biodegradation at field sites is highly sensitive to weather effects on ambient and groundwater temperature. The magnitude of such sensitivity is also dependent on site-specific conditions such as distribution of the contaminant in the soil.

An Integrated, State-of-the-Art Approach for Evaluating Monitored Natural Attenuation

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Background/Objectives. Former waste disposal activities at Naval Air Station North Island in San Diego, California resulted in the accumulation of NAPL in the shallow subsurface at Site 5, Unit 2 (the Site). Groundwater at the Site is impacted with petroleum hydrocarbons and chlorinated solvents. Tetrachloroethene and trichloroethene, the only chlorinated ethenes found in the NAPL, are completely degraded to cis-1,2-dichloroethene (cDCE) and vinyl chloride (VC) within some 20 feet downgradient from the NAPL. First-order degradation rates vary from 17/year for cDCE to VC and 10/year for VC to ethene, respectively. These are some of the fastest degradation rates ever observed under “natural” conditions and are brought about by a unique set of hydrogeologic and biogeochemical conditions. The presence and disposition of mobile NAPL at this Site complicated the analysis of monitored natural attenuation (MNA) because total chlorinated ethene concentrations have fluctuated greatly over time. Maximum total chlorinated ethene concentrations in groundwater ranged from 550,000 µg/L in 1998 to 14,000 µg/L in 2003 to 587,000 µg/L in 2005 to 3,312 µg/L in 2013. Thus, it was not possible to prepare compelling plots of decreasing solute concentration versus time because there was the fear that a rising water table might result in increasing solute concentrations. Although total chlorinated ethene concentrations exhibited this large variation, which equates to significant variations in mass loading, the downgradient extent of the solute plume has not changed over time; in fact the center of mass for the solute plume has migrated back toward the source and even the highest chlorinated ethene solute concentrations ever observed were completely degraded within 200 feet along the flowpath. Because of the difficulty in showing decreasing solute concentrations over time, MNA was met with significant resistance from regulatory agencies who insisted engineered remediation was required even though strong evidence of chlorinated ethene degradation was observed. Therefore, more robust evaluation of MNA was performed.

Approach/Activities. In order to properly evaluate MNA and to determine the amount of time required for complete Site remediation, an integrated approach using state-of-the-art analytical and computational techniques was utilized. In addition to the standard techniques for evaluating the efficacy of MNA, including an evaluation of contaminant concentrations over time and space and biogeochemistry, several additional techniques were utilized. These included an evaluation of contaminant mass in place (CMIP), compound-specific isotope analyses (CSIA), molecular biological tools, and CO_2 radiocarbon analyses. Once the amount of CMIP was determined and degradation confirmed, the Navy’s Natural Attenuation Software (NAS) was used to simulate the degradation of Site contaminants and estimate the time required for complete Site remediation via intrinsic bioremediation. In addition, an evaluation of the environmental impacts of various remediation approaches was made using SiteWise.

NAS was developed in collaboration with the Naval Facility Engineering Command, USGS and Virginia Tech University.

SiteWise™ was developed jointly by the Navy, Army Corps of Engineers, and Battelle

Results/Lessons Learned. Supporting natural attenuation under the best of circumstances can be difficult. This presentation shows how to integrate the latest tools to prepare a compelling case for MNA at sites where the analysis of MNA is problematic. Using the techniques presented in this presentation, MNA coupled with institutional controls was ultimately selected and approved by the regulators as the most efficacious remediation approach for this Site.

Back to Contents

The Missing Mass Problem—Untangling Fate and Transport Processes in Aquifers

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Background/Objectives. At sites where we have constructed multiple high-resolution mass discharge transects, from the source zone to the leading edge, there is a consistent pattern of decreasing mass discharge along the flow path. We will term this missing mass the *mass discharge deficit*. There are three potential contaminant sinks that can contribute to the mass discharge deficit: 1) reversible diffusive storage and partitioning in lower-permeability zones, which generates back-diffusion after source removal or attenuation, 2) quasi-permanent sequestration by irreversible sorption or mineral assimilation, and 3) destructive attenuation through biological or abiotic reaction mechanisms. Highly resolved hydrogeology and contaminant distribution datasets are now providing a basis for estimating the magnitude of each of the three sinks.

Approach/Activities. We will present mass transport distribution and attenuation results from two chlorinated solvent sites with contrasting hydrogeologic structures: both sites are alluvial aquifers, one formed from generally low-permeability sediments interspersed with sandy lenses and the other formed from higher-permeability sands interspersed with silty lenses. In both cases, a significant fraction of the total solvent mass was stored in the lower-permeability strata. Also in both cases, groundwater velocities in the high-permeability transport pathways were dramatically higher than the corresponding bulk aquifer groundwater velocities.

Results/Lessons Learned. With the highly resolved aquifer structure and contaminant concentration distribution in-hand, we were able to perform analytical calculations to assess mass exchanges across the storage/transport zone interfaces. From these calculations, we present three observations: 1) net migration of contaminants from high-permeability transport pathways into lower-permeability storage zones appears to be the dominant mechanism creating the mass discharge deficit; 2) residence times for contaminants that enter the lower-permeability zones may be quite long and slow-rate biotic and abiotic attenuation processes may be a factor in long-term plume attenuation, however; 3) contaminant exchange rates between higher-conductivity transport zones and lower-conductivity storage/attenuation zones may be quite large, relative to destructive attenuation rates, making the attenuation process difficult to detect through field data analysis.

Can Natural Attenuation Make a Dent in a Complex Mixture DNAPL Source Area?

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Background/Objectives. Installation Restoration (IR) Site 9 at North Island Naval Air Station in Coronado, California (the Site) is a 50-acre site bordering San Diego Bay that includes a former chemical waste disposal area that operated from the late 1940s until the mid-1970s. An estimated 8 to 32 million gallons of liquid wastes were disposed there, and today groundwater beneath the Site remains variably impacted with a complex mixture of chlorinated solvents and ketones including trichloroethene (TCE), cis-1,2-dichloroethene (cDCE), vinyl chloride (VC), 1,1-dichloroethene (1,1-DCE), 1,1,1-trichloroethane (1,1,1-TCA), acetone, 2-butanone (methyl ethyl ketone [MEK]), and 4-methyl-2-pentanone (methyl isobutyl ketone [MIBK]). VOC concentrations in the source area strongly suggest that dense nonaqueous phase liquids (DNAPLs) are present, with maximum concentrations typically as follows: cDCE 460 mg/L, TCE 240 mg/L, VC 72 mg/L, MEK 68 mg/L, MIBK 66 mg/L, 1,1-DCE 55 mg/L, and 1,1,1-TCA 42 mg/L. Contamination at the Site is spread across an approximate 100-foot thick geologic sequence that consists of unconsolidated sand, dense silty sand, and a 5-foot thick silt layer that occurs at approximately 50 feet below ground surface (bgs). A clay layer approximately 20 feet thick occurs underneath the sandy aquifer, which appears to limit the migration of VOCs vertically. Shallow groundwater at the Site is non-saline, and a freshwater/saltwater interface (FWSWI) is encountered at approximately 15 to 20 feet bgs. The presence of saltwater in the subsurface has not impeded vertical migration of VOCs, which extends to the top of the clay layer.

Approach/Activities. The U.S. Navy has initiated a comprehensive investigation to evaluate natural attenuation processes in the DNAPL source area and the groundwater plume at the Site. The investigation includes aquifer microcosms assays, compound-specific isotope analyses (CSIA), biomarker sampling for specific dechlorinating bacteria, and repeated site-wide sampling for groundwater quality. The microcosm assay is evaluating biotic and abiotic degradation in high-strength groundwater (VOC concentrations > 500 mg/L) from the shallow and deep source area (both brackish and saline [sulfate-rich] groundwater), as well as a location from the shallow downgradient plume. For the CSIA tests, a novel CSIA method is being developed by the University of Oklahoma to measure enrichment of 13C during anaerobic biodegradation of ketones. Groundwater samples from the Site will be analyzed for 13C-enrichment in ketones with distance from the source area.

Results/Lessons Learned. Results of site-wide sampling indicate that VOC concentrations in groundwater have declined by more than 50% at the majority of monitoring wells between 1998 and 2013. In general, the ketones appear to attenuate rapidly downgradient of the source. Part-per-million levels of ethene have been detected in the most contaminated portion of the source area, indicating that microbial dechlorination processes are ongoing despite the presence of dissolved phase VOC concentrations > 500 mg/L. The microcosm assays and CSIA tests will be completed by March 2015, and the results will be presented at the Biosymposium in May.

An Integrated Approach for Deducing Degradation Pathways at Sites Contaminated with Chlorinated Ethylenes

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Background/Objectives. Bioremediation, both natural and engineered, has emerged as the preferred remediation approach at many sites contaminated with chlorinated ethylenes. A number of prognostic and diagnostic tools are available, yet guidance documents to assist site owners in selecting the most efficacious bioremediation approach are limited. Although the value of substrate additions (i.e., biostimulation) to enhance contaminant degradation has been demonstrated, this approach may not be needed at sites where monitored natural attenuation (MNA) is sufficient to meet remedial goals. Both remediation costs and associated environmental impacts will increase as more invasive and aggressive treatment options are implemented. Therefore, selection of the most appropriate bioremediation approach can result in substantial savings of capital investment and operation & maintenance (O&M) costs. Furthermore, avoiding unnecessary aquifer amendments, such as substrates and inocula, minimizes undesirable secondary impacts such as pH changes, formation of greenhouse gases, and reduced aquifer permeability. On the other hand, aggressive bioremediation can significantly shorten remedial timeframes, thereby reducing O&M costs as well as long-term environmental impacts. This paper presents an integrated approach that guides the user through a deductive processes that allows identification of degradation pathways for chlorinated ethylenes and selection of the most efficacious bioremediation approach.

Approach/Activities. Protocols exist for the evaluation and implementation of MNA and biostimulation, yet, there is no clear guidance on how to choose between MNA, biostimulation, and bioaugmentation; a shortcoming that causes unnecessary expenses and potentially detrimental environmental impacts. In addition, the existing protocols are dated and do not consider the state-of-the-art prognostic and diagnostic tools that assist in decision-making. A systematic framework that effectively aids site owners in selecting the best bioremediation approach was developed under a project sponsored by ESTCP. This framework represents an extension of the 1998 USEPA Technical Protocol for Evaluating the Natural Attenuation of Chlorinated Solvents and (i) incorporates quantitative information of *Dehalococcoides mccartyi* biomarker genes, (ii) uses Compound-Specific Isotope Analysis (CSIA) results, (iii) considers the contribution of abiotic transformation of contaminants, and (iv) recognizes that natural attenuation is an important component of integrated remediation strategies. The new approach allows identification of existing degradation mechanisms, taking into consideration a site’s biogeochemical profile. In addition, the approach takes into account site management requirements such as time constraints for regulatory compliance, cost, and risk tolerance.

Results/Lessons Learned. The new framework integrates groundwater geochemical and contaminant data with quantitative real-time PCR (qPCR) and CSIA information, along with the current understanding of biological and abiotic degradation mechanisms, to deduce degradation pathways. This integrated approach is encapsulated into a robust Excel® tool, BIOPATH, that is useful for identifying relevant degradation pathways at a site. Furthermore, BIOPATH guides users in determining whether MNA, biostimulation, or bioaugmentation combined with biostimulation is the efficacious remedial approach to meet specific cleanup goals.

Natural Attenuation of Non-Volatile Contaminants at the Oxic/Anoxic Interface in the Vadose Zone

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Most microbial activities takes place at the interfaces and there is a growing awareness that most natural attenuation happens at the fringes of contaminant plumes. When anoxic polluted groundwater encounters the overlying vadose zone it forms an oxic/anoxic interface often at the capillary fringe. Aerobic biodegradation of volatile contaminants in the vadose zone has been studied extensively and it is clear that microbial activity in the capillary fringe can prevent vapor. In contrast, the biodegradation of non-volatile groundwater contaminants in the vadose zone is less well understood. Aniline (AN) and diphenylamine (DPA) are non-volatile contaminants often found in dye and munitions production sites. Both compounds are biodegradable under oxic conditions but not in anoxic plumes

In this study, we determined the potential for biodegradation of AN and DPA at the oxic/ anoxic interface in the capillary fringe. Laboratory multiport columns that represented the unsaturated zone were used to evaluate degradation at the oxic/ anoxic interface.
In the presence of AN and DPA degrading bacteria the biodegradation fluxes of both contaminants were estimated to be 113 ± 26 mg AN • m^{-2} • hr^{-1} and 76 ± 18 mg DPA • m^{-2} • hr^{-1}at the oxic/ anoxic interface. Low effluent concentrations released from the column indicated that natural attenuation of AN and DPA in the capillary fringe can substantially increase the loss of mass from the plume. Oxygen and contaminant profiles along with enumeration of bacterial populations indicated that most of the biodegradation took place within a narrow zone in the capillary fringe. The results extend the understanding of the role of interfaces in natural attenuation and support the idea that the capillary fringe is a key type of fringe whose contribution must be considered.

Natural Attenuation Pathways for Chlorinated Alkane Mixtures: Evaluating the Role of *Dehalogenimonas* in Reductive Dechlorination

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Background/Objectives. A portion of the contaminated groundwater plume at a superfund site located in south Louisiana (USA) contains a mixture of 1,2-dichloroethane (1,2-DCA), 1,1,2-trichloroethane (1,1,2-TCA), and vinyl chloride. While the anaerobic biodegradation pathways for these contaminants have been relatively widely reported for cases in which the contaminants are present as single contaminants, less is known about the contaminant-contaminant interactions that can influence transformation when these contaminants are present in mixtures. In support of the remediation decision-making process for the site, a variety of laboratory-based studies were conducted to assess the composition of the microbial community inhabiting the groundwater, its contaminant transformation potential, and factors that can limit the transformation rate of specific chlorinated alkanes present in contaminant mixtures.

Approach/Activities. Community DNA extracted from site groundwater was used for construction of 16S rRNA gene libraries and as template in PCR and quantitative real-time PCR (qPCR) reactions employing genus-specific primers. Enrichment cultures were established to assess the contaminant transformation potential of the indigenous microbial population and to identify intermediate and terminal degradation products. qPCR was employed to track growth of *Dehalogenimonas* and *Dehalococcoides* during contaminant transformation and facilitate identification of the microbes responsible for transforming key compounds. Because an important contaminant transformation role was found to be played by a previously uncharacterized species in the bacterial genus *Dehalogenimonas*, additional pure-culture experiments were performed to assess pathways and contaminant-contaminant interactions.

Results/Lessons Learned. Analysis of 16S rRNA gene libraries and the use of genus-specific primers in PCR demonstrated that the microbial community in site groundwater contains bacteria clustering within the organohalide respiring genera *Dehalogenimonas* and *Dehalococcoides*. Enrichment cultures inoculated with site groundwater demonstrated that viable microbes indigenous to the site have an ability to transform 1,2-DCA to the non-toxic final product ethene via dihaloelimination. 1,1,2-TCA was found to be transformed to the intermediate product vinyl chloride which was subsequently transformed to ethene. The presence of 1,1,2-TCA was found to substantially influence the rate of 1,2-DCA dechlorination when contaminants were present in mixtures. The use of genus-specific primers in qPCR allowed identification of the complimentary functional roles played by *Dehalogenimonas* and *Dehalococcoides* in contaminant transformation. Sequencing of PCR amplicons revealed the presence of bacteria with 16S rRNA gene sequences not closely related to previously described *Dehalogenimonas* species. Characterization of a pure culture, *Dehalogenimonas* sp. strain NSZ-14, complimented the mixed-culture experimental results and allowed comparison to contaminant-contaminant interactions observed in laboratory enrichment cultures comprised of mixed populations as well as field-scale observations.

Role of Magnetite in the Abiotic Degradation of TCE in Aerobic Groundwater at the Hopewell Site

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Background/Objectives. The Hopewell Precision NPL site is located in Hopewell Junction, New York. The source of contamination is on the Hopewell Precision facility. A plume of groundwater contamination extends about 1.5 miles from the source. The area surrounding the Site is mostly residential. All of the houses are served by private drinking water wells and septic systems. The primary contaminant in groundwater in the down gradient residential area is TCE. Point-of-entry treatment (POET) systems have been installed in 41 homes where TCE was found in well water at concentrations in excess of 5 µg/l.

Over the last ten years, TCE concentrations in groundwater have attenuated. In February 2003, the highest concentration of TCE at the site was 250 µg/L. In March 2013, the highest concentration was 42 µg/L. The low concentrations and a reasonable rate of attenuation over time make Monitored Natural Attenuation a realistic option as a component of the final remedy.

The groundwater is primarily extracted from glacial outwash deposits. The mineral magnetite is commonly found in glacial sands. Magnetite can react with TCE and transform it to oxidized products which are then ultimately transformed to carbon dioxide. The magnetic susceptibility of a sample of sediment is a reasonable proxy for the content of magnetite. Core samples were acquired and analyzed for magnetic susceptibility to determine if abiotic degradation of TCE on magnetite would explain the rate of natural attenuation of TCE in the groundwater.

Approach/Activities. Core samples were collected adjacent to the well screen of 12 monitoring wells that sampled the TCE plume. The cores extended across the screened interval. The core samples were subdivided into 75 sub-cores, and the sub-cores were analyzed for their magnetic susceptibility. The distribution of magnetite was uniform. The average of the magnetic susceptibility of the sub-cores at each of the 12 locations varied 1.2E-07 to 2.7E-07 m^3kg^{-1}. The average magnetic susceptibility for all 12 locations was 1.8E-07 m^3kg^{-1} with a standard deviation of 4.5E-08 m^3kg^{-1}. Rate constants for attenuation of TCE on magnetite are available from microcosm studies that were done with sand from a similar aquifer in Minnesota. Based on the level of magnetic susceptibility in the sediment at the Hopewell site, TCE should degrade with a first order rate constant of 0.15 per year, or a half-life of 4.8 years.

The REMChlor computer application was used to construct a model of the TCE plume at the site. The predictions of the model were compared to concentrations of TCE in the 12 monitoring wells. To match the observed distribution of TCE in groundwater at the site, the first order rate constant for degradation of TCE would need to be 0.065 per year, or a half-life of 11 years.

Results/Lessons Learned. The magnetic susceptibility of the sediment explained the observed rate of natural attenuation of TCE in the groundwater.

Abiotic Reaction & Diffusion of TCE in Rock Matrices

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Background. Chlorinated solvents in rock matrices can serve as a long-term contaminant source in fractured bedrock aquifers, sustaining groundwater plumes for extended periods of time. The intensity and longevity of the groundwater plume will be impacted by the diffusional flux between the rock matrix and adjacent conductive fractures, as well as the fate of contaminants residing within the rock matrix itself. This will be related to the effective diffusion coefficient and the contaminant reaction rate. Naturally occurring degradation processes, particularly abiotic dechlorination processes, have hitherto not been investigated in detail to assess potential impacts on processes such as uptake into the rock matrix, and the potential for back-diffusion to sustain plumes.

Approach. Minimally disturbed rock cores were collected from the former Naval Air Warfare Center in Trenton, NJ. Subsequent laboratory testing was performed on rock cores that had not been exposed to TCE, as well as on rock core that had been exposed to TCE for decades. Laboratory testing included measurement of effective diffusion coefficients within the rock, as well as assessment of abiotic reaction between TCE and ferrous minerals. The impacts of the magnitude of the effective diffusion coefficient and abiotic rate constant on contaminant uptake into the rock, as well as plume longevity, were subsequently evaluated.

Results. Results showed that diffusional flux through the rock matrix was dependent upon both the rock matrix porosity as well as bedding plane orientation. First order abiotic reaction resulting in the complete dechlorination of TCE was observed for all rock types examined. Decades of exposure to TCE did not result in any substantial decrease in abiotic dechlorination activity. Ethene, ethane, acetylene, and propane were the observed abiotic reaction products. While the measured rates were slow compared to dechlorination rates typically considered “useful” for natural attenuation, the relative rates of dechlorination compared to diffusive flux in the rock matrix suggest that these naturally occurring abiotic dechlorination process will likely have a large impact on contaminant migration into or out of rock matrices.

Abiotic reaction was shown to have an impact on the extent of TCE uptake into the rock matrix, as TCE in rocks exhibiting relatively large abiotic reaction rates did not migrate substantially from the fracture face into the matrix. Numerical modeling showed that the natural attenuation timeframes of the sources emanating from the rock matrix were very sensitive to both the effective diffusion coefficient and the first order abiotic rate constant. Overall results of this study show that accurate determination of both the effective diffusion coefficient relevant to bedding, and ferrous iron facilitated abiotic dechlorination, are essential for understanding the impacts of rock matrices on natural attenuation timeframes. For many rock types, rock matrix processes may not be the cause of sustained sources in fractured bedrock.

Back to Contents

Sequential Reducing/Oxidizing/Reducing Conditions Enhances Natural Attenuation at Naval Air Station Whiting Field, FL

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Background/Objectives. Historic co-disposal of petroleum hydrocarbons and solvents during and immediately after WW II at NAS Whiting Field, FL, has resulted in legacy contamination of groundwater by BTEX and chlorinated ethene compounds. The large mass of BTEX compounds in the contaminant source area results in strongly reducing conditions. Much of the contaminant plume, however, is largely oxic (DO~1-2 mg/L). The discharge area of the plume is in an anoxic wetland, exposing contaminants to sequential reducing/oxidizing/reducing conditions along aquifer flowpaths. An experimental laboratory study was undertaken to document the contribution of reducing and oxidizing processes to the natural attenuation of contaminants at this site.

Approach/Activities. Aquifer sediments of deltaic origin were collected within the contaminant plume using vibracoring technology at depths ranging from 60 to 120 feet below land surface. Oxic and anoxic microcosms were constructed using aquifer sediments amended with [UL ring-^{14}C] benzene and [1, 2-^{14}C] cis-dichloroethene (DCE). Additional microcosms were constructed using streambed and wetlands sediments collected from the discharge area of plume.

Results/Lessons Learned. Oxic microcosms constructed with aquifer sediments showed rapid oxidation of both benzene and DCE to $^{14}CO_2$. Anoxic aquifer sediment microcosms also showed significant benzene and DCE oxidation to $^{14}CO_2$, but at a slower rate. Streambed sediment microcosms showed rapid mineralization of benzene to $^{14}CO_2$ under oxic and anoxic conditions as well as mineralization of DCE to $^{14}CO_2$ under oxic conditions. The wetlands sediments, which were actively methanogenic, showed little benzene oxidation, but significant reduction of DCE to ^{14}C-ethene in addition to mineralization to $^{14}CO_2$ and ^{14}C-methane. The results of this study show that the observed sequence of redox processes drives reduction of TCE to cis-DCE in the petroleum-hydrocarbon contaminated source area, oxidation of cis-DCE in the migrating plume, and reduction of cis-DCE in the groundwater discharge area. The reducing/oxidizing/reducing conditions that are encountered along the flowpath confer a substantial natural attenuation capacity to this aquifer system.

Field Comparison of NSZD Assessment Methods: Gradient Method and Two CO_2 Flux Methods

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Background/Objectives. Natural Source Zone Depletion (NSZD) is increasingly used as a component of LNAPL site assessment and remedial strategy. NSZD evaluations can be used to quantify the rate of LNAPL depletion via natural processes. Comparing this rate to actual or expected recovery or degradation rates achievable by active treatment is useful for evaluation of the relative benefit of active remediation. At sites where the effects of active remediation are/or would be less than natural depletion rates, a compelling argument against continuing or implementing active remediation can be made on grounds of efficacy and sustainability.

Approach/Activities. Two approaches, the gradient method (based on concentrations of oxygen and/or CO_2 in soil gas and soil vapor diffusivity) and carbon dioxide flux method (based on measurements of CO_2 flux from the ground surface to the atmosphere), are commonly used to estimate NSZD rates. Both methods were used to assess NSZD rates at multiple locations within a natural gas processing facility in Texas. CO_2 flux was measured using two methods concurrently: a soil flux chamber and infrared gas analyzer, collecting a series of short-term measurements, and CO_2 sorbent traps, collecting a single longer-term time-averaged measurement. Supplemental data to support interpretation of results, including temperature measurements, atmospheric and soil gas pressure data, and precipitation data, were collected and reviewed as part of data analysis.

Results/Lessons Learned. Results indicate that NSZD rates estimated at most locations were generally comparable between the different methods. The results also indicate the importance of quantifying natural processes in background conditions. The current methods used to correct for background conditions will be comparatively evaluated. Differences between each method's results provides insight into factors that influence the representativeness of each measurement approach; these factors will be discussed, along with conditions that make a site particularly favorable or unfavorable for use of each measurement approach.

Natural Source Zone Depletion Rates from Subsurface Temperature Data: A Quantitative Analysis

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Background/Objectives. Natural source zone depletion (NSZD) represents a combination of natural processes that reduce the mass of petroleum hydrocarbon light non-aqueous phase liquid (LNAPL) through phase change and biodegradation. NSZD is increasingly being considered an important component of LNAPL management, as measurements of NSZD rates can serve as a benchmark for determining the relative benefit of active, engineered remedial alternatives (ITRC, 2009).

Current methods of measuring NSZD are based on measurement of soil gas concentrations of oxygen and/or carbon dioxide with soil gas diffusivity, and/or carbon dioxide flux. These methods rely on stoichiometric relationships for hydrocarbon degradation and field measurements to estimate oxygen consumption or carbon dioxide production. These testing mechanisms have limitations in application, primarily at sites with surface caps, e.g., gas stations, where the influx of oxygen or efflux of carbon dioxide is controlled by small-scale permeable features.

The biologically mediated NSZD processes that destroy hydrocarbons and alter the composition of soil gas (e.g., consume oxygen and produce carbon dioxide) also release heat creating temperature anomalies above the natural soil temperature profile. Recent research has focused on measuring temperature in and around LNAPL-affected areas and characterizing thermal anomalies (areas of warmer temperature) associated with exothermic NSZD processes.

Thermal anomalies can be measured in an existing monitoring well network through long-term deployment of dataloggers or instantaneous readings with a thermocouple. This relatively inexpensive data collection can identify where aerobic biodegradation is occurring. Although, thermal anomalies are relatively easy to observe and document, correlations of the extent and magnitude of an anomaly to an NSZD rate are just now being developed.

Approach/Activities. A model was constructed to calculate heat flux associated with thermal anomalies identified in LNAPL source zones and, correspondingly, the rate of hydrocarbon degradation generating the excess heat in the subsurface. Temperature signals from heat sources and sinks unrelated to NSZD processes, such as seasonal variability in radiant heating and cooling at ground surface, are filtered out of the analysis, and the model allows for input of thermal properties of soil and aquifer matrices. The model is calibrated using previous experience and published data. Rates estimated using temperature will be compared to estimated NSZD rates developed through other methods.

Results/Lessons Learned. The presentation will discuss the development and use of the thermal model to quantify NSZD rates along with the findings of sensitivity evaluations and estimation of background soil temperatures at a site. The use of temperature to evaluate NSZD rates has the potential to cost-effectively quantify natural LNAPL depletion at most sites and provides an alternative where soil gas gradient and soil gas flux methods are impractical.

Reductive Dechlorination of Vinyl Chloride in the Absence of *Dehalococcoides mccartyi*

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Background/Objectives. Vinyl chloride (VC), a human carcinogen, is a daughter product of tetrachloroethene (PCE) and trichloroethene (TCE) reductive dechlorination, which are common groundwater contaminants. At many sites, microbial reductive dechlorination of PCE and TCE can be achieved (e.g., biostimulation); however, formation of VC due to incomplete reductive dechlorination to environmentally benign ethene remains a grand challenge for site management and aquifer restoration. Currently, only members of the obligate organohalide-respiring *Dehalococcoides mccartyi* (*Dhc*) group are known to completely dechlorinate VC to innocuous ethene. Consequently, site assessment and monitoring efforts focus exclusively on *Dhc* biomarkers. The goal of this study was to identify the population responsible for VC-to-ethene reductive dechlorination in an enrichment culture that tested negative for the presence of *Dhc* biomarker genes.

Approach/Activities. Microcosms were established with trester (i.e., solid wastes derived from the wine making process) collected near Stuttgart, Germany. The microcosms received lactate (5 mM), hydrogen (*ca.* 0.33 atm; 829.2 µmol) as electron donors, and VC (*ca.* 516.3 µM) as electron acceptor. Transfers occurred once VC was completely dechlorinated to ethene and a sediment-free enrichment culture was obtained. VC, ethene, and hydrogen were measured by gas chromatography. Metagenome sequencing, high-throughput sequencing of 16S rRNA gene amplicons, and PCR and qPCR were applied to characterize the community structure and dynamics of the VC-dechlorinating culture.

Results/Lessons Learned. The enrichment culture dechlorinated VC to ethene and the activity could be transferred in defined medium. Multiple efforts failed to detect *Dhc* biomarker genes whereas the expected PCR amplicons were obtained with control DNA extracted form a consortium containing *Dhc*. The 16S rRNA gene amplicon data indicated the enrichment of a population phylogenetically related to the genus *Dehalogenimonas* (*Dhgm*). The enumeration of *Dhgm* 16S rRNA genes demonstrated that this populations grew concomitant with VC to ethene reductive dechlorination. Metagenome sequencing of the enrichment culture corroborated the absence of *Dhc* and the dominance of a *Dehalogenimonas* population. These findings demonstrate that the ability to grow with VC as respiratory electron acceptor is not limited to *Dhc*, and some members of the *Dhgm* genus can couple VC-to-ethene reductive dechlorination to growth. Detailed characterization of the VC-dechlorinating *Dehalogenimonas* sp. is ongoing. These findings have implications for site assessment and monitoring, as well as bioremediation of sites impacted with chlorinated ethenes.

Natural Source Zone Depletion Rate Measurements to Support LNAPL Remediation Decision-Making

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Background/Objectives. The Interstate Technology and Regulatory Council (ITRC) recommends using NSZD rate determination as an "*objective benchmark by which to compare the relative effectiveness of different remedial alternatives".* TRC has performed NSZD rate measurements at a variety of sites to support LNAPL remediation decision-making.

Approach/Activities. The carbon dioxide trap provides an integrated measurement of carbon dioxide flux from the ground surface, which can be converted to a rate of fuel hydrocarbon biodegradation. Measurements of soil gas flux by means of carbon dioxide traps have been made at seven LNAPL sites located in five different states. The type of LNAPL has varied from gasoline to diesel fuel. At two of these sites, a minimum of four quarterly NSZD rate measurements have been performed. At one site, a second line of evidence on NSZD rate is being generated through subsurface thermal flux monitoring.

Results/Lessons Learned. Generating multiple NSZD rates at individual sites and measuring NSZD rates at a portfolio of sites allows for valuable insights into both ZSZD rates and the most appropriate methodology for making the measurements. Of primary importance is the methodology employed to correct for background sources of CO2, and the number of sampling locations and events.

Popular approaches for product recovery often result in significant expenditures with little product removal. Furthermore, the endpoint of product recovery efforts is often a point of contention and hurdle to gaining regulatory agency consensus that corrective action is complete. Ultimately, the findings from this and similar studies have the potential to spark a paradigm shift for the management and regulatory closure of hydrocarbon-impacted sites. This presentation will also cover the status of efforts to gain regulatory agency concurrence on NSZD rates and appropriate incorporation of NSZD rate information into LNAPL site management decision-making.

Natural Source Zone Depletion Rate Measurements to Support Determination of an Appropriate LNAPL Recovery Endpoint

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Background/Objectives. Historic fuel releases at a pipeline terminal resulted in accumulation of fuel in the form of light, nonaqueous phase liquid (LNAPL) over an area of approximately 20 acres. The site is located in the Missouri River floodplain. An LNAPL recovery system (single pump total fluids recovery) was installed and operated. Natural Source Zone Depletion (NSZD) rate measurements are being made to support determination of an appropriate endpoint of LNAPL recovery system operations.

Approach/Activities. The carbon dioxide trap provides an integrated measurement of carbon dioxide flux from the ground surface, which can be converted to a rate of fuel hydrocarbon biodegradation. Quarterly measurements of carbon dioxide flux by means of carbon dioxide traps are being performed for a period of two years. Efforts are being made to develop a second line of evidence for the NSZD rates through subsurface thermal flux monitoring. The NSZD rates are being evaluated in a mass balance approach that incorporates LNAPL mass estimates based on extensive LNAPL thickness measurements and associated specific volume calculations, a program of soil coring and petrophysical analysis, and the volume of LNAPL removed in recovery system operation.

Results/Lessons Learned. The C14 method of correcting for background carbon dioxide flux has proved more reliable and accurate than the method based on measuring total carbon dioxide flux at a background location. Quarterly measurements are providing insight into temporal variability in carbon dioxide flux, and the magnitude of uncertainty in NSZD rates based on a single round of carbon dioxide flux measurements. Based on carbon dioxide flux measurements made to date, the NSZD rate appears to be on the order of 2,000 to 3,000 gallons of LNAPL per acre per year, much greater than the rate of LNAPL removal via recovery system operation.

The thermal signature resulting from LNAPL biodegradation has been measured via continuous multi-depth temperature monitoring via probes installed both within the LNAPL zone and at a background location. Work is underway to convert the thermal flux into an LNAPL biodegradation rate.

The presentation will include results of a mass balance evaluation. Estimates of the mass of mobile LNAPL present at the site prior to LNAPL recovery operations will be based on LNAPL accumulation measurements made at approximately 50 monitoring wells and associated LNAPL specific volume values. An LNAPL mass estimate for a later point in time will be based on LNAPL saturation measurements performed on soil samples collected at multiple depth intervals from approximately 50 soil borings installed within the LNAPL smear zone. The decrease in LNAPL mass derived from these estimates will be compared to the LNAPL recovery volume and NSZD rates measurements derived from carbon dioxide flux and thermal flux measurements.

Back to Contents

Investigating the Feasibility of Monitored Natural Attenuation at a Former Manufactured Gas Plant

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Background/Objectives. Indispensable lines of evidence documenting plume stability and demonstrating decreasing trends in contaminant concentrations and analysis of geochemical parameters are often insufficient to gain stakeholder approval of monitored natural attenuation (MNA), particularly at complex sites. Environmental molecular diagnostics (EMDs) can provide additional valuable critical lines of evidence to evaluate the feasibility and performance of MNA. In this study, EMDs will be employed along with traditional groundwater monitoring to determine if benzene and naphthalene biodegradation is occurring and to evaluate MNA as a corrective action at a former manufactured gas plant (MGP). At the site, excavation of the former coal tar pit and relief holder foundation removed the primary contamination source but residential NAPL is present as staining, sheens, tar coatings and tar blebs in lenses and subsurface voids beneath the former source area due to vertical migration. Benzene and naphthalene have been detected at relatively high concentrations (10 mg/L) in monitoring wells directly influenced by residual NAPL and groundwater impacts extend to a deeper hard limestone aquifer. However, contaminant concentrations decrease precipitously with distance from the NAPL and the dissolved plume does not extend offsite despite the timeframe of MGP operation (late 1890s to 1953).

Approach/Activities. Two EMDs will be employed to evaluate MNA at the former MGP site: high-throughput qPCR arrays (QuantArrays) and stable isotope probing (SIP). On selected groundwater samples, QuantArrays will be used to simultaneously quantify a broad spectrum of functional genes responsible for aerobic and anaerobic biodegradation of alkanes, BTEX, and PAHs. To definitively determine whether in situ biodegradation of benzene and naphthalene is occurring, stable isotope probing (SIP) will be conducted at a total of seven monitoring wells within the dissolved plume including four monitoring wells in the weathered limestone aquifer and three wells screened in the hard limestone aquifer. For SIP studies, a passive sampler (Bio-Trap) amended with ^{13}C-benzene or ^{13}C-naphthalene is suspended in the screened interval of each monitoring well for approximately 60 days. Upon recovery, quantification of ^{13}C enriched dissolved inorganic carbon (DIC) and phospholipid fatty acids (PLFA) is performed to assess biodegradation by measuring ^{13}C contaminant mineralization and incorporation into microbial biomass.

Results/Lessons Learned. Field work is scheduled to begin in September 2014. All results will be received by February 2015. Concentrations of naphthalene dioxygenase (NAH), ring hydroxylating toluene monooxygenase (RMO/RDEG) and phenol hydroxylase (PHE) genes are frequently orders of magnitude greater within a dissolved plume than in the background locations at sites undergoing MNA. Functional genes encoding enzymes for anaerobic biodegradation of toluene (*bssA*), methylnaphthalene (*nmsA*), and alkanes (*assA*) are also frequently prevalent within the dissolved plume, particularly in source areas influenced by residual NAPL. Although not yet performed, comparison of QuantArray results for groundwater samples obtained from background and impacted monitoring wells will reveal whether growth of microbial populations capable of aerobic and anaerobic biodegradation of BTEX and PAHs is evident within the dissolved plume at the site. In addition, quantification of ^{13}C enriched PLFA and DIC will demonstrate whether in situ biodegradation of benzene and naphthalene has occurred. Overall, traditional groundwater monitoring combined with the QuantArray and SIP results can provide convincing lines of evidence and greatly improve stakeholder confidence in MNA as an effective site management strategy.

Enhanced MNA—An Effective Closure Strategy

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Background/Objectives. Conventional monitored natural attenuation (MNA) relies primarily on the dissolution of the leading edge of contamination followed by the gradual dissolution of higher concentrations up gradient of eth contaminant plume. This is time consuming and not cost effective. The Enhanced Monitored Natural Attenuation (EMNA) strategy provides a cost effective and faster approach to achieving regulatory closure.

The objective of this paper is to present the EMNA strategy in detail and describe case studies where EMNA was successfully applied.

Approach/Activities. The EMNA combines MNA with two additional strategies to speed up contaminant degradation and significantly shorten the time to achieve regulatory closure. The first strategy is to combine MNA with an effective in-situ additive that will accelerate remediation through mass removal, treat multiple compounds simultaneously, and degrade contaminants upon implementation. The second strategy is to combine MNA with a risk based closure using background contaminant levels instead of MCLs or action levels.

Various additives have been used with varying degrees of effectiveness. Nano materials have been successfully used at several sites to implement EMNA. The exceptional efficiency of nano materials in degrading and sequestering environmental pollutants is attributed to the enormous surface possessed by nano materials and their ability to remain suspended in water for extended periods of time allowing maximum contact with contaminants and facilitate transport through soil and groundwater media. Soil and aquifer media pose a filtration effect on groundwater passing through and therefore impedes the mobility of solid particle additives that have to be carried by groundwater. The movement of nano particles is largely governed by Brownian movement thereby allowing nano particles to flow freely in porous media.

EMNA can be further enhanced by determining a realistic and practical contaminant concentration to achieve regulatory closure. Instead of MCLs or arbitrary action levels, background levels can be used in combination with risk based site evaluations combined with toxicological and epidemiological evaluations. Regulators are more inclined to accept this approach for brownfield sites in the Northeast United States, the Rust Belt and Department of Defense facilities where current background levels can be elevated due to legacy waste disposal practices.

Results/Lessons Learned. Conventional MNA is time consuming and often not cost effective, especially in situations, such as brownfields, where time to achieve regulatory closure is very important. The Enhanced MNA strategy provides a cost effective and faster approach to achieving regulatory closure.

This paper describes the EMNA approach in detail and presents case studies where EMNA has been successfully applied.

Life-Cycle of a “TPH” Plume: Nature and Estimated Toxicity of Polar Metabolite Mixtures in Groundwater at Biodegrading Fuel Release Sites

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Background/Objectives. A large proportion of organics measured as extractable TPH (e.g., EPA Method 8015B or equivalent; TPHd/DRO or TPHmo/ORO) in groundwater at biodegrading fuel release sites is composed of polar compounds (polars). While they can result from other sources, polars found within the source area and downgradient are typically metabolites from petroleum biodegradation. To avoid erroneously quantifying the polars as petroleum hydrocarbons, polars can be separated from hydrocarbons by performing a silica gel cleanup (SGC) on the sample extract prior to TPH analysis. Some regulatory agencies have been hesitant to allow SGC because of uncertainty about the nature and toxicity of the polars removed. This study was conducted to provide “targeted” quantitative and “non-targeted” qualitative data on the nature of the polars present in groundwater at these sites and an evaluation of the toxicity of the polars mixture. Our initial results from this study using groundwater samples from sites with highly-biodegraded sources were presented at the 2013 Battelle Biodegradation Conference; since that time, we have expanded the study to include groundwater plumes from less-biodegraded sources. The study update now provides a reasonably comprehensive understanding of the life-cycle of the mixture of organics measured as extractable “TPH” in groundwater at these sites.

Approach/Activities. Groundwater samples from five fuel terminals with biodegraded plumes and from five service station sites with elevated BTEX plumes were quantitatively analyzed using GC-MS for 76 individual plausible biodegradation metabolites for which human health toxicity information and analytical standards were available. The polars in each sample were also tentatively identified using GC-MS and GCxGC-MS in non-targeted mode, and were categorized by polar family and structural class. A ranking system was developed for evaluating the potential human chronic oral toxicity of the different classes of identified polars consistent with systems developed by USEPA and the United Nations. Aquatic toxicity testing (EPA Methods 1001, 1002 and 1003) using groundwater samples from several sites is ongoing.

Results/Lessons Learned. Up to 100% of the organics in groundwater measured as TPHd/DRO were polars and not dissolved hydrocarbons. The individual target metabolites were infrequently detected usign GC-MS above reporting limits of generally 10 ug/L. More than 1300 unique metabolites were tentatively identified using GCxGC-MS. The mixture of metabolites in groundwater consisted of primarily organic acids/esters, with variable alcohols and ketones, and very few phenols and aldehydes. The vast majority of the metabolites identified are in structural classes of “Low” toxicity to humans. This work demonstrates that the overall trend for the metabolites over time with continued biodegradation is toward (1) a higher proportion of acids/esters, and (2) a lower toxicity profile. Results indicate that SGC should be used routinely to separate hydrocarbons from polars if the TPH results are to be compared to hydrocarbon-based regulatory criteria, because the low-toxicity metabolites have RfDs of 0.1 to 1.0 (or higher) versus the aromatic hydrocarbons with RfDs of 0.03 to 0.04. Overall, the complex mixtures of metabolites in groundwater are unlikely to present a significant risk to human health if groundwater was ingested.

Long-Term Management of Monitored Natural Attenuation for a Hydrocarbon Plume, Lessons Learned

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Background/Objectives. Use of Monitored Natural Attenuation (MNA) as a remedial approach for groundwater plumes of hydrocarbons and other chemicals is growing. Regulatory approval of MNA typically requires a thorough and complete assessment, delineation of constituents of concern, understanding of fate and transport (F&T) processes, and knowledge of nearby receptors. This data is used to develop site-specific remedial goals and a long-term monitoring program to validate data and assumptions used in F&T modeling. While these technical requirements are usually well understood, the long-term implementation of MNA as a remedial approach has revealed that there are other key aspects and future considerations associated with long-term plume management. A summary of the many challenges encountered during long-term management of a hydrocarbon plume for which MNA is utilized as the remedial approach are reviewed.

Approach/Activities. Assessment performed in the early 1990's of a 1968 pipeline fuel release in central-southern Mississippi revealed a mile-long hydrocarbon plume. Assessment results identified the plume extent and characterized ongoing biodegradation processes. F&T modeling and a review of remedial options lead to a recommendation of using MNA as the remedial approach. The regulator accepted this approach and long-term monitoring began in 1999.

Results/Lessons Learned. The 16-year long implementation of MNA for a hydrocarbon plume has shown a number of changes to external influences that are not typically considered or expected at the time when MNA is being planned. The external influences that changed included regulatory changes (personnel, regulations, and remedial goals), technical changes (sampling techniques, analytical techniques, detection levels), changes of groundwater movement (climatic changes, unauthorized pumping from nearby wells, property development), and the how these changes can impact long-term plume and MNA management.

Multiple Lines-of-Evidence Approach Used to Suspend Pump-and-Treat and Shift to Monitored Natural Attenuation: Fruit Avenue Plume Superfund Site, Albuquerque NM

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Background/Objectives. The Fruit Avenue Plume Superfund site is a groundwater plume containing trichloroethene (TCE). Natural attenuation (NA) was selected in 2006 to replace pump-and-treat (P&T) as the remedy for the eastern portion of the plume located down-gradient of the recently installed P&T system. The P&T system operated for seven years recovering 11 kilograms of contaminant mass from 238 million gallons of groundwater. Although the P&T remedy component was highly valued by stakeholder community, by late 2012 the system was no-longer contributing towards achievement of the remedial goals established for site groundwater.

Approach/Activities. A multiple lines-of-evidence approach was used to demonstrate that NA is an active and important component of the groundwater remedy that could be expanded as the primary remedy for the whole site. TCE degradation (biotic and abiotic) and non-degradation (adsorption, diffusion, dispersion) processes were investigated by examining multiple lines-of-evidence that included: 1) TCE and TCE breakdown product concentration and distribution trends, 2) NA indicator parameter distribution, 3) carbon isotope distribution, 4) microbiological analyses, and 5) aqueous mineral equilibrium modeling with down-hole magnetic susceptibility. Degradation rates were estimated, and the degradation rates were used in a groundwater flow and contaminant transport model to simulate future migration and to estimate when remedial goals would be met. The NA evaluation results supported a shift from P&T to NA as the sole remedy for the site. A report describing the technical evaluation was reviewed by EPA, State of New Mexico, and local regulatory technical representatives, and meetings held to build consensus for suspension of P&T operations.

Results/Lessons Learned. The P&T system was placed in standby mode in May 2013 and is being maintained as a contingency remedy until long-term monitoring and the second 5-year review confirm the effectiveness of NA as a the sole response action, after which the P&T system will be decommissioned. The evaluation revealed that P&T operations were adversely effecting TCE degradation processes by injecting treated water with high dissolved oxygen (from air stripper treatment) and high sulfate (from sulfuric acid scale control) concentration water within the TCE plume footprint. The evaluation also revealed the importance of using a multiple lines-of-evidence approach to identify the existence of abiotic NA processes that may be more predominant in some aquifer settings.

Back to Contents

Natural Attenuation Evaluation Using Multiple Lines of Evidence, Fruit Avenue Plume Superfund Site, Albuquerque NM

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Background/Objectives. The Fruit Avenue Plume Superfund site is a groundwater plume containing trichloroethene (TCE). A pump and treat (P&T) system was installed in 2006 to treat TCE contaminated groundwater present in the central portion of the plume near the presumed source area. A natural attenuation (NA) evaluation was conducted to evaluate whether NA, which was selected as the response action for the downgradient portion of the plume, could be expanded as the primary remedy for the whole site.

Approach/Activities. TCE degradation (biotic and abiotic) and non-degradation (adsorption, diffusion, dispersion) processes were investigated by examining multiple lines-of-evidence. Detailed results of each technical evaluation will be included on the poster.

Based on the results of a MAROS evaluation, TCE and cis 1,2-dichloroethene (cis-DCE) concentrations and plume mass are declining, the plume is decreasing in length and growing wider, and the center of mass is advancing downgradient. Up to one-half of the chlorinated solvent mass has been transformed to cis 1,2-DCE through NA processes and vinyl chloride (VC) is not present.

Natural attenuation geochemical indicator parameter results (dissolved oxygen, ferrous iron, sulfide, carbon dioxide, methane, redox potential, alkalinity, and chloride) provided information that was helpful in identifying treated water from injection of P&T effluent as a source of oxygen and sulfate enriched water that was inhibiting NA within the central portion of the plume. The NA indicator parameters also identified conditions attributed to the mixing of anaerobic groundwater from low-flow, fine-grained sediments with aerobic groundwater from high-flow, coarse-grained sediments when aggressive well purging methods are used for sample collection.

Compound-specific isotope analyses (CSIA) revealed that groundwater is enriched with $\delta^{13}C$ relative to virgin TCE product by an amount which can only be caused by degradation processes. The $\delta^{13}C$ of cis-DCE is depleted compared to virgin product indicating that it is being formed by TCE degradation. Because $\delta^{13}C$ of cis-DCE did not exceed that of virgin product, limited evidence of cis-DCE degradation was observed.

Microbiological testing (PLFA) revealed low biomass levels but with favorable microbial categories accounting for 50 to 95 percent of the biomass present. Aqueous mineral equilibrium modeling, down-hole magnetic susceptibility testing, and plume degradation patterns provide evidence of abiotic degradation and a degradation rate was estimated.

Point decay rates were calculated from TCE concentration trends and degradation rates were estimated from CSIA data. The degradation rates (-0.022/yr to -0.029/yr) were used in a groundwater flow and contaminant transport model to simulate plume migration and to predict when remedial goals would be met.

Results/Lessons Learned. This NA evaluation illustrated that degradation processes are providing important contributions to remediation at the site. NA as a sole response action is projected to achieve remedial goals within a reasonable timeframe and without reaching the site boundary, even if the P&T system is shut down.

Strategies for Managing Contaminated Properties: Integrating Chemical and Biological Remediation

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Background/Objectives. Preliminary groundwater sampling in 2007 showed initial chlorinated hydrocarbon contamination above New Jersey Department of Environmental Protection (NJDEP) Groundwater Quality Standards (GWQS) in both shallow and deep groundwater aquifers. Source concentrations in the deep aquifer were between 1.3-71,000 ug/L on-Site and 160-170,000 ug/L on the adjacent property. The main objective of the project is mass reduction of trichloroethene (TCE) concentrations within the source of the plume to approximately 10 ug/L using potassium permanganate (KMnO4) injections. Once mass reduction of the source of the plume has been achieved, we plan to enhancement aerobic degradation using findings of a proposed biotreatability study.

Twenty-four injection wells (16 deep and 8 shallow) were installed below the proposed building foundation. Quarterly groundwater sampling has been ongoing since 2011 to track the movement of KMnO4 and the effectiveness of the injections. Now in its fourth year a reduction in TCE concentrations within the source plume including non-detect values in some source wells has been noted.

Approach/Activities. Groundwater sampling completed in 2010 established a baseline against which the results of the KMnO4 injections could be compared. Quarterly sampling since installation of the ISCO system in 2011 has shown a decrease in TCE concentration in several of the source area wells. This suggests that the use of KMnO4 is successful in oxidizing TCE given onsite conditions. Once concentrations of TCE are reduced to approximately 10ug/L, injections will subside and monitored natural attenuation (MNA) will begin. A biotreatability study is scheduled for March 2015 to determine the quantity and type of bacteria present on site. Based on results we will be researching options to provide optimal conditions for aerobic microbiological degradation of the non-source plume.

Combined treatment of the source of the plume using KMnO4 and the non-source plume using MNA may allow for complete remediation of contamination on the site.

Results/Lessons Learned. Based on current groundwater results, we can surmise that KMnO4 injections have successfully reduced the concentration of TCE onsite. At the time of the presentation we will have a better understanding of the indigenous bacterial population onsite and will present our plan for enhancing biodegradation based on our findings.

Back to Contents

Sampling Groundwater Monitoring Wells: Is What's in the Pipe Representative of the Formation?

Panel Discussion Wednesday/Track D

Moderator
Rick Cramer (AECOM)

Panelists
Michael Barcelona (Western Michigan University)
Sandy Britt (ProHydro Inc)
Murray Einarson (Haley and Aldrich)
John Gillespie (Air Force Civil Engineer Center)
Noah Heller (BESST, Inc.)

It is imperative that the groundwater data we collect represents the formation being sampled in order to support sound remediation decision-making. Yet, there are cases where analytical results are representative of what is in the casing but are not representative of the formation. Several technologies for passive groundwater sampling have been developed in the past decade. There are many examples of how these technologies reduce groundwater monitoring costs while generating data that is comparable to low-flow sampling techniques, considered the "gold standard" in our industry. However, new applications of flow-weighted technologies developed in the groundwater production industry bring up some healthy questions challenging the efficacy of passive sampling technologies as well as low-flow sampling results. A group of the world's leading experts on hydrogeology and groundwater monitoring will share their opinions during this discussion.

The following are among topics expected to be addressed:

- Under what conditions does groundwater chemistry in a monitoring well represent the groundwater in the screened formation?
- What are the flow dynamics in a groundwater monitoring well and how does this impact groundwater chemistry?
- Does low-flow sampling always result in groundwater samples representative of the screened formation?
- How does passive groundwater sampling address this issue of representative samples?
- What is the impact of screen length on representative groundwater monitoring?
- How does the efficacy of these data impact groundwater remediation decisions?

Back to Contents

Results of 2D Numerical Modeling Study of the Influence of Methane Generation from Ethanol-Gasoline Blends on Vapor Intrusion

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Background/Objectives. The aerobic biodegradation of BTEX and other petroleum hydrocarbons is recognized as a significant process for attenuation of these compounds in the vadose zone, but the influence of methane generation from degradation of ethanol in motor fuels on fate and transport of BTEX has been less well characterized. Previous studies by the authors demonstrated the use the MIN3P-DUSTY model for 1-D simulations for gasoline containing ethanol. The objectives of this study are to better understand 2D transport for a broad ethanol range (E0-E85) and the influence of ethanol degradation kinetics, building foundation and soil properties, and building size. Additionally, the influence of transient conditions and contaminant source depletion on vapor intrusion to indoor air is assessed.

Approach/Activities. Initial simulations were conducted to verify MIN3P-DUSTY model behavior for different building foundation conditions and to compare the results to model predictions reported for the Abreu 3D model. Because the model includes transport through a concrete foundation, a literature search of concrete properties was completed. The processes modeled include methane generation from ethanol degradation, gas diffusion, advection and oxygen-limited aerobic degradation. The model is designed to assess such factors as the methane generation rate, the additional oxygen demand from methane, and the soil gas advection caused by methane generation. To support application to vapor intrusion assessment, a sensitivity analysis was performed for a range of ethanol blends, foundation and soil properties, building size, and distances between the building and contamination source. Additionally, simulations were performed to understand the effect of source depletion and transient conditions on vapor transport and attenuation factors, and to evaluate the effect of a spatially variable surface boundary condition to simulate the influence of wind forces.

Results/Lessons Learned. The 2D model simulations indicate the potential for significant hydrocarbon and oxygen fluxes through the concrete foundation depending on source concentrations and assumptions for concrete properties. For E10 simulations, pressures up to 140 Pa and a significant advective component for benzene transport are predicted. As the ethanol content is increased, there is a progressive increase in the calculated attenuation factor for non-depleting scenarios, but depleting scenarios indicate the depletion time scales are on the order of months for ethanol. As a consequence, significantly lower gasoline vapor attenuation factors are predicted highlighting the importance of transient behavior and source depletion for understanding the influence of ethanol on BTEX biodegradation. Key input parameters to the model are soil and foundation properties and source-building separation, with building conditions having lesser importance, for the range of input parameters considered.

Fate of Methane and Ethanol-Blended Fuels in Soil: Laboratory and Field Experiments

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Mirann Tsumura, Leah Zivalic, and Kate Scow (University of California, Davis, CA, USA)

Background/Objectives. We are conducting a series of densely monitored controlled release field experiments to fill key knowledge gaps regarding subsurface methane and ethanol/gasohol fate. Our research questions include the quantification of natural biodegradation rates in the field, an improved understanding of life cycle of ethanol-degrading microbial communities and the subsurface conditions they create, the lag time between ethanol release and degradation, interactions between mixed fuel constituents (e.g. ethanol and BTEX), temperature dependency and seasonal variability of methane generation, and the fate of degradation products including methane gas. Our research site is within the UC Davis Putah Creek Riparian Reserve in Davis, CA; climate is semi-arid and soils are sandy loams and silts.

Approach/Activities. We are conducting three types of controlled release experiments in the field: 1) Gas mixture, a continuous release of methane, sometimes with other gases included, with the composition and release rate changing over time to allow examination of various hypotheses, 2) E10 (gasoline with 10% ethanol): a continuous release of E10 NAPL at rate equal to documented low rate releases from underground storage tanks (USTs) that are difficult or impossible to detect with current practical approaches (<0.04 gallons per day); 3) E85: release at same rate as the E10 release. In the field experiments, gas or NAPL is released from a stainless steel drive point with 0.5 cm slotted section at 1 m bgs; we monitor temperature, pressure, moisture content, and soil gas composition in the soil, and efflux of carbon dioxide, methane, oxygen, water vapor, and other species to/ from soil to atmosphere. Periodic coring allows examination of the microbial community composition with depth. Laboratory microcosm and column tests assisted in planning the E10 and E85 field experiments above, evaluated the effect of moisture content on methane oxidation, and allowed testing and refinement of the monitoring approaches in the field

Results/Lessons Learned. The methane release experiment has been ongoing since 7 July 2014. We have found that up to 40% of the methane released can be accounted for by efflux from soil to the atmosphere. The percentage in the efflux depends on the rate of release, to date, and, based on literature and our microcosms with methane-spiked PCRR soils, we hypothesize that the very low moisture content of the soils in this drought year limits in situ methane oxidation. We will test this hypothesis by monitoring the experimental plot under an irrigation regime. Efflux of carbon dioxide accounted for up to 20% of the E10 release rate under our lab column conditions, which we believe were oxygen-limited compared to the field conditions. We also detected low molecular weight hydrocarbons in the column efflux, though the concentrations were small and the total efflux accounted for a very small fraction of the E10 release rate. On the basis of the lab tests, we are designing the field experiment for E10 release, which will be started in early 2015. Similar lab tests are planned for E85 release scenarios, with a goal of designing and beginning a field E85 release in 2015. Selected results of these experiments will be discussed in the conference presentation.

Controls on Ethanol and BTEX Distribution and Fate Following a Major Release

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Jay Grosskleg (Federated Cooperatives Limited, Saskatoon, SK, Canada)

Background/Objectives. A 65,000 L release of a 98% ethanol - 2% gasoline blend occurred in a highway ditch adjacent to agricultural properties. It is estimated that approximately 25,000 L were recovered at the surface by first responders. A subsurface investigation was undertaken to determine the distribution and fate of the approximately 40,000 L that infiltrated from the bottom of the ditch through the underlying clay soils. This investigation revealed an impacted area roughly 70 m long, 12 m wide and less than 0.5 m deep. Groundwater at the site occurs at approximately 5.2 meters below grade. Based on the information available regarding transport of ethanol in the subsurface, it was anticipated prior to the assessment work that we would see downward migration of the plume to the groundwater table. It was further anticipated that we would see a zone of reduced or absent microbial activity in the core of the plume due to the inhibitory nature of elevated concentrations of ethanol on the microbial population. Further it was anticipated based on current literature that at the periphery of the plume, the lower concentrations of ethanol would result in preferential biodegradation (limited by available electron acceptors / nutrients) at resulting in minimal degradation of the BTEX components. The soil data collected in the investigation appears to confirm that fact. What was not anticipated was that the ethanol plume would remain largely immobile from the time of the release. The main objective of this study was to examine the properties of the ethanol and soils at the site to determine the causes for this as it has the potential to change the prevailing understanding of the fate and transport of this chemical in the subsurface.

Approach/Activities. The presence of ethanol lowers the interfacial tension of water and hydrocarbon mixtures, which allows the fluid to enter smaller pores. These fluids, trapped by capillary forces, are less likely to be displaced. It was not possible to collect all the data necessary to conduct an empirical study. Rather, a numerical model was used to simulate the invasion of the spill assuming Raoult's law applies to phase partitioning and parameters controlling the infiltration of the spill fluid. The model was conditioned by “calibrating” the distribution of the studied 40,000 L release and exploring the sensitivity of various parameters. Different soil conditions were imposed on the model to determine the relative sensitivity that various parameters exert on spill invasion and attenuation. Certain parameters were varied for each soil considered (clay, silt and sand) to establish their effect on spill behavior and natural biodegradation.

Results/Lessons Learned. Ethanol persisted in the core of the spill area, presumably because the high concentrations either inhibited intrinsic biodegradation or were toxic to soil microbial population. Within the impacted area, nutrient concentrations were generally low. There was some evidence that more robust biodegradation occurred on the periphery of the spill area, presumably due to access to atmospheric oxygen replenishment. The conceptual site model needs to take into account both the soil conditions and the characteristics of the fluids in order to lead to an appropriate management strategy.

Physical Model Experiments and Simulations of Releases of Alcohol Blended Fuels

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Background/Objectives. The objective of this research is to improve the current understanding (through both physical model experiments and numerical simulation studies) of the physical-chemical impacts of alcohols on the distribution and transport characteristics of dissolved alcohol and NAPL resulting from releases of alcohol blended fuels to the subsurface. This research extends our previous work on numerical simulations of spills of ethanol-blended fuels to include the results of recent experiments and also to extend the use of experiments and simulations to investigate the characteristics of fuels containing other alcohols.

Approach/Activities. Two-dimensional laboratory-scale experiments were conducted to characterize phase separation, NAPL mobilization and redistribution as well as ethanol transport resulting from spills of ethanol blended fuels. Fixed volume spills of varying ethanol fuel composition (E25, E50, and E85) were injected into a model aquifer under water-saturated conditions. Hydrophobic and hydrophilic dyes were used to track the transport behavior of the alcohol plumes as well as the migration and distribution of the NAPL phase. In addition to visualization data, pore water concentrations of ethanol and dissolved hydrocarbon concentration associated with the ethanol plume were also measured. Simulations were also conducted with a multiphase, multicomponent finite difference numerical model (UTCHEM) to quantitatively evaluate the impact of key physical-chemical properties that influence the fluid-phase transport in porous media. A key component of the numerical model is a phase equilibria module which models the equilibrium partitioning of components in the gasoline-alcohol-water system. The simulation results were compared with the results of the laboratory physical model experiments.

Results/Lessons Learned. NAPL source: Saturations and pore water concentrations for NAPL, water, and ethanol suggest that, for fuels with higher ethanol content, more NAPL will be mobilized due to both cosolvency and phase mobilization. In addition, the volume of media impacted by residual NAPL (that remains after ethanol is transported from the source of the spill) increases with ethanol content. Results further indicate that for intermediate to high ethanol contents, the residual NAPL that is formed has a low NAPL saturation in the center and a high saturation at the edges. The variation in the size, shape, and saturation of the residual NAPL for different fuel blends may have a significant impact on pore water concentrations and longevity for BTX emanating from NAPLs that remain following ethanol fuel releases. Ethanol plume: As the ethanol fuel content increases, more vertical migration can occur due to buoyancy. For high ethanol content fuels, a significant amount of the ethanol could become trapped near the water table. This vertical migration for high ethanol content fuels (E50 and E85) has implications for where to locate and how to monitor ethanol and BTX plumes from sources of ethanol fuel spills. In addition to these results for ethanol, the results of current experiments and simulations of fuel blends of other alcohols will be presented for comparison.

Back to Contents

Methanogenic Biodegradation of Different Types of Biodiesel: Impacts on Benzene Biodegradation and Microbial Communities

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Background/Objectives. Biodiesel production has significantly increased due to concerns over climate change and energy security. It can have different characteristics depending on the type of source material and alcohol (methanol versus ethanol) used in transesterification, which produces a methyl ester (ME) and ethyl ester (EE) biodiesel, respectively.

Biodiesel is often blended with other fuels. As it is with any other fuel, failures during production, transport, and use can result in the contamination of soil and groundwater. Although ME biodiesel has been shown to be biodegradable, this can be problematic since it also negatively impacts benzene biodegradation, which is often the regulatory driver at fuel hydrocarbon contaminated sites. However, no studies have examined the biodegradability of EE biodiesel, its impact on benzene biodegradation, and the microbial community shifts that occur during their biodegradation. As such, laboratory experiments were conducted in order to address these questions.

Approach/Activities. Microcosms were setup using approximately 17 g of sediment collected downgradient from an Agrochemical industry effluent with 100 mL of anaerobic media in 125-mL serum bottles. Microcosms were purged for 30 minutes with nitrogen gas and sealed with Teflon-lined septa and aluminum crimp caps. Afterwards, the batch reactors were incubated statically, upside down, in the dark, and at 25 °C.
Tests included biodiesel alone, biodiesel + benzene, ‘as is’ and autoclaved controls. Two different source materials (sunflower oil (SF) and waste frying oil (WF)) and two alcohols (methanol and ethanol) were used to produce three different biodiesels: waste frying oil ethyl ester biodiesel (WFEEB), sunflower oil methyl ester biodiesel (SFMEB), and sunflower oil ethyl ester biodiesel (SFEEB). The initial amounts of benzene and biodiesel in the microcosms were approximately 1.5 mg/L and 60 mg/L, respectively.
Headspace samples were periodically removed and analyzed for methane and benzene quantification. Aqueous samples were collected for the determination of long chain fatty acids (LCFA). Finally, microbial community shifts between the three different biodiesel types in the presence and absence of benzene were monitored by extracting total DNA in time series aqueous subsamples. Bacteria and Archaeal community shifts were evaluated using the fingerprint denaturing gradient gel electrophoresis (DGGE) technique.

Results/Lessons Learned. Acknowledgements: This work was supported by FEDER funds through the Operational Program for Competitiveness Factors - COMPETE and National Funds through FCT – (Portuguese Science and Technology Foundation) under project numbers PTDC/AAG-TEC/4403/2012 and PTDC/AAC-AMB/113973/2009.

Municipal Wastewater Treatment and Biofuel Production: Effects of Selected Pharmaceuticals on Lipid Productivity and Transcriptomic Responses of Microalga *Chlorella vulgaris*

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Background/Objectives. In the search of alternative energy sources, microalga-based technologies are currently developed to provide a new generation of biofuel. The cultivation of microalgae in wastewater as the growth medium may offer the dual benefit of wastewater remediation and sustainable biofuel production. The potential of microalgal biomass to be converted into biodiesel depends on the accumulation of neutral lipids, mainly triacylglycerides. However, the presence of toxic contaminants in municipal or industrial wastewater could negatively affect the biomass growth and/or modify the pattern of lipid accumulation in algal cells. Beside conventional contaminants, municipal wastewater has been shown to contain detectable concentrations of pharmaceuticals originating from human excretion and domestic disposal. Pharmaceuticals are biologically active compounds that may affect living organisms at very low doses.

Approach/Activities. In this study, we explored the potential of cultivating microalgae in municipal wastewater for the removal of selected contaminants and the production of biodiesel. The effect of a suite of pharmaceuticals such as acetaminophen, atenolol, carbamazepine, erythromycin, estrone, gemfibrozil, ibuprofen, sulfamethoxazole, and tetracycline commonly found in municipal wastewater on biomass growth and lipid accumulation in the microalga, *Chlorella vulgaris*, was evaluated. The algal biomass growth was monitored by the optical density (680 nm) and triacylglyceride (TAG) content of cells was measured by GC-MS after conversion into fatty acid methyl esters (FAME). The molecular responses of *C. vulgaris* upon exposure to selected pharmaceuticals was investigated through gene expression (transcriptional) analysis using reverse-transcription real-time PCR.

Results/Lessons Learned. Exposure to pharmaceuticals did not result in observable effects on algal growth at concentrations below 25 µM, except for sulfamethoxazole and tetracycline, which showed inhibitory effects at 0.4 and 6.25 µM, respectively. The gene expression analysis will help gain further understanding of key genes and regulatory mechanisms involved in the lipid metabolism of *C. vulgaris* and how they will be affected in the presence of pharmaceuticals as emerging contaminants (The results will be available at the time of presentation). Results from this research are expected to help develop and optimize innovative alga-based technologies combining the benefits of wastewater treatment, sustainable biofuel production, and mitigation of carbon dioxide emissions.

Back to Contents

Isotope Fractionation Caused by VOC Water-Phase Diffusion during Air-Sparging Treatment—Implications to Biodegradation Assessment

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Background/Objectives. While performing groundwater remediation treatment, compound-specific isotope analysis (CSIA) can provide unique insight into processes responsible for contaminant removal. For instance, for an air sparging system, CSIA can help to distinguish VOC volatilization from biodegradation. However, to apply CSIA, all processes creating an isotope fractionation must be identified, and eventually quantified. During air sparging, the mass transfer of the dissolved VOC by diffusion towards the air channel occurs and might be associated with an isotope fractionation. The main objective of this study was to investigate the effect of water-phase diffusion on the carbon isotope ratio by conducting column experiments, and evaluate the implication for biodegradation assessment.

Approach/Activities. Two types of laboratory experiments were carried out. In the first experiment, carbon isotope fractionation factor for water-phase diffusion of benzene was determined. The approach used a 2-cell glass apparatus separated by a HDPE porous filter (1 to 1.6 um). Accordingly, benzene molecules were allowed to transfer from one cell to the other only by diffusion. The second set of experiments was conducted in a column designed to perform air sparging treatment of water containing dissolved benzene (75 mg/L). The column was filled with alluvial sand to ensure benzene biodegradation. Water samples were taken at two depths in the column and were analyzed for $\delta^{13}C$ and $\delta^{2}H$.

Results/Lessons Learned. $\delta^{13}C$ data for benzene confirmed an isotope fractionation caused by water-phase diffusion which was of smaller magnitude than those observed during gas-phase diffusion and biodegradation. Positive isotope shifts were also observed during the air sparging treatment and the shift magnitude reflected a combination of both water-diffusion and biodegradation processes. This study demonstrates that the use of CSIA to evaluate VOC removal process during air sparging treatment should be interpreted with caution. The diffusion-related 13C-isotope fractionation is contrasting with air-water and air-NAPL partitioning, but is similar to biodegradation.

Use of ^{13}C and ^{37}Cl Stable Isotopes to Estimate TCE Biodegradation Rates

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Background/Objectives. Compound-specific isotope analysis (CSIA) was conducted to better understand natural biodegradation and chemical migration pathways between chlorinated volatile organic compound (CVOC)-impacted areas at an industrial facility. CSIA provided independent support of biodegradation as the dominant chemical degradation mechanism, based on the data fit with the Rayleigh model for chemical degradation. Analysis of the stable isotope data included a basic evaluation of overall trends and correlation of isotope fractionation and CVOC concentrations followed by a more detailed evaluation of biodegradation rates along groundwater flowpaths.

Approach/Activities. Groundwater samples for CVOCs, as well as ^{13}C and ^{37}Cl stable isotopes, were collected from 24 monitoring wells completed in a multi-layer unconsolidated aquifer. The occurrence of natural biodegradation is supported by decreasing concentrations and evidence of breakdown products, geochemical indicators, and microcosm studies. The general CVOC plume distribution is characterized by the presence of elevated concentrations of TCE and TCA in a shallow aquifer and elevated concentrations of cis-1,2-DCE and VC in an intermediate aquifer. Four steps were involved in quantifying biodegradation using CSIA: evaluating the stable isotope data for fit with the Rayleigh model, determining the source isotopic signature, selecting an appropriate isotopic enrichment factor, and calculating the extent of biodegradation and conversion to a biodegradation rate. Groundwater analytical results included five chlorinated compounds (TCE; cis-1,2-DCE; VC; 1,1,1-TCA; and 1,1-DCA) further evaluated by isotope analysis that included the $\delta^{13}C$ and $\delta^{37}Cl$ values for these chlorinated compounds. Graphs of $\delta^{13}C$ and $\delta^{37}Cl$ versus the natural log concentration of each CVOC from all samples, as well as within each aquifer, showed a trend indicative of the Rayleigh correlation, with values of $\delta^{13}C$ or $\delta^{37}Cl$ in downgradient wells enriched (less negative) by 2‰ or greater as compared to values in the upgradient well. Comparison of groundwater sample data for $\delta^{13}C$ and $\delta^{37}Cl$ with a range of published values for undegraded (source) TCE and 1,1,1-TCA product suggests releases to multiple flow zones.

Results/Lessons Learned. CSIA was useful for the estimation of biodegradation rates for TCE in the shallow and intermediate aquifers. The most negative value of $\delta^{13}C$ was -25‰ for TCE occurring at a select shallow well. The lowest value of $\delta^{37}Cl$ was 1.18‰ for TCE occurring in a select intermediate well. These values fall within or near the range of published values for undegraded product. Using assumptions of the flow path and groundwater flow rates, the Rayleigh equation was used to estimate the fraction remaining after biodegradation (f), the extent of biodegradation or abiotic transformation ($1-f$), and ultimately, the rate of biodegradation (λ). The rate of biodegradation (λ) along the groundwater flow path was estimated from the CVOC concentration in the groundwater sample, the extent of biodegradation ($1-f$) from ^{13}C and ^{37}Cl isotope data, and the estimated travel time between two monitoring points along the groundwater flow path. In the shallow and intermediate aquifers, first-order biodegradation rates for TCE ranged from 0.00002 to 0.1083 d^{-1}, with an average rate of approximately 0.0001 to 0.0226 d^{-1}; which is consistent with the range of values from published literature.

CSIA Confirms Anaerobic Biodegradation of Bis(2-chloroethyl)ether (BCEE) in Groundwater at an Active Chemical Facility

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Background/Objectives. Historical operations at an active chemical manufacturing facility have resulted in groundwater impacted with a number of chlorinated compounds including BCEE (bis(2-chloroethyl) ether) and BCIE (bis(2-chloro-isopropyl) ether). Monitoring data collected since 2002 indicated that concentrations of these compounds in groundwater are either stable or decreasing with time and that groundwater conditions are generally conducive to anaerobic biodegradation. However, very little information was available, particularly about the fate of BCEE and BCIE, which would determine technical feasibility and cost of different groundwater remedy alternatives especially Monitored Natural Attenuation (MNA).

Approach/Activities. Compound Specific Isotope Analysis (CSIA) of ^{13}C from select monitoring wells demonstrated that BCEE and BCIE were transforming naturally under the prevailing anaerobic groundwater conditions. However, chlorinated compounds have been shown to transform abiotically via chemical reactions with natural sulfide minerals that could be present in an aquifer. Microcosm experiments were required to examine two transformation scenarios of BCEE and BCIE in a controlled laboratory environment (1) anaerobic biodegradation using saturated soil samples from the site in order to grow populations of native microbes (2) abiotic transformation via sulfide chemical reactions. Enrichment factors and 2-D CSIA data (^{13}C vs ^{37}Cl) were obtained from the BCEE microcosm experiments, but the microcosm results for anaerobic biodegradation of BCIE were inconclusive.

Results/Lessons Learned. BCEE microcosm CSIA data was compared with field groundwater CSIA data to distinguish the primary processes contributing to the observed concentration reductions in groundwater at the site. Results from this comparison indicate that anaerobic biodegradation is contributing significantly to the observed reductions in concentrations of BCEE. To our knowledge, this is the first time that CSIA has been used to demonstrate anaerobic biodegradation of BCEE. Evidence that these contaminants are anaerobically biodegrading in groundwater will be critical to selecting a cost-effective remedy for managing the groundwater plume.

Application of CSIA at Chlorinated Solvent Sites

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Background/Objectives. Studies have shown compound-specific isotope analysis (CSIA) can be used to assess the source and fate of chlorinated solvent compounds and their breakdown products in groundwater. The practical application of CSIA to assess the extent of degradation at contaminated sites can have a high degree of uncertainty if the source isotopic composition and enrichment factors are not known, since there is a large range reported in the literature for both of these critical values. Because of the sequential degradation of chlorinated ethenes during reductive dechlorination, degradation assessment based on the Rayleigh equation is not applicable. Even limited transformation of parent solvent can increase the uncertainty in forensic applications due to isotope fractionation. In this presentation, we focus on using carbon isotope mass balance to reduce the uncertainty in application of CSIA at solvent sites.

A small number of studies have discussed the utility of carbon isotope mass balance for demonstrating degradation beyond vinyl chloride. Carbon isotope balance ($\delta^{13}C_{CE}$) is simply the concentration weighted average of the isotope signatures of all chlorinated ethenes in the stepwise dechlorination process. If degradation beyond vinyl chloride has not occurred, then $\delta^{13}C_{CE}$ is equal to the carbon isotope ratio of the parent solvent (PCE or TCE). Therefore, carbon isotope balance can be used to estimate the $\delta^{13}C_o$ value of parent solvent. Enriched $\delta^{13}C_{CE}$ values compared to the parent solvent then provide unequivocal evidence for degradation of chlorinated ethenes beyond vinyl chloride.

Approach. CSIA was performed at three different sites where groundwater was impacted by TCE and/or PCE. These analyses were performed initially as separate projects completed between 2010 and 2015. In order to assess the extent of biodegradation of PCE and TCE, a carbon isotope balance was performed. To assess whether different sources for chlorinated ethenes were present, two dimensional isotope plots were prepared to assess whether distinct isotopic “signatures” could be observed.

Results. Site#1 is a TCE-release located in the Central Valley of California. The lowest $\delta^{13}C_{CE}$ value was -31.9‰ in the suspected release area and showed an increasing trend with distance to -22.2‰ approximately 2,000 feet downgradient, proving degradation of TCE, cDCE and VC. Chlorine and hydrogen isotope ratios were constrained to a narrow range and did not conclusively indicate a different source, and were not substantially affected by biodegradation. Site #2 is a mixed solvent release in a highly industrialized area of southern California. Groundwater samples from another nearby TCE-release site (Site 2b) were also characterized. Similar to Site #1, chlorine and hydrogen isotope ratios were constrained to a narrow range and did not conclusively indicate a different source, and were not substantially affected by biodegradation. The $\delta^{13}C_{CE}$ values provided conclusive evidence for complete mineralization at some locations, but at other locations, it was more difficult to assess since the source could have been the release at Site 2a (TCE source -22‰), Site #2 (likely lighter than -22‰), or another Site. Site#3 is a PCE-release located in an industrialized area. At this Site, $\delta^{13}C_{CE}$ values increased from -23.5‰ to approximately -18.5‰ proving biodegradation, and corresponded with an increase in $\delta^{37}Cl$ from +0.5 ‰ to +5.5‰. Mixing in monitoring wells was shown to obscure the isotope signature at many wells installed within the source zone, based on CSIA performed on adjacent depth-discrete samples. In summary, CSIA proved to be a powerful tool for demonstrating MNA, particularly due to carbon isotope balance.

Use of Multi-Isotope Tracers to Evaluate Biodegradation of Petroleum Hydrocarbons Enhanced by Sulfate Application

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Background/Objectives. Petroleum hydrocarbon (PHC) contamination in shallow aquifers results in the rapid consumption of oxygen creating anaerobic conditions. Addition of electron acceptors such as nitrate and sulfate in microcosm experiments has been shown to accelerate anaerobic biodegradation of some aromatic compounds such as benzene in PHC contaminated groundwater. Field studies where sulfate has been applied using a gallery application system and under natural conditions (recharge of high sulfate concentration groundwater) have confirmed the results of the laboratory studies. Our study explored the use of new tools that can improve the monitoring of a land sulfate application system to remediate PHC contaminated groundwater. These new tools include: CSIA to evaluate the degree of biodegradation of BTEX, sulfur and oxygen isotopes in sulfate, and carbon isotopes in dissolved inorganic carbon (DIC) to monitor the progress of sulfate reduction; and biomarkers (metabolites and mRNA) to provide specific information on the degradation of benzene and toluene under aerobic/anaerobic conditions. This new tool box was tested in a pilot test study performed at the Borden site in Canada.

Approach/Activities. The pilot-scale experiment was performed in the sandpit area at the University of Waterloo Groundwater Research Facility at CFB Borden located near Alliston, ON. A multicomponent PHC source zone (3 m x 3 m) was emplaced in 2012 between 1 and 3 m below ground surface inside a sheet pile walled experimental gate. Simulation tools were used to design an optimal sulfate dosage method that would satisfy the reagent delivery and remediation requirements. Three episodes of sulfate release (5 m^3 of 5-20 g/L Na_2SO_4, and 0.3 g/L $(NH_4)_2SO_4$) at the ground surface were conducted over an 8-month period. A host of multilevel monitoring wells in conjunction with a real-time resistivity data collection system was employed to continuously track sulfate patterns and migration. Treatment performance was evaluated based on changes in the PHC mass discharge across a downgradient monitoring fence line. Groundwater samples were collected during the pilot study for ^{13}C and ^{2}H, and ^{34}S and ^{18}O analyses on BTEX and sulfate, respectively. The production of CO_2 during biodegradation of PHCs was monitored by measurement of concentration and isotopes patterns of DIC. Samples were also collected for microbiological analyses including metabolites and mRNA.

Results/Lessons Learned. Monitoring the fate of PHCs at and downgradient of the source during successive injection of a high volume of a concentrated sulfate solution is challenging. However, the isotopic enrichment patterns observed for BTX and sulfate provided definitive information to evaluate the fate of PHCs in the groundwater. These data showed the occurrence of PHCs biodegradation associated with sulfate reduction. The concentration and isotope patterns observed for DIC are also linked to PHCs biodegradation. The microbiological data showed both, the occurrence of biodegradation under aerobic and anaerobic conditions in the PHC plume.

Back to Contents

Interpreting Field Data based on Trends from a One-Dimensional Model of Contaminant Isotopic Ratios Subject to Degradation and Advective Flow

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Background/Objectives. At many sites compound specific isotope analysis (CSIA) is employed to help inform the site-conceptual model. This can be done to help direct remediation work or to answer forensic questions about where a plume originated. This has been explored for continual sources by Breukelen, Hunkeler and Volkering (*Env. Sci. Tech.*vol. 39, pp. 4189-4197). However, at many sites there is no longer a source to the dissolved phase. This project will explore the implications of that model for sites where the source is no longer active.

Approach/Activities. The subject sites had been managed for many years, but questions had arisen that required definitive answers. Some questions were strictly concerned with remediation: “At this trichloroethene site are the trichloroethene, cis-dichloroethene and vinyl chloride all degrading?” Other questions focused on forensics: “Can the location of the original source be determined for a plume which extends across a property boundary and potentially has a center-of-mass very far from the origin?” It was proposed that CSIA data be used to answer these questions.

Using the model proposed by Breukelen, Hunkeler and Volkering, a database of profiles of isotopic ratio versus distance for a set of plume ages will be developed for various scenarios. Scenarios to be explored will include ones where the degradation is entirely reductive, others where the degradation is “stalled” or stopped at the conversion of trichloroethene to cis-dichloroethene, others where the pathway is partially reductive and partially oxidative, and others where the pathway is part biological reduction and part abiotic.

Results/Lessons Learned. The profiles generated from these scenarios will form a database that will be used to help identify scenarios which explain the observations from three sites. The value to the site management in knowing both plausible and implausible scenarios will be discussed.

Isotopic Fractionation in the Terminal Electron Acceptors during Biodegradation of Benzene and Toluene

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Background/Objectives. NOVA Chemicals has various levels of known organic contaminants in soils and groundwater at its ethylene manufacturing facilities. The objective of this project was to evaluate if chemical and isotopic techniques can be used to identify the processes involved in biodegradation of these contaminants and possibly to enhance the efficiency of these contaminant removal processes.

Approach/Activities. The project consisted of a series of laboratory experiments aimed at coupling various redox processes to the biodegradation of benzene and toluene. Redox processes such as denitrification and bacterial sulfate reduction often facilitate the biodegradation of benzene and toluene. Specifically nitrate and sulfate can serve as the terminal electron acceptors by nitrate-, and sulfate reducing bacteria during biodegradation. In the laboratory experiments, the isotopic fractionation factors for bacterial sulfate reduction and denitrification were assessed under anaerobic conditions and for varying concentrations of nitrate, sulfate, benzene and toluene.

Results/Lessons Learned. The biodegradation of benzene and toluene was observed under redox conditions favoring denitrification and bacterial sulfate reduction. This was evidenced in the laboratory experiments by the decreasing concentrations of: benzene or toluene and sulfate or nitrate over time. Isotope enrichment factors of -14.6‰ for bacterial sulphate reduction and -34.6‰ for denitrification were obtained. The use of isotope enrichment factors in the terminal electron acceptors as a tracer for biodegradation is a new and novel approach and can be implemented in the management strategy for any bioremediation project.

Extending the Applicability of Compound-Specific Isotope Analysis to Low Concentrations of 1,4-Dioxane

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Background/Objectives. A critical process of natural attenuation is contaminant degradation. At many sites, it is most difficult to demonstrate degradation of 1,4-dioxane, which is often present at chlorinated solvent sites but is considered to be recalcitrant in the subsurface. Little is known about the fate of 1,4-dioxane at low concentrations in the subsurface, because most laboratory and field studies have involved concentrations in the 1,000 microgram per liter (µg/L) range. Compound-specific isotope analysis (CSIA) is a powerful tool for providing evidence of contaminant degradation of many groundwater contaminants including fuel-related hydrocarbons, oxygenates and chlorinated solvent compounds. For example, CSIA has been proven to be a very important tool to document biodegradation of another organic contaminant with similar chemical properties to 1,4-dioxane – methyl-tert-butyl ether (MTBE), thought to be resistant to biodegradation 15 years ago. CSIA is now a primary technique used to show that MTBE degrades under both engineered and natural conditions. The same could be true for 1,4-dioxane if a reliable and practical method for performing CSIA on groundwater samples can be developed; the currently available methods are generally not reliable below concentrations of 50 µg/L. The objective of this research is to develop a method for performing CSIA at concentrations as low as 1 µg/L, so that it can be applied at sites with dilute 1,4-dioxane plumes.

Approach. A method was developed for concentrating dilute aqueous concentrations of 1,4-dioxane onto a synthetic carbonaceous resin with a high sorption capacity for 1,4-dioxane, and then extracting the 1,4-dioxane with solvent to yield a much more concentrated solution. The first phase of testing involved assessing whether fractionation of the $^{13}C/^{12}C$ ratio of 1,4-dioxane occurred during loading and extraction from the resins. Six mass loading and extraction experiments were performed with 50 mL of 1,4-dioxane diluted to approximately 1g/L and loaded onto approximately 1 gram of resin. In each case, the resin material was fully saturated with 1,4-dioxane. Small aliquots of solvent (2 mL) were used to extract the 1,4-dioxane mass from the resin. Mass recoveries ranged from 91.0 to 98%. Stable carbon isotope ratios of the extracts and samples of the pure 1,4-dioxane were analyzed at the University of Waterloo Stable Isotope Laboratory.

The next steps for this research involve repeating the tests at successively lower concentrations to determine the limit of applicability for carbon and hydrogen isotope ratios and assessing the variation of $^{13}C/^{12}C$ and D/H ratios of 1,4-dioxane in groundwater samples from multiple field sites.

Results. The $\delta^{13}C$ value of pure 1,4-dioxane used to prepare aqueous solutions was -33.3 ‰. The different extracts from separate batch extractions yielded a mean $\delta^{13}C$ value of extracted 1,4-dioxane of -33.6 ± 0.3 ‰. Extraction efficiency from the resin did not impart any systematic effect on $\delta^{13}C$ values. These tests provide confidence that the concentration method does not fractionate carbon isotope ratios of 1,4-dioxane. Similar experiments are being performed at lower concentrations of 1,4-dioxane and on D/H ratios and sampling methods for trapping 1,4-dioxane from dilute groundwater samples.

Back to Contents

State of the Practice: Molecular Biological Tools, Leaps Forward and Lessons Learned

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Background/Objectives. From metagenomics through transcriptomics to proteomics and metabolomics, the advances in molecular biological tools (MBTs) over the past 30 years have been truly astounding. DNA and RNA extractions on environmental samples are now commonplace and qPCR is a routine component of site management. qPCR has given rise to QuantArrays, advances in next generation DNA sequencing technologies seem nearly continuous, and widespread environmental proteomics may be just over the horizon. The presentation will report on the technological advances in the molecular biology but will also attempt to highlight lessons learned, research needs and potential pitfalls of environmental molecular diagnostics (EMDs) in the "Omics Era".

Approach/Activities. In 2013, the Interstate Technology and Regulatory Council EMD team published online documents offering guidance on the application of MBTs for environmental remediation. The presentation builds upon these summaries to describe new technologies not included in the ITRC documents including high-throughput qPCR arrays (QuantArrays), applications of next generation sequencing (NGS), and advances in proteomics. However, the underlying purpose of MBTs in environmental remediation – accurate determination of whether biodegradation of specific contaminants is possible and whether those functions are active at the site – is sometimes lost amidst the "omics" revolution. To address this emerging issue, a literature review of MBT applications in bioremediation was conducted. The recommendations and research needs published over the last 30 years by leading researchers, practitioners, and expert panels were then compared to the current state of the practice to identify lessons learned, lingering questions, and misconceptions.

Results/Lessons Learned. Great strides have been made in our ability to assess the potential for contaminant biodegradation. Not only has qPCR quantification of *Dehalococcoides* become a fundamental part of assessment at chloroethene sites but quantification of functional genes involved in aerobic cometabolism of chlorinated compounds and biodegradation of petroleum hydrocarbons is much more common. Despite these advances, barriers to increased use and utility of MBTs remain. While efforts have been made to standardize protocols, sample collection, extraction, reaction conditions and quality control parameters differ notably between laboratories potentially hindering confidence in the MBTs as a whole. Identification of new biomarkers has been repeatedly identified as a research need. With recent identification of genes involved in anaerobic benzene biodegradation and additional reductive dehalogenases, progress has certainly been made. Moreover, pure culture and environmental proteomics will greatly aid in biomarker identification and validation. Finally, expert panels have also cited lack of rate information and limited decision-making impact as barriers to increased use of MBTs in environmental remediation. NGS has been demonstrated as a great investigative tool to examine microbial community composition but function does not always follow phylogeny and all MBT results must viewed in the context of their ability to contribute to site management decisions. However, with analysis of databases compiling extensive, widespread and long-term use of MBTs most notably qPCR, we are now in a much better position to begin to address these issues and in the relatively short term, proteomics results may better correlate to biodegradation rates and allow progress toward predictive models.

The Molecular Tool Box: Current and Future Applications to Improve Microbial Remedies

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Background/Objectives. The discovery of specialized anaerobic bacteria that use chlorinated compounds as respiratory electron acceptors (i.e., organohalide respiration) has been the basis for productive bioremediation applications. Many key players contributing to reductive dechlorination at chlorinated solvent sites have been discovered, and organism- and process-specific biomarker genes have been identified. Quantitative real-time PCR (qPCR) assays emerged as the Environmental Molecular Diagnostics (EMD) tool of choice to assess and monitor reductive dechlorination processes. Since the enumeration of genes (i.e., DNA targets) merely indicates the potential for a process of interest to occur, the information has limited value to assess actual activity. The greatest challenge for EMD applications is to establish links between biomarker abundances and process rates, so that contaminant longevity can be predicted.

Approach/Activities. To demonstrate the value of current EMD tools, qPCR and contaminant concentration data from over 700 wells impacted with chlorinated ethenes were analyzed. A correlation analysis was performed to link contaminant and ethene concentration information with *Dehalococcoides mccartyi* (*Dhc*) biomarker gene abundances. Recent technological advances enable high-throughput qPCR applications, and hundreds of target genes and transcripts can be analyzed simultaneously in a highly parallel format. Further, environmental proteomics has matured into a technology applicable for monitoring biomarker proteins in environmental matrices, including groundwater. The value of these new tools for bioremediation was explored and demonstrated at field sites.

Results/Lessons Learned. Correlation analysis enhanced the value that *Dhc* biomarker gene-centric qPCR offers for bioremediation monitoring. At a majority of wells where ethene was detected, the abundance of the vinyl chloride (VC) reductive dehalogenase (RDase) genes *bvcA* or *vcrA* was elevated. Elevated ratios of *Dhc* 16S rRNA genes to total bacterial 16S rRNA genes and of the sum of the VC RDase *vcrA* and *bvcA* genes to *Dhc* 16S rRNA genes were strong indicators for detoxification of chlorinated ethenes to ethene. The application of environmental proteomics at a chlorinated solvent site informed about nutritional limitations, and targeted biostimulation enhanced *Dhc* dechlorination performance. The analysis of dechlorinating consortia and groundwater samples demonstrated the value of high-throughput qPCR applications, and provided new insights into the reductive dechlorination process. The integrated application of biomarker gene-, transcript-, and protein-centric EMD application generates additional valuable information regarding the microbiology responsible for contaminant detoxifcation. Such information is critical for selecting the most promising remedy, support efficient site management, and provide more reliable time lines for achieving site closures.

Using CSIA to Document Biodegradation of *cis*-DCE and Vinyl Chloride in Groundwater

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Background/Objectives. The Naval Facilities Engineering Command Southwest has evaluated the natural attenuation of chlorinated solvents at a site on Naval Air Station North Island, near San Diego, California, USA. At the site, land had been created by backfilling an inlet with sediments that were dredged from the bay. The new land was used in part for disposal of waste, including chlorinated solvents. A water table aquifer formed in the fill. The groundwater that was contaminated with volatile organic compounds including TCE is termed IR Site 5-Unit 2.

At the site, natural biological reductive dechlorination is transforming TCE to *cis*-DCE and vinyl chloride. There was some question of the extent to which the *cis*-DCE and vinyl chloride were being further degraded to ethylene or ethane. At most sites ethylene and ethane are further degraded and do not accumulate to stoichiometric concentrations in groundwater.

Approach/Activities. When *cis*-DCE or vinyl chloride is degraded, the ratio of the stable isotopes of carbon is changed in the material that remains after degradation. This fractionation of the isotopes can be measured by compound specific isotope analysis (CSIA). The extent of degradation can be related to the extent of fractionation. Groundwater was sampled from a series of wells that extended from the source of the contamination to the toe of the plume. The concentrations of *cis*-DCE and vinyl chloride were determined, and the isotopic ratio of carbon ($\delta^{13}C$) in the compounds was determined. To evaluate the data, they were compared on a plot that depicts the extent of fractionation that would be expected if attenuation was not caused by degradation, and also depicts the extent of fractionation that would be expected from biological reductive dechlorination. The plots can reveal the occurrence of degradation, and provide an estimate of the relative extent of attenuation caused by degradation as opposed to dilution and dispersion.

Results/Lessons Learned. In wells at the source of the TCE contamination, CSIA provided minimal evidence for degradation of cis-DCE and no evidence for degradation of vinyl chloride. At wells in the mid-point of the plume, CSIA provided evidence for extensive degradation of both *cis*-DCE and vinyl chloride. Degradation could account for one-half to one-third of the total attenuation. Further down the plume, CSIA could document degradation, but the apparent attenuation due to degradation was less, and attenuation due to dilution or dispersion was more important. This is expected. It is likely that various flow paths in ground water are heterogeneous in the rate of degradation. Flow paths with less degradation will make a relatively greater contribution to the total concentration in down gradient wells.

Metagenomic and Metagenetic Approaches Applied to Enhanced Anaerobic Reductive Dechlorination of Polychlorinated Biphenyls: Linking Structure and Function

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Background/Objectives. Polychlorinated biphenyl (PCBs) manufacture and industrial use have been banned for decades, and yet, environmental contamination continues to pose serious health risks. PCBs are a 209 congener chemical family formed by a biphenyl backbone potentially chlorinated at 1 to 10 positions. PCBs can be completely degraded by bacterial communities under sequential anaerobic and aerobic conditions as anaerobic reductive dechlorination is more effective with highly substituted PCBs and aerobic degradation more effective with low chlorine number PCBs. Our goal here was to explore the microbial community structure and function involved in effective PCB dechlorination

Approach/Activities. Anaerobic conditions were induced in one soil and two sediments polluted with PCBs at different concentrations by the addition of molasses, lactate, or soy bean oil. These substrates are known to induce anaerobic conditions that could lead to anaerobic dechlorination. To evaluate bacterial diversity and community structure, two metagenetic approaches were used to characterize the biodiversity by ribosomal intergenic spacer analysis (RISA) and phylogenetic microarrays based on the 16S rRNA gene. In addition, PCB composition and total mass were measured. Two different metagenomic approaches were also applied: 1) Reads were compared to nucleic and proteic sequences annotated as dehalogenases or known as affecting dehalogenation processes; and 2) A non *a priori* method was done by comparing sequencing results and bacterial databases.

Results/Lessons Learned. Correlations were calculated between our metagenetic (diversity/structure) and metagenomic (potential functions) results at the genus level. We were able to reconstruct partial pathways that may be involved in the dechlorination process as a function of the organic substrate added. For example, in the soil treated with soy bean oil, the function related to fatty acid metabolism increased and this increase was correlated to fatty acid degraders. By combining these results, we propose possible cooperation between bacteria during the degradation of PCBs. Metagenomics and metagenetics together provide details concerning microbial community involvement in metabolic pathways.

Use of Metaproteomics for Detection of Peptides Involved in In Situ Degradation of Energetic Contaminants

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Background/Objectives. Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is a widely used explosive, and it is recognized as a contaminant of concern at several Department of Defense (DoD) cleanup sites. RDX has a lower sorption potential to soil compared to other compounds commonly used in military explosive formulations, which may lead to an increased potential for RDX migration to and contamination of groundwater. The biological degradation pathways that impact the fate and transport of RDX are not well understood. New advanced molecular tools such as proteomics have a great potential to provide important information, which can be used to document the natural attenuation of RDX and/or to design more effective bioremediation strategies to accelerate the rate of biotransformation under anaerobic conditions (via co-metabolic processes) or under aerobic conditions (via bioaugmentation).

Approach/Activities. Here, we propose a protein-based approach that offers a viable alternative for quantifying rates of natural attenuation or *in situ* bioremediation (under varying redox conditions). Quantification of protein levels provides the advantage of direct correlation of bioremediation activity since gene copy numbers and transcript levels do not necessary correlate with protein levels of the target gene.

Results/Lessons Learned. The primary results identify a variety of peptides that may serve as biomarkers of RDX degradation. The proteomic approach has the potential to provide a wealth of new information regarding the microbial community structure, as well as protein function and activities within the subsurface.

Understanding Technetium Immobilization in the Subsurface at the Hanford Site

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Background/Objectives. Environmental bacteria play a role in reducing contaminants to less soluble forms. The purpose of this work is to identify the chemical and biological reactions that occur and potentially influence the mobility of Technetium (Tc-99) in the subsurface. Tc-99 is a by-product of nuclear fission processes and has a relatively long half-life ($t_{1/2}$=212,000 years), additionally, it is highly soluble and mobile in groundwater and is most often remediated through pump and treat systems. The oxidized form of Tc-99 (Pertechnetate, $Tc^{VII}O_4^-$) is highly soluble and very mobile, while the reduced form of Tc-99 (Technetium-oxide, $Tc^{IV}O_2 \cdot nH_2O$) is insoluble. Significant portions of the element are present at Department of Energy Sites such as Hanford. Complex interactions within the subsurface have made clean-up efforts for Tc-99 challenging. More importantly, it is difficult to predict or estimate the interactions and impacts of the complex, mixed microbial communities found in the environment.

Approach/Activities. We have set up controlled batch experiments to examine a selection of organisms (*Anaeromyxobacter dehalogenans* strain CP-C, *Geobacter sulfurreducens* strain PAC, *Geobacter daltonii* strain FRC-32, and *Shewanella oneidensis* strain MR1) that have a known metal reducing capabilities, for their ability to reduce Tc-99 to less soluble forms. An additional organism, *Cellulomonas* strain ES6 was chosen based on the origin of isolation from the Hanford site. Organisms were evaluated under anaerobic conditions both as isolates and in mixed consortia with and without the presence of iron-bearing mineral substrate. The substrate was selected based on the sediment present in the contamination plume the 200 Area at the Hanford Site. Experiments were monitored using qPCR, VOA analysis, ICP and biomass by total protein.

Results/Lessons Learned. Initial data collected has shown that the presence and type of substrate may increase the reduction of Tc-99 to less mobile forms. Preliminary qPCR data on the consortium has shown that while the inoculum is prepared with the relative numbers of each species being equal, different species become dominant as the experiment proceeded. Data collected from these experiments will allow for (a) a better understanding of the mobility of Tc-99 in the subsurface, (b) better predictions of contaminant fate and transport over time, and (c) the development of long term remediation strategies for Tc-99. Additionally, information collected will be used to develop a systems-based metabolic model with predictive capabilities; the model will be based on molecular methods for detection of bacterial species variation in the Tc-99 contaminated groundwater.

Back to Contents

Novel Genera Identified as Vinyl Chloride Assimilating Microorganisms using Stable Isotope Probing

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Background/Objectives. Vinyl chloride (VC) is a common contaminant reported in soils, surface water and groundwater. This chemical is classified as a human carcinogen, having a Maximum Contamination Level of 0.002 mg/L and Public Health Goal of zero mg/L set by US EPA. The objective of the current study is to identify the microorganisms able to assimilate VC in aerobic, VC oxidizing enrichment cultures.

Approach/Activities. Using enrichment cultures derived from contaminated groundwater we examined the microbial community involved in VC assimilation under aerobic conditions via stable isotope probing. For this, aerobic microcosms were amended with labeled (^{13}C) and unlabeled (^{12}C) VC and DNA was extracted twice (day 3 and 7) during the experiment. The extracted DNA was ultracentrifuged and fractioned. The DNA from the heavy fractions from both the labeled and unlabeled VC amended microcosms was subject to high throughput sequencing (MiSEQ Illumina). Specific primers were designed for the phylotypes responsible for label uptake using Primer-BLAST. The new primers were tested for specificity using Sanger sequencing. These primers were used in quantitative PCR assays across the buoyant density gradient to confirm label uptake.

Results/Lessons Learned. The enrichment culture degraded VC within 7 days. The heavy fractions (between 1.75 and 1.78 g mL^{-1}) were dominated by the genera *Nocardioides, Sediminibacterium, Aquabacterium,* and *Variovorax* at both time points, indicating these phylotypes were responsible for label uptake. While *Nocardioides* has been previously reported as an aerobic VC degrader, the other genera represent novel microorganisms associated with VC degradation. The primers designed for *Sediminibacterium* and *Aquabacterium* were highly specific to their target sequences. The qPCR assays for both genera at both time points also confirmed their assimilation of the label. Ongoing work involves primer design and specificity testing for *Variovorax*.

Development of Loop Mediated Isothermal Amplification (LAMP) for Rapid Detection of *Dehalococcoides* spp. in Groundwater Samples

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Background/Objectives. Typically, real time PCR (qPCR) based on the TaqMan probe or DNA binding dyes is used to quantify and monitor the in situ activity of *Dehalococcoides* spp. To date, a wide range of qPCR protocols to quantify 16S rRNA genes as well as reductive dehalogenase genes such as *vcrA, tceA* and *bvcA* are available. Although qPCR methods have been successful for monitoring reductive dechlorination, alternate molecular methods that are faster and cheaper, may make quantification of reductive dehalogenase genes in ground water samples easier. In this study, we developed LAMP for rapid and specific quantification of the vinyl chloride reductive genes (*vcrA* and *bvcA*), in commercial reductive dechlorinating cultures as well as groundwater DNA templates.

Approach/Activities. LAMP primers and a fluorescent probe were designed for vinyl chloride reductive genes (*vcrA* and *bvcA*) in *Dehalococcoides* spp. using Primer Explorer V4. The method was applied to commercial reductive dechlorinating cultures (SDC-9 and KB-1) and groundwater DNA templates. Threshold times and sensitivities were determined by creating a 10 fold dilution series for both template types. Detection limits were evaluated using plasmid standards for both genes. All experiments were performed on a real time PCR thermal cycler.

Results/Lessons Learned. Amplification was observed using LAMP primer sets for templates prepared from cultures SDC-9 and KB-1 as well as groundwater. Preliminary data indicates that LAMP was able to detect the vinyl chloride reductive genes (*vcrA* and *bvcA*) in *Dehalococcoides* spp. below 10^7 gene copies/L, the accepted threshold for natural attenuation. The presence of PCR inhibitors in groundwater templates may explain the slightly higher detection limit compared to SDC-9 and KB-1 templates. Future research will focus on developing the LAMP assay for the detection of 16S rRNA gene as well as other reductive dehalogenase genes (*pceA* and *tceA*) in *Dehalococcoides* spp., identifying PCR inhibitors in groundwater templates and mitigating their effects on amplification.

Advancing Phosphorous Speciation with Improved Mineral Libraries for X-Ray Absorption Spectroscopy

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Background/Objectives. Understanding phosphate speciation and solubility are of importance due to their role in agricultural productivity, in water quality, and as limiting nutrients for microbial remediation of hydrocarbons in subsurface environments where electron acceptors are plentiful. In cold climate calcareous soils of western Canada, the dominant phosphate species are calcium phosphate minerals. The end species, apatite, is insoluble and poses challenges to remediation processes. Magnesium (Mg) has been shown to substitute into the structure of some calcium phosphates and both increases solubility and slows the formation of insoluble end species. Little is known of the mechanisms and extent of magnesium substitution in calcium phosphate minerals.

Approach/Activities. The study utilizes XANES in phosphorous speciation opposed to the more conventional method of sequential extraction. This method is preferable to sequential extractions as it directly obtains solid state P speciation in soil. XANES utilizes synchrotron radiation to determine the chemical form of phosphorous, without sample alteration, and is sensitive to concentrations of 100 mg P/kg soil. However, there is a gap in phosphorous K-edge XANES spectra libraries in determining whether Mg/Ca mixed species are present. XANES results will be supported by elemental analysis through X-ray fluorescence, speciation through Fourier Transform Infrared spectroscopy, and through X-Ray Diffraction.

Results/Lessons Learned. This study determined speciation using synchrotron-based X-Ray Absorption Near Edge Spectroscopy (XANES). A range of Ca and Ca/Mg phosphate minerals was synthesized and a XANES spectral library was produced at the Canadian Light Source synchrotron. The library was used to determine P speciation in remediation samples that are part of an NSERC/FCL bioremediation research project in Saskatoon, SK where Mg saturation of soils was utilized as a treatment to enhance phosphate solubility. These measurements at the molecular-scale will validate the field-scale approach of producing Mg-substituted calcium phosphates in real world samples as part of remediation.

Diversity and Activity of Organohalide-Respiring Bacteria in PCB-Contaminated Activated Sludge and Toxicity of Digested Biosolids

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Background/Objectives. Polychlorinated biphenyls (PCBs) are persistent organic pollutants, which are hydrophobic molecules that adsorb to particles in the sludge present in wastewater treatment plants (WWTP). At a Baltimore WWTP, the wastewater undergoes aerobic biological removal of organic matter and enhanced biological treatment to remove nitrogen and in addition to chemically removing phosphorous through precipitation. The dewatered sludge is digested anaerobically in order to recover the energy as methane before the sludge is dried, pelletized and sold as fertilizer. Recycled sludge (biosolids) applied as fertilizer to farmland or with structural purpose for soil enhancement might unintentionally provide toxic contaminants (such as PCBs) present in the incoming wastewater thus causing an entry point for bioaccumulation in the food chain. The use of biosolids recycles valuable nutrients in the form of carbon, nitrogen and phosphorous that all are beneficial for soil enhancement and plant production. The objective of this study was to evaluate the diversity and activity of organohalide respiring bacteria in PCB contaminated activated sludge and digested biosolids to evaluate the change PCB congener pattern and thereby the change in toxicity throughout the waste water treatment process.

Approach/Activities. Samples were collected at three times during the year at five locations within the Baltimore WWTP and analyzed for: dry matter content, presence of PCBs (via gas chromatography) and the abundance and activity of PCB dechlorinating bacteria. DNA was extracted and selectively amplified by PCR using the specific primer set 348F/884R, enumerated via Q-PCR and identified via DHPLC/sequencing. Microscopic analyses were performed to analyze the spatial arrangement of dechlorinating bacteria in the sludge using fluorescence in situ hybridization with specific probes for PCB dechlorinating bacteria, DAPI staining and microscopic examination with CLSM and SEM.

Results/Lessons Learned. Organohalide respiring bacteria were identified in all sludge samples with (no. of organohalide respiring cells/g dry matter): Influent: $7.3x10^{6}$; recirculating activated sludge: $3.5x10^{11}$; dewatered sludge before digestion: $1.3x10^{11}$; post anaerobic digestion: $6.8x10^{7}$. DNA was not recovered from dried biosolids due to the high temperature treatment aimed at reducing presence of pathogenic bacteria. The decrease in abundance after anaerobic digestion might be due to the temperature conditions from mesophilic to thermophilic. According to results based on EPA method 8082 (detection limit: 0.5 µg/kg) PCBs were not detected in any samples. However, the high abundance of organohalide respiring bacteria that can thrive at low PCB concentrations seems to contradict this observation. This was also supported by the high diversity of organohalide respiring bacteria, since up to ten species were identified throughout the plant with the highest diversity in the dewatered sludge and the lowest in the recirculating activated sludge experiencing alternating aerobic and anaerobic conditions. The PCB concentration in the sludge was between 0.2 and 1.4 µg/kg. The degradation products and toxicity profiles showed that the toxicity of the 12 dioxin-like congeners increased throughout the plant. Potential improvements for biological transformation during the process are being investigated to reduce the PCB content as well as the toxicity during wastewater treatment.

Microbial Community Characterization at Bioremediation Sites Using Next Generation Sequencing

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Background/Objectives. Next generation sequencing (NGS) is increasingly used to provide detailed microbial community characterization in public health, medical, wastewater treatment, industrial fermentation and resource extraction scenarios. The growing availability of NGS is also making this increasingly affordable technology practical for bioremediation monitoring and performance assessment. While NGS protocols are robust, the ability to analyze and interpret results in a practical and meaningful way requires ongoing use and observations at a variety of remediation sites to better understand the benefits and limitations of NGS approaches.

Approach/Activities. In this study, NGS using a 454 pyrotag platform, and primers targeting 16S rRNA genes, were employed to characterize eubacteria and archaea from four geographically distinct chlorinated solvent bioremediation sites in the Pacific Northwest (PNW), Alaska (AK) Kansas (KS) and Florida (FL). All sites were bioaugmented and at various stages of remediation. Archived DNA samples spanning several years were used for the analyses. The resulting sequences were analyzed using cluster analysis, to compare the microbial communities over time and between sites, and non-metric multidimensional scaling (NMDS) to provide correlations to geochemical parameters.

Results/Lessons Learned. NGS returned an average of 8,000 reads per sample, providing detailed microbial community profiles. Cluster analysis indicated that samples from the same site generally grouped together and indicated that the microbial communities at the FL and KS sites were most similar but distinct from those at the AK and PNW sites. Based on the number of operational taxonomic units (OTUs) the AK site had the lowest microbial diversity and the FL site had the highest. Cluster analysis indicated that microbial community at the FL site became the most similar to the bioaugmentation culture injected at the site and may indicate that conditions at the FL site were most compatible with colonization by the culture. Observations of OTU frequency indicated that changes in the abundance of individual microorganisms could be significant, and could be correlated to specific changes in site geochemistry. NMDS analysis indicated that dissolved hydrocarbon gases (methane, ethane, ethene), oxidation reduction potential (ORP) and groundwater temperature were strongly correlated with microbial community structure, while other factors including pH, conductivity and time post-bioaugmentation had more subtle impacts. This study demonstrates that NGS can be used to better understand microbial communities in bioremediation systems and the technology's usefulness will undoubtedly increase in tandem with our ability to meaningfully interpret NGS results.

Microbial Characterization of Soil using Molecular Methods and Traditional Culturing for Assessment of Natural Attenuation of Mixed Contaminants

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Background/Objectives: Natural attenuation is a promising alternative for soil remediation, but its use requires providing lines of evidence for processes such as biodegradation. One such line of evidence is identification of microbes present in the soil that are known to biodegrade the contaminants of interest (COIs). Bacteria and fungi with known abilities to biodegrade COIs can be identified either by traditional culturing methods, or using molecular methods which do not require culturing. The objective of this effort was to assess the potential for biodegradation of COIs in soil using traditional culturing techniques combined with sequencing of the 16S or ITS regions of the cultured bacteria and fungi as well as molecular methods such as terminal restriction fragment length polymorphism (TRFLP), quantitative polymerase chain reaction (qPCR). The microbiome was also characterized via mass sequencing of ribosomal RNA genes.

Approach/Activities: Soil was collected from the Santa Susana Field Laboratory (SSFL). Liquid-propulsion rocket engine tests and nuclear energy research at the site led to contamination of the soil with polychlorinated biphenyls (PCBs), dioxins, polycyclic aromatic hydrocarbons (PAHs) and non-PAH petroleum hydrocarbons (PHCs). Soil samples were collected from 30 different locations at the SSFL site with a wide range of COI concentrations. DNA was extracted directly from soil samples and amplified using PCR for TRFLP analyses and RNA gene sequencing analysis. The qPCR analysis (Microbial Insights®) was conducted on two soil samples using 18 gene targets for the degradation of PHCs and PAHs, as well as the target gene for *Dehalococcoides* (an anaerobic dechlorinating bacteria). Bacteria and fungi were also isolated on plates containing model compounds to serve as substrates similar to each COI.

Results/Lessons Learned: From the culturing experiments, 45 microorganisms were isolated, sequenced, and identified. These included 14 unique bacteria and 7 unique fungal species. Of these, 10 bacterial species and 5 fungal species were previously reported to biodegrade the site COIs, or belong to genera reported to biodegrade the COIs. According to TRFLP analysis, soil type exerted more effect on the microbial community structure than the presence of any COI. No specific TRFLP peaks were significantly correlated with any COI. According to qPCR analysis, SSFL soils contain large populations of microbes capable of degrading PHCs aerobically. Anaerobic PHC, anaerobic PAH, and aerobic PAH targets were not detected. A small amount of *Dehalococcoides* was detected in one of the samples. The rRNA gene sequencing analysis revealed a diverse soil microbial population spanning many genera, but no strong correlation was observed between species abundance or presence and specific COIs. Collectively this study suggests that microbes present in SSFL soils are capable of biodegrading PHCs, but not PAHs, PCBs, or dioxins. Results are consistent with companion microcosm experiments which found little biodegradation of the chlorinated COIs in SSFL soils incubated in the laboratory.

Back to Contents

Time versus Money: A Quantitative Approach to Selection of Groundwater Monitoring Frequency

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Background/Objectives. Every year, hundreds of thousands of wells at contaminated groundwater sites are sampled in order to characterize changes in contaminant concentrations. The annual cost of this monitoring likely exceeds $1 billion. Despite the enormous cost of monitoring contaminated groundwater sites, there are few methods available to select appropriate monitoring frequencies. Those methods that are available generally do not quantify the trade off between monitoring frequency and accuracy in characterization of the long-term change in concentration.

Approach/Activities. We have utilized the statistical properties of regression analysis to quantify the relationship between monitoring frequency and accuracy and confidence in characterization of the long-term change in concentration. When using regression analysis to estimate the long-term trend (either linear or first-order) both the accuracy (as expressed by the 95% confidence interval for the trend) and the confidence (as expressed by the p-value) are proportional to the standard error of the regression. In addition, there is a quantifiable relationship between the standard error and i) the number of monitoring results used to characterize the trend and ii) the time between each monitoring event. As a result, the effect of both the number of monitoring events and the time between monitoring events on the accuracy and confidence of the long-term trend can be quantified.

Results/Lessons Learned.
For any given monitoring frequency (e.g., quarterly monitoring), the accuracy and confidence in the long-term trend doubles when the number of monitoring events is increased by about 60% (e.g. from 10 events to 16 events). For any given number of monitoring events, the accuracy and confidence in the long-term trend doubles when the time between monitoring events is doubled (e.g., from 10 quarterly events to 10 semiannual events). Taken together, these two relationships quantify the trade-off between time and money for characterizing the long-term trend in groundwater contaminant concentrations. Deceasing the monitoring frequency by 50% while increasing the total monitoring time by 25% results in no change in accuracy or confidence of the trend but decreases monitoring costs by 38%. For example, five years of semiannual monitoring (10 events) will provide the same level of accuracy and confidence in the long-term trend as four years of quarterly monitoring (16 events). Although the magnitude of the long-term trend and the magnitude of short-term variability do affect the absolute accuracy and confidence of the long-term trend, these site-specific factors do not affect the trade-off between time and money.

Ternary Diagrams of BTEX Concentrations to Evaluate Remediation Performance: Examples from a Former Refinery Site

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Background/Objectives. When a contaminated site is undergoing engineered remediation, it can be useful to track not only contaminant concentration levels, but also to determine the removal mechanisms that are responsible for decreasing concentrations. Various mechanisms can cause decreases in measured groundwater contaminant levels that are unrelated to the engineered remediation systems. If decreases in contaminant levels are due to physical (non-destructive) mechanisms, such as volatilization, dilution, sorption, or dispersion, the potential for dissolved concentration rebound is higher than if the contaminants are being degraded through biological or chemical mechanisms. In order to optimize the effectiveness of engineered remediation systems, it is desirable to assess, during system operation, those mechanisms impacting contaminant concentrations in groundwater. One strategy for determining the dominant removal mechanism is to evaluate the ratio of removal rates of different BTEX compounds. Theory and empirical data from field studies both indicate that the removal rates for different compounds depend on the removal mechanism. The evolution of the proportion of selected compounds can thus be used to indicate which removal mechanism is dominant.

Approach/Activities. Ternary diagrams can be used to plot the ratios of dissolved BTEX compounds in monitoring wells, and to show the trajectory of these ratios over time. Expected mechanism-specific trajectories were established based on aerobic and anaerobic biodegradation rates in previous review papers, and based on a volatilization model. This method was tested on historic groundwater monitoring data from a former refinery site with a robust air sparging system. The site has been extensively studied, and the available data spans over 25 years for some wells. Ternary diagrams of benzene/toluene/ethylbenzene and benzene/toluene/total xylene concentrations were used to assess removal mechanisms at monitoring wells where dissolved BTEX was detected over multiple years. The ternary diagrams for two monitoring wells located within the radius of influence of the air sparge wells clearly show the effect of air sparging on the evolution of contaminant ratios. Several other wells with decreasing concentrations outside the radius of influence of the air sparge system showed trajectories indicative of anaerobic biodegradation or no discernable trend, which indicates dilution/dispersion effects.

Results/Lessons Learned. The application of ternary diagrams to existing BTEX data from a remediation site showed evidence of anaerobic biodegradation, aerobic biodegradation, volatilization, and dilution/dispersion as the dominant removal mechanism at different wells on the site. This tool enabled us to assess which wells were directly impacted by the air sparge system. This method will be explored in future studies, where we plan to apply ternary diagrams along with other diagnostic tools, such as compound specific isotope analysis and molecular biological tools, to assess the effectiveness of remediation systems during operation to help optimize remediation efforts.

Quantifying Enhanced Anaerobic Bioremediation of Chlorinated Solvents

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Background/Objectives. Enhanced anaerobic bioremediation (EAB) using injected carbon amendments has become a common practice at chlorinated sites where natural sources of bioavailable organic carbon are insufficient for effective and sustained rates of reductive dechlorination. Whether EAB is employed as a primary remediation strategy or considered as a transition technology prior to employing a more passive approach (e.g., Monitored Natural Attenuation, MNA), decision making is hampered by data limitations to determine when such transitions can take place. Short-term sustainability of EAB is typically evaluated using dissolved-phase concentrations of total organic carbon (TOC) and dissolved oxygen (DO) and is limited to empirically-based methods. A promising and low cost metric for evaluating short-term and long-term sustainability of EAB is potentially bioavailable organic carbon (PBOC). Previous research demonstrated strong correlations at MNA sites between PBOC concentrations in aquifer sediments and TOC and DO levels in groundwater systems. We hypothesize that PBOC is effective in differentiating residual injected organic carbon substrates, both soluble substrates (e.g., lactate) and slow-release substrates (e.g., emulsified vegetable oil or EVO), bound to some degree to aquifer materials. To test this hypothesis, we investigated PBOC at EAB sites and conducted laboratory experiments to verify key assumptions. As addition data to support to this hypothesis, we assessed the impact of EAB on microbial communities using DNA extraction and sequencing.

Approach/Activities. Aquifer sediment was collected at two EAB sites treated with EVO injections. PBOC was measured in background locations and compared to the concentration and distributions of PBOC at treated areas and at various distances located downgradient of groundwater flow away from EVO injection points. Data analysis included comparison of PBOC results to site geochemical parameters. Laboratory experiments were conducted using EVO-treated soil in flow-through columns to evaluate the loss of TOC and obtain measurement of PBOC over time. The impact of EAB on the composition of the total and metabolically active microbial communities and their diversity was also evaluated using a subset of the total samples by targeting bacterial 16S rRNA genes using Illumina DNA sequencing techniques. The aim was to identify dominant microbial community members associated with active dechlorination and to provide a comparison of the broader bacterial diversity among samples.

Results/Lessons Learned. Results of the field survey showed statistically valid distinctions between PBOC in treated areas and background concentrations of PBOC at both EAB sites. Greater levels of PBOC (1-2 orders of magnitude) were present in aquifer sediment at EVO-treated sampling sites compared to non-treated sediment. At one site where samples were collected along the groundwater flow path, decreasing PBOC with distance was observed at locations downgradient of EVO injections. Results of the laboratory column experiment confirmed the hypothesis that PBOC is effective in measuring residual amended carbon. Data enabled quantification of mass balance and rates of mass transfer. At present, results of the next-generation sequencing of microbial communities of EAB site samples are pending but results will be available when updating of abstracts is permitted. Overall, the results confirm the hypothesis, suggesting that PBOC has merit in support of decisions regarding the efficacy of carbon injections and when evaluating the long-term sustainability of EAB.

Big Data Analysis to Select the Best Remedial Technology to Meet Remedial Objectives

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Background/Objectives. Can we use data analytics to identify technologies best suited to meet remediation goals at contaminated groundwater sites? The objective of this study is to develop a statistical methodology to determine the optimal technology for a groundwater site given select characteristics. The methodology will be developed using a large dataset of groundwater samples and hydrogeological data from numerous sites treated for contamination in the United States. The hypothesis is that sites with similar chemical and hydrogeological characteristics should perform equally with similar remedial technologies.

Approach/Activities. The approach proposed in this study includes clustering all sites based on select aquifer characteristics where initial contaminant concentrations (at time zero of remediation) are defined. Further sub-clustering will be based on remedy “performance” defined as the temporal trends observed for concentrations of contaminants during remediation. For each site observation, concentrations of contaminants of interest in groundwater are analyzed via multivariate time-series analysis to reduce dimensionality and visualize the multivariate trend. This visual representation is then converted to a signature that can be used in the clustering analysis. Remedial technologies used in each subcategory can then be evaluated by testing the distribution across site-categories to determine with statistical significance the technology that predicts a specific performance.

Results/Lessons Learned. Operational and monitoring data for hundreds of thousands of sampling locations were obtained from two datasets. Integrating the data has presented challenges with entity resolution, defining representative samples, and dealing with data quality issues and censored data. Although the project is still ongoing, we show with preliminary data how the clustering is performed and present the algorithm used to convert multivariate time-series data to string symbols and the statistical test to determine the technology associated with each site and performance. This work demonstrates the application of various data mining techniques to reduce the dimensionality of site operational and monitoring data. Specifically, clustering multivariate time-series analysis is proposed. Although many statistical applications have used time-series data to cluster objects by a set of features, only a few applications have clustered multivariate time-series data and none, to our knowledge, have been applied in the analysis of environmental monitoring data.

When and Where are High-Resolution Data Required? Sequence Stratigraphy to Determine Depositional Environment and Data Requirements for Optimized Remediation

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Background/Objectives. Sedimentary aquifer systems are the end product of transport, deposition, and burial of sediments in a wide variety of depositional environments from alluvial fan to basin plain. The processes of transport, deposition, and preservation of sediment active in each depositional environment are different, and determine the character, orientation, and dimensions of aquifer and aquitard elements present in an aquifer system, and hence the need (or lack thereof) for “high-resolution” characterization. Sequence stratigraphy is methodology that provides an effective means of identifying depositional environments in existing remediation site data. Several project case studies representing different depositional environments are presented. In each case the aquifer architecture is documented and the level of vertical and lateral data resolution required to adequately characterize the system is discussed. Historically, simplifying assumptions of homogeneity and isotropy of aquifer systems have been made in design of groundwater remedies including containment, pump and treat, and in-situ remedies and these assumptions resulted in implementation of remedies incapable of achieving requirements. Realization that simplifying assumptions are limiting the ability to achieve remediation goals has resulted in the need to acquire additional high-resolution site data to characterize aquifer heterogeneity. Application of sequence stratigraphy and facies models for depositional environments provides a complementary approach to predict styles and degree of heterogeneity in aquifers and aid in optimization of high resolution data collection programs.

Approach/Activities. Existing data from groundwater remediation sites corresponding to fluvial, alluvial fan, aeolian barrier island, back-barrier lagoon, and mixed aeolian/ fluvial are reformatted to reveal grain size trends in the lateral and vertical sense and are examined using a sequence stratigraphic approach to address remedy performance and site management strategies. Case studies are presented from each environment, their aquifer and aquitard dimensions documented, and the need for high resolution data collection discussed.

Results/Lessons Learned. The processes of transport, deposition, and preservation of sediment active in each depositional environment are different, and determine geometric and sedimentologic properties of aquifer and aquitard elements present in an aquifer system. Aeolian and back-barrier systems where sands are derived from aeolian dune systems seaward tend to be sheet-like in nature, and hence a high degree of vertical resolution may be required, but a low degree of lateral resolution is sufficient to adequately characterize plume morphology and contaminant distribution. In contrast, fluvial deposits consist of sinuous and lenticular sand bodies encased in relatively lower permeability channel margin, overbank, and floodplain deposits have a high potential for off-gradient groundwater flow and contaminant transport, as well as matrix contaminant storage and hence require significantly higher data densities in both the vertical and lateral sense. Identification and accurate interpretation of depositional environments in aquifer systems provides a predictive framework for data acquisition and remedy implementation, improves efficiency throughout the characterization and remediation lifecycle, significantly reducing cost and time to closure.

Back to Contents

A Review of the Basis for Environmental Sample Holding Times and an Experimental Evaluation of Alternative Stabilization Techniques for Polycyclic Aromatic Hydrocarbons

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Background/Objectives. The efficient shipment of environmental samples from international locations is often impacted by transportation issues that may influence the scientific integrity of the samples. Delays due to remote collection sites, customs clearance, poor shipment communications, weather delays at airports, and other factors can result in the delivery of samples to the laboratory that exceed the US Environmental Protection Agency (USEPA) holding times and/or temperature requirements which most environmental professionals view as sound requirements to ensure no target analyte degradation prior to extraction. These requirements are generally accepted by the scientific and regulatory community as defensible standards for monitoring sample integrity, which when exceeded raise issues associated with the validity of the final chemical measurement.

One objective of this study was to review the scientific basis and technical foundation for currently accepted USEPA sample holding times for polycyclic aromatic hydrocarbons (PAHs) in water, sediment and tissue samples, and to identify current published research that may provide alternate viable approaches for the preservation of environmental samples that are less sensitive to temporal and temperature issues often associated with international sample shipments.
The second objective was to test the most optimal preservation methods designed to stabilize PAHs in environmental matrices and provide longer sample holding times at ambient temperatures without compromising sample integrity and data quality.

Approach/Activities. A review was conducted to determine whether the fundamental basis for the development of holding time criteria by the USEPA was valid. Subsequently, holding time studies at room temperature in water and sediment matrices were conducted in accordance with ASTM D4515-85 using two preservation methodologies (sodium azide, low pH). The degradation of the 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) including 1 and 2-methylnaphthalene was monitored in preserved sea water and marine sediments at room temperature by EPA method 8270d.

Results/Lessons Learned. Current PAH holding times defined in the mid-1980s are based primarily on administrative requirements rather than laboratory based validation studies. Although, there has been substantial research concerning the validity of volatile organic compound holding times, little work has been performed or published to validate PAH preservation criteria. Based upon literature review, prescribed holding times for PAHs in water could be extended from the present 7 days when stored at 2-6^{o}C to 21 days when first acidified then stored at 4^{o}C. Moreover, increased acceptable holding times from 14 days for PAHs in sediment to 92 days has been documented. This research examines the reliability of two alternative preservation methods for sediment and water samples and their implications for the generation of more reliable environmental data collected in remote locations.

Enhancing Data Quality, Validity, and Reporting Speed with a Mobile Solutions Tool

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Background/Objectives. Environmental remediation and sustainability projects typically require collection and analysis of large volumes of field data. With the widespread availability of mobile devices, the opportunity exists to streamline data collection and concurrently improve quality by reducing errors associated with transcribing handwritten information or manually organizing data. Although numerous input devices and software are in the marketplace, the mobile tool presented here focuses on a simple, flexible, and customizable system using standard equipment such as tablet computers and readily available software.

Approach/Activities. A system was developed and tested using Microsoft InfoPath® (Windows®-based form creation software) which allows direct submission of the data to online web portals, such as Microsoft SharePoint® libraries. Key quality improvement features included dropdown menus and constrained data fields which showed errors or provided screen tips to the user. After submission, data are immediately accessible and can be exported in a database or tabular format. One significant feature is that the data fields (such as groundwater pH, conductivity, turbidity, temperature readings) are automatically transferred to the corresponding columns or fields in the online web portal. This process is more rigorous than simply copying a file to a remote location, as individual data fields are preserved. Forms can be easily customized to include instrument readings, notes, photographs, and GPS locations. Testing was specifically conducted in an offline mode in the field, such that an internet connection at remote sites was unnecessary. Submission of the forms to the online location is completed when an internet connection (such as a mobile hotspot) becomes available, and can be automated with pre-populated website locations or email addresses.

Results/Lessons Learned. Multiple platforms have been tested and are being implemented (Android™, iOS™, Windows) which has created a “bring your own device” (BYOD) environment. Primary challenges during implementation included the need to train field personnel accustomed to traditional data collection methods, development of backup systems to prevent data loss, and hardware requirements such as devices that are readable in outdoor lighting and able to withstand weather conditions and dropping. Efficiency and time savings were documented in several separate efforts by minimizing or eliminating post-field transcription and processing. Dropdown lists and constrained fields improved overall data quality by reducing errors in sample identifiers and providing initial data validation in the field. In summary, this system has several advantages, including use of common electronic input devices, readily available software with little need for custom programming, accurate data entry, and fast, simple submission to the user’s online data management system.

Innovative Sampling Technique for Site Characterization at an Active Manufacturing Facility

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Background/Objectives. A confidential manufacturing facility had a release of dielectric oil from transformers located in the basement of the facility. Traditional drilling techniques using a hydraulic probe drilling rig were used to investigate the nature and extent of the release. During this initial investigation, artesian conditions were encountered. Heaving sands and flowing water made well installation difficult and an adequate well seal could not be completed in at least one of the well locations. The difficult site conditions resulted in longer than expected drilling durations and a higher than expected volume of polychlorinated biphenyl (PCB) remediation waste. Tetra Tech developed an innovative approach to complete the site investigation in these difficult site conditions at a lower cost than traditional drilling techniques.

Approach/Activities. Tetra Tech completed a site conceptual model based on initial investigation results and developed an innovated step-wise site investigation approach that included ground penetrating radar (GPR), pilot testing of GORE® Modules and vapor pins, and hand-installed soil borings and temporary wells. The GPR survey identified anomalies in the subsurface that could be interpreted of areas of non-aqueous phase liquid (NAPL). These areas were selected for further investigation. A pilot test consisting of GORE® Modules and modified vapor pins was conducted in strategic locations to determine the accuracy of the GPR survey. In total, 11 sample points were advanced in the basement during the pilot test. NAPL was observed in five of the 11 locations and three samples were collected and analyzed for PCBs. The locations of PCB containing oil were successfully identified during the pilot test. Tetra Tech updated the site conceptual model based on these results and designed and implemented a temporary well installation program to further delineate areas of PCB containing oil in the subsurface. In total, 34 sample points were advanced. NAPL was observed in 15 of the 34 locations and 14 samples were collected and analyzed for PCBs. The extent of PCB containing oil was successfully delineated during this phase of work.

Results/Lessons Learned. Four innovative field methods were implemented with varying success. The GPR survey revealed anomalies in the subsurface; however, these anomalies did not appear to correlate to areas of NAPL. The GORE® Modules were ineffective in detecting PCBs, possibly due to the presence of NAPL and/or the low volatility of PCBs. The modified vapor pins and hand-installed soil borings were effective sample ports for the collection of groundwater and NAPL levels and samples for qualitative and quantitative analysis. Using these innovative and relatively non-invasive site investigation techniques resulted in the successful delineation of PCB containing NAPL in the subsurface at a third of the cost of traditional drilling methods.

SERDP Study Explores Well Flow Dynamics for Active and Passive Sampling

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Background/Objectives. Low flow purging and sampling techniques were introduced to limit purge volumes, reduce turbidity and agitation during sampling, and to improve repeatability. Passive, no-purge, samples likewise have been introduced to improve sampling by limiting waste generation, and improving cost structures. How do these methods reflect aquifer concentrations? Do they represent aquifer concentrations differently?

Approach/Activities. Strategic Environmental Research and Development Program (SERDP) project ER-1704 tested passive and dynamic sampling procedures in the lab, in the field, and in model domains to better understand flow dynamics in wells. Three short-screen (5-10ft) wells were installed in locations where differing degrees of contaminant stratification was known though isolated zone sampling. The wells were outfitted with sensors, passive grab sampling devices (Snap Samplers) and a low flow rate pump. Low flow purging and sampling was conducted, with parameter measurements recorded at 3-6 minute intervals using an uphole flow-through cell. Sensors were deployed in the well above and below the pump intake to record downhole parameters. Snap Samplers were deployed above and below the pump intake to collect physical samples before and after purging. The wells were purged at low flow rates (minimized drawdown) for up to 6 well volumes, with 20-36 VOC chemical analysis samples collected from the discharge during the course of the well purge. Modelled flow in wells was also explored to further illustrate field observations.

Results/Lessons Learned. Results describe a flow field where water flows largely horizontally from the formation to the well, then flows vertically in the well bore to the pump intake during pumping; and also vertically due to tiny density contrasts when not pumping. In many cases, several well volumes were required to clear the well and reach chemical steady state. “False” stability is a concern in early purge times as slow parameter drift may reflect continued contaminant concentration change. Additionally, steady state was a fragile condition. Pump discharge reflected water entering the pump from above and below, which in some cases was chemically very different. Changes to flow rate disrupted this fragile condition, changing discharge concentrations over a range of 50% or more until the stable condition was re-established. Ultimately, maintenance of steady flow rate, very stable parameter measurements (i.e. no slow drift), and several well volumes purged is required to obtain flow-weighted average samples using a low-flow purging approach. Passive sampling approaches usually yielded similar results without purging, but care was necessary to understand whether stratification in the aquifer was maintained or homogenized in the unpurged well, or if stratification was partially maintained. Determination of these effects required substantial effort and is probably not warranted for standard monitoring. However, the study is informative in that it explains some of the dynamics associated with why passive and active samples often yield similar chemical results, and illustrates why practitioners still must always pay attention to seemingly unimportant details such as slow purge parameter drift.

Using Predictive Uncertainty Analysis to Optimize an In Situ Bioremediation System Design and Control: Field Scale Application

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In situ bioremediation is a commonly used remediation technology to clean up the subsurface of a petroleum-contaminated site. The process control of such a system is complex and may involve more than one objective. This study discusses the development of a simulation model-based, dynamic, and multi-objective predictive control system for generating cost-effective control strategies for a bioremediation site, which involves substantial uncertain data.

To investigate remediation performances, a subsurface model was employed to simulate contaminant reactive transport. In the first step, a nonlinear optimization model was formulated to evaluate different remediation strategies. Based on the uncertainty involved in some model parameters, a prediction system was constructed to provide all possible outputs for the proposed remediation design. By using the prediction system, the optimal strategy to achieve the remediation objective can be directly located. In the second step, the method has been developed to handle the diminution of uncertainties involved in new parameter acquisition during the bioremediation process. An interactive decision-making tool is built for process control. The method includes generation of a set of optimal control strategies and identification of the optimal control strategy to satisfy the decision maker's particular preferences on tradeoff between cost and efficiencies.

The developed system has been applied on real site data. Application of the proposed approach to a bioremediation process in a real site, which involves substantial uncertain data, indicated that it was effective in dynamic optimization and real-time process control of the in situ bioremediation systems.

The proposed in situ bioremediation process optimization is done through the application of common groundwater flow and reactive transport models (MODFLOW, MT3DMS, PHT3D) in conjunction with publicly available tools (PEST) for predictive uncertainty analysis to provide to modelers and decision maker with a cost effective tool which is transferable from the present study to other site managed by in-situ bioremediation.

The Death of the Myth of Long-Screened Wells!
A Unique Methodology to Assess Large Dilute Plumes

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Background/Objectives. The generally accepted truth about long-screened wells is that they are not reliable for groundwater monitoring due to significant mixing within wells that are greater than 10' of screen length. Therefore, the analytical results of groundwater samples from long-screened wells are not believed to be representative of the zonal groundwater distribution in the surrounding formation. However, field procedures have been developed by Izbicki and others to profile the groundwater flow dynamics and chemistry of long-screened wells that defines the chemistry of the formation. In this case study, a large, dilute VOC plume is characterized by conducting depth discrete sampling of existing long-screened monitoring wells. A monitoring well with 125' of continuous well screen was profiled using the USGS method (USGS open file report, 1999) to determine if low-flow purge and sample methodology could be used to collect depth-discrete chemistry data representative of the formation.

Approach/Activities. The well profiling results reported for this case study are based on the same well profiling approaches that groundwater producers have used for decades to determine zonal flow and the location of zonal contributions of undesirable chemical constituents from production wells. Groundwater producers profiled wells by means of spinner log tools for flow, and jar sampling tools for water sampling within production wells. Over the past decade, the industry has seen significant reductions in the tool size and sensitivity of these instruments, thus allowing for use of the miniaturized technologies in production wells without pump removal with limited annular access and, in our study, a smaller diameter monitoring well.
The purpose of performing a flow profile for flow conditions inside the long-screened well was to use the flow data to perform a mass balance on the co-located depth-dependent groundwater samples. The flow surveys use a very basic idea where the in-pipe groundwater velocity is measured – in this case by means of tracer rhodamine red FWT 50. The tracer has a low specific gravity of 1.035 g/cc and when diluted in water asymptotically approaches the specific gravity of water (1g/cc). Therefore, the tracer is essentially neutrally buoyant and can be used to track groundwater movements over a wide range of velocities.

Results/Lessons Learned. Based on the results of the flow profiling analysis of a long-screened well, low flow purge and sampling methodology is appropriate to collect depth-dependent groundwater chemistry data that is representative of the surrounding formation proximal to the well screen in this study area. This is invaluable when attempting to characterize the nature and extent of a large, dilute VOC plume. For large dilute plumes, short-screened wells do not characterize the entire impacted section at any one location, and nesting several short-screened wells is very costly. However, profiling long-screened wells provides a high resolution vertical characterization of the plume that is not attainable with other technologies. The results of this technology provide insights on what groundwater sampling methodologies result in data representative of the formation versus methodologies that are only indicative of what is in the well casing (i.e., passive groundwater sampling methods).

3-D Mapping of Subsurface Microbial Activity for Complete CSM

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Background/Objectives. A complete conceptual site model (CSM) needs to include a good understanding of subsurface microbial activity, as this factor can significantly affect overall remedial strategy as it relates to active cleanup, monitored natural attenuation (MNA), or some combination of both. Additionally, the presence and degree of bioactivity can affect technology selection, and potentially contaminant transport mechanisms at impacted sites. Historically, it has been difficult to assess the complex three-dimensional (3-D) distribution of microbial colonies in the subsurface using only one-dimensional (1-D) drilling tools due to the heterogeneity in geology, and complex nutrient and contaminant distributions. An electrical subsurface scanning process has been recently proven to be capable of providing high data density 2-D and 3-D mapping of microbially active zones in the subsurface.

Approach/Activities. Two types of project sites will be discussed. Specifically, LNAPL impacted sites (fuel leaks) without bioamendents added, and DNAPL sites (chlorinated solvents) with and without bioamendments. The ability to integrate electrical subsurface scanning data with drilling data to provide an understanding of the presence and effects of bioactivity will be discussed.

Results/Lessons Learned. Successful remediation and site closure of environmentally impacted sites can be performed more effectively and often at lower cost when the CSM includes an understanding of bioactivity. The integration of biochemical data from discrete soil/groundwater samples obtained via drilling methods and higher data density electrical scanning datasets provides a more complete understanding of biogeochemical zonation for inclusion in the CSM. The requirements for data integration for real-world NAPL sites will be discussed, as well as strengths and weaknesses of the methodology.

Development of an Innovative Approach for Characterizing Non Aqueous-Phase Liquid (NAPL) in a Heterogeneous Subsurface Environment

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Background/Objectives. Historical industrial activities at the BF Goodrich Superfund Site in Calvert City, KY, resulted in a significant volume of NAPL, primarily ethylene dichloride (EDC), being released to the subsurface. A remedial investigation (RI) was conducted at the Site, which is bordered by the Tennessee River, to define the nature and extent of contamination resulting from the historical releases, and to assess the current and potential future risk to public health, welfare, and the environment. A primary objective of the RI was to delineate the extent of NAPL and evaluate the potential for NAPL migration.

Approach/Activities. RI-related field activities, including well installation and sample collection in various media, were performed to evaluate the nature and extent of contamination. During these activities, the delineation of NAPL was performed by utilizing lines of evidence (LOEs) to determine the presence of NAPL at a given monitoring location. Eight different LOEs were evaluated for the Site, including: visual observation of NAPL, NAPL saturation, soil partitioning, dye testing, NAPL vapors, groundwater saturation threshold, Site use/Site history, and other factors (e.g., NAPL sheens, staining, etc.). A total of 4,069 unique NAPL monitoring locations were identified and evaluated. The delineation process first evaluated the prevalence of various NAPL indicators to generate a score to rank the probability of NAPL occurrence at a given monitoring location, and classified the location into one of three categories: confirmed NAPL zone, potential NAPL zone, and not a NAPL zone. Within the potential NAPL category, three threshold levels were subsequently established to indicate which of the potential NAPL locations could be reasonably classified as confirmed NAPL. Of the 4,069 NAPL locations, 309 were assigned confirmed NAPL, 493 were assigned potential NAPL, and 3,267 were assigned no NAPL status. The rankings were subsequently used to develop a three-dimensional (3D) model of the NAPL distribution at the Site. From this 3D model, two-dimensional (2D) NAPL distribution maps and 3D NAPL plume maps were prepared to assist with visualization of the NAPL plumes, and NAPL volume estimates were generated.

Results/Lessons Learned. The location and extent of NAPL impacts are consistent with historical releases that occurred at the Site. NAPL migration is associated with several lithologic units present beneath the Site, with a notable unit of interbedded sand, silt, and clay lenses oriented parallel to the shoreline of the Tennessee River facilitating lateral NAPL migration away from source areas to downgradient discharge points. The total estimated volume of NAPL-impacted soil at the Site ranges from 1.1 to 3.5 million cubic yards, depending on the confirmed NAPL threshold level.

Back to Contents

Contaminant Mass Discharge Reduction Measured Using an Existing Pump-and-Treat System as a Compliance Metric for Source Treatment

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Background/Objectives. Remedial performance has traditionally been measured by comparison of contaminant concentrations in soil and groundwater to numerical standards; however, use of contaminant mass discharge as an interim metric for remedial performance is gaining acceptance within the remediation industry and regulatory community. The Time Oil Well 12A Superfund Site in Tacoma, Washington is the first known site to use contaminant mass discharge reduction as a compliance goal in a Record of Decision (ROD). The site has been undergoing remediation since 1983 to address soil and groundwater contamination, principally chlorinated volatile organic compounds (VOCs) including dense non-aqueous phase liquids (DNAPL), that pose a risk to the City of Tacoma municipal water supply. The original ROD (1983) involved wellhead treatment at Well 12A (a City of Tacoma municipal water supply well). A ROD Amendment (1985) involved soil excavation, soil vapor extraction, and operation of a groundwater extraction and treatment system (GETS). After 25 years of remedial action, a review of the existing remedy for the site concluded that it was inadequate to achieve groundwater restoration in a time frame sufficient for the City of Tacoma's projected future water use. A second ROD Amendment (2009) specified that a 90% reduction in contaminant mass discharge from the source area to the dissolved phase plume would be achieved by adding excavation of shallow soils and filter cake, in situ thermal remediation, and enhanced anaerobic bioremediation (EAB) for source treatment.

Approach/Activities. In order to implement the multi-component remedy, it was necessary to measure and gain regulatory acceptance of the pre-remedial action baseline mass discharge from the site and to establish the criteria and methods for the post-remedial action measurement. Multiple methods were evaluated and ultimately a pumping test method using the existing GETS was selected. Extraction rates were optimized to achieve capture of a representative volume of the source treatment area and obtain an integrated measurement of contaminant concentrations from that volume. A key component of the evaluation involved a statistical analysis of the GETS VOC data to develop a strategy to define when adequate data had been collected to support the conclusion that mass discharge measurements were stable to within an acceptable range of variability.

Results/Lessons Learned. After nearly six months of pumping, the project team reached consensus that the mass discharge measurements were sufficiently stable and a baseline mass discharge of 403 grams per day was established. Excavation, in situ thermal remediation, and EAB injections have been completed and the team is currently monitoring progress towards achievement of the objective. The results of the first 12 months of groundwater sampling and interim pumping of the GETS, used to assess progress towards the achievement of the objective, will be presented.

Flux-based Mass Balance Framework to Assess Enhanced Bioremediation Outcomes

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Background/Objectives. Enhanced in situ anaerobic bioremediation is emerging as a sustainable and cost-effective treatment option for the remediation of chlorinated solvents in groundwater--particularly at locations with extreme geological complexities such as fracture networks. However, the lack of field verified demonstrations could limit the application of enhanced bioremediation due to uncertainties related to field-scale plume responses, treatment timing, and the correlation between DNAPL mass removal to changes in groundwater quality. Mass balance analyses are important for optimizing bioremediation system design parameters and preventing investments in costly remedial efforts that may have a negligible impact on long term reductions in mass discharge. The assessment of the relationship of mass flux and DNAPL distribution in sites before and after bioremediation will provide improved site management guidance. Field scale results and mass balance analyses are presented for a fractured media site in California subject to enhanced in situ anaerobic bioremediation: Edwards Air Force Base, Site 37.

Approach/Activities. The study uses a mass balance framework to characterize changes in mass discharge from DNAPL source zones at the field site at different stages of treatment. Bioremediation is currently underway at Site 37 using Passive Flux Meters (PFMs), interwell partitioning tracer studies, and push-pull tests. Sequential testing at multiple transects down gradient of the DNAPL sources before and after enhanced bioremediation will be performed. A mass balance analysis will be performed to assess changes in mass discharge due to the enhanced bioremediation approach.

Results/Lessons Learned. We will discuss how the mass balance results from another bioaugmentation site in California were used to guide the flux characterization of the more geologically complex Edwards site. Data from the previous field study indicate significant declines in mass discharge from source zones after bioremediation. Flux-based mass balance assessments are used to verify the effectiveness and sustainability of bioaugmentation at both sites.

Determining Mass Flux and Natural Attenuation of a Legacy Groundwater VOC Plume Discharging into San Diego Bay

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Background/Objectives. Installation Restoration (IR) Site 9 at North Island Naval Air Station (NASNI) in Coronado, California (the Site) is a former chemical waste disposal area where an estimated 8 to 32 million gallons of liquid wastes were disposed between the late 1940s and mid-1970s. Today, groundwater beneath the 50-acre site remains variably impacted with a mixture of volatile organic compounds (VOCs) consisting primarily of chlorinated ethenes and ketones, and the VOC plume extends from the disposal area to the western Site boundary at San Diego Bay. Shallow groundwater beneath NASNI is tidally influenced and hydraulically connected with San Diego Bay and the Pacific Ocean. The VOC plume intercepts both the shallow freshwater aquifer as well as the underlying brackish/saline groundwater down to depths of 100 feet below ground surface (bgs). Previously, the Navy performed an investigation to screen offshore sediments for potential evidence of VOC impacts from IR Site 9 groundwater. That investigation detected part-per million levels of vinyl chloride (VC) and cis-1,2-dichloroethene (cDCE) in offshore sediment porewater at depths of 1 and 5 feet into the sediment, providing a strong indication that Site groundwater was reaching the San Diego Bay sediment pore water. The localized occurrence of VC and cDCE in the offshore sedimentssuggests that biodechlorination is occurring in the Bay sediments. An ecological risk assessment found that discharge of Site groundwater does not pose an unacceptable risk to fauna in the Bay. Presently, the Navy has initiated a comprehensive investigation to identify and map groundwater discharge zones in the subterranean estuary at Site 9, and to quantify the effect of natural attenuation processes on destruction of Site VOCs in Bay sediment porewater.

Approach/Activities. The investigation is focused on measuring contaminant fate and transport mechanisms and determining contaminant mass loading into San Diego Bay. The investigation includes: trident probe mapping of groundwater discharge zones, sediment porewater sampling; seepage meter deployments to quantify groundwater discharge rates and VOC mass fluxes; installation and sampling of temporary nested piezometers to collect time-series measurements of geochemical and physical conditions in offshore sediment porewater over a complete spring-neap tidal cycle; compound-specific isotope analysis (CSIA) to measure 13C-enrichment in VOCs as they migrate through the offshore sediments; and, a laboratory microcosm study to quantify biotic and abiotic transformation of VOCs in the offshore sediment porewater. The investigation consists of more than 170 trident probe sample points, 30 offshore porewater sampling locations, 21 seepage meters, 10 temporary piezometer nests (screened at 1, 5, and 8 feet into the sediments).

Results/Lessons Learned. Results from the first transect of trident probe sample points advanced in 2014 indicate that the maximum concentration of VOCs in San Diego Bay sediment pore water adjacent to Site 9 have decreased by 2 to 3 three orders of magnitude relative to 1998/2000. The results suggest that natural attenuation has played a significant role in limiting discharge of Site VOCs to the Bay over the past 15 years. A robust dataset from the full investigation will be ready by May 2015 and presented at the Battelle Biosymposium.

High-Resolution Site Characterization in a Complex Deltaic Setting

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Background/Objectives. Traditional and TRIAD explorations were used to define upper and lower chlorinated solvent (cVOC) groundwater plumes within a multi-layered deltaic geologic sequence. These explorations included: monitoring wells, discrete groundwater samples and limited Waterloo and MIP profiling. However, after an initial ISCO remedial effort, rebound in groundwater concentrations were reported. While rebound is known to occur following remedial actions, the reason for the rebound was less obvious. This presentation will focus on the use of HRSC techniques to further identify potential geologic and geochemical conditions influencing rebound (e.g., insufficient characterization, greater mass than estimated, back diffusion from silty/clay units, vertical hydraulic gradients, poor additive distribution and natural chemical sinks) to provide a more holistic understanding of the nature and extent of the cVOC contaminant plumes and a hexavalent chromium plume.

Approach/Activities. The design of the HRSC program focused on establishing discrete transects perpendicular to the site plumes. The spacing of the points was designed to provide a greater level of detail so that subtle changes within the multi-layered deltaic formation geochemistry could be better understood. The number of transects proposed was based upon the location of the primary and secondary source zones and to determine future injections. The HRSC program focused on collecting real-time indirect vertical measurements using a MIP profiling tool equipped to measure changes in geologic conditions (electrical conductivity) and geochemical changes (FID, PID, ECD and XSD). Profile extents were adjusted during the explorations to define contaminant limits. Cross sections were developed by superimposing the HRSC data along with historical, groundwater grab samples, monitoring wells and geology. These assessments were used to identify where additional groundwater grab samples and wells would be located within sections of the plume where elevated readings were identified in thin (12 to 18-inch thick) deltaic lenses. The groundwater was analyzed for natural attenuation parameters, cation/anions, and other parameters that could inhibit the effectiveness of the additive injected. The grab samples were collected over a 2-foot zone to target the greatest mass; whereas, wells were screened over 5-feet to determine if the longer well screens underestimated the contaminant mass present.

Results/Lessons Learned. HRSC identified that the general footprint of the plumes remained the same; however, the mass within the core was greater. Thin highly concentrated lenses (12-24 inches thick) not previously identified were located 18-inches above a well meeting remedial criterion. The data also identified contaminants present in less permeable units likely resulting in back-diffusing and may account for the rebound observed within those monitoring wells installed in lower permeable units. Targeting the zones with the greatest mass and natural oxidant demand required greater oxidant loading than previously anticipated under the more conventional site characterization. Since the contaminants were present in thin zones, many of the existing monitoring well data (based on 5-foot screens) underestimating the total mass present.

Back to Contents

High-Resolution Site Characterization: The State of the Practice

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Background/Objectives. The passage of CERCLA in 1980 created, nearly instantly, what is today a $9 billion annual industry which is still growing. Knowledge of the fate and transport of industrial chemicals in the subsurface was extremely limited in the 1980s and most of the early practitioners in the new industry came from, or were influenced by, the water supply and wastewater disposal fields. The conceptual models and scales of measurement from these fields were inappropriate for assessment and remediation of chemicals in the subsurface as recognized by a few early pioneers like C.V. Theis and John Cherry. These models and approaches became embedded in the field and are still prevalent today. In the 1980s, pumping and treatment (P&T) of groundwater comprised between 80% and 90% of Superfund groundwater remedies. In large measure these remedies failed to meet the goal of aquifer restoration and as of 2011 P&T comprised only 20% of remedies. Understanding of the nature of contaminant behavior in the subsurface has increased tremendously, largely due to academic research, and new, more effective investigatory and remedial technologies have been developed. The 14th Edition of the Superfund Remedy Report (November 2013) stated that "…the continued increase in the selection of in situ groundwater technologies suggests a role for recently-developed characterization techniques, such as high-resolution site characterization (HRSC)". HRSC has great promise to shorten project life cycles, improve Conceptual Site Models, increase remedy effectiveness and reduce life cycle costs.

Approach/Activities. HRSC requires making measurements at scales that encompass the spatial structure of the key variables (e.g., hydraulic conductivity, contaminant concentration, geochemistry). This requires small sampled volumes and close sample spacing. HRSC is best applied using transects normal to the direction of transport. Application of Triad Approach principles reduces the time and costs associated with HRSC. Appropriate use of technologies such as Waterloo^{APS}, Membrane Interface Probe, LASER Induced Fluorescence, on-site laboratories, geophysical techniques, detailed chemical profiling of aquitard materials and others facilitate the collection of the types and density of data which allow for the level of understanding of site conditions which is required for successful and cost effective selection, design and implementation of the combinations of remedial technologies required to meet remedial goals.

Results/Lessons Learned. HRSC results allow for more "surgical" application of remedial technologies thereby making remedies more cost effective. However, application of a single "high resolution" technology does not result in a high resolution investigation. Multiple tools and techniques are required to address the various questions posed by a given site.

High-Resolution Characterization of DNAPL Source Zone Architecture in Clay Till

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Background/Objectives. Characterization of dense non-aqueous phase liquid (DNAPL) source zone architecture is essential to develop accurate site specific conceptual models, delineate and quantify contaminant mass, perform risk assessment, and select and design remediation alternatives. The activities of a distribution facility (1965-83) for perchloroethene (PCE) and trichloroethene (TCE) at the Naverland site near Copenhagen, Denmark, have resulted in PCE and TCE DNAPL impacts to a fractured clay till and an underlying fractured limestone aquifer/bedrock. The scope of the investigations was to evaluate innovative investigation methods and characterize the source zone hydrogeology and contamination to obtain an improved conceptual understanding of DNAPL source zone architecture in clay till and bryozoan limestone bedrock. This presentation will focus on the clayey till.

Approach/Activities. A wide range of innovative and current site investigative tools for direct and indirect documentation and/or evaluation of DNAPL presence were combined in a multiple lines of evidence approach. The approach was initialized with surface geophysics to determine the surfaces of the clayey till and the underlying limestone aquifer. Based on the geophysical investigations and the site history membrane interphase probing (MIP) and soil gas surveys were used for delineation of the most contaminated part of the source area. In the DNAPL source area intact coring with subsampling for quantitative soil analysis, PID and hydrophobic dye tests (Indigo Blue and SudanIV) was carried out and followed by installation of NAPL FACT FLUTe liners.

Results/Lessons Learned. Though no single technique was sufficient for characterization of DNAPL source zone architecture, the combined use of membrane interphase probing (MIP); coring with quantitative subsample analysis, SudanIV test, and PID; and NAPL FACT FLUTe gave good insight in the source zone architecture in the clayey till. Surface geophysics with ground penetrating radar (GPR) and seismic reflection and refraction (SRR) combined with geologic information supplemented the conceptual understanding of transport and distribution of DNAPL in the fill, clayey till and the interface to the limestone. The DNAPL source zone architecture in the clay till was consistent with conceptual expectations.

Acknowledgements. The authors would like to acknowledge the Capital Region of Denmark for site access and data as well as funding.

Improving Mass Flux Estimates through Hydrofacies Analysis

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Background/Objectives. Mass flux continues to gain popularity in our industry, but use of conventional investigation methods leads to mass flux estimates with large uncertainty if not significant errors. This is because conventional methods fail to capture the complex heterogeneity and permeability structure that results from natural geologic processes – often 4 or more orders of magnitude variability. A mass flux estimate based an average permeability across an aquifer flux transect can miss the majority of the flux.

Approach/Activities. To improve mass flux estimates, we propose the use of hydrofacies analysis: aquifer zones that are depositionally related and have a similar mass transport behavior. These hydrofacies are identified using "next generation" site investigation tools at high resolution within a borehole. The resulting profile of aquifer permeability and hydrofacies reliably separates transport zones from storage. This information, coupled with high resolution groundwater sampling, allows for an accurate depiction of "relative" mass flux along atransect. Advanced permeability profiling tools (like the Geoprobe® Hydraulic Profiling Tool and the Waterloo® Advanced Profiling System) enable practitioners to characterize hydrofacies and aquifer structure at a level of detail not previously achievable through conventional methods. The complex aquifer structure revealed by the permeability profiling tools allows the characterization of hydrofacies that may have otherwise gone unnoticed.

Results/Lessons Learned. We recommend using permeability profiling transects to map hydrofacies trends, and then applying classical geologic methods of stratigraphic correlation and facies trend analysis to interpret aquifer architecture. The relative permeability derived from this approach can be combined with high resolution groundwater sampling to create a detailed representation of hydrostratigraphy and relative mass flux. The resulting detail can be used to optimize monitoring networks and focus remediation systems.

The concepts are developed and illustrated using a series of case studies.

Field Testing of a High-Resolution Chlorinated DNAPL Logging System

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Background/Objectives. Chlorinated solvent NAPLs are famous for being difficult to delineate in the subsurface. We have developed and recently field tested a high-resolution laser-induced fluorescence (LIF) characterization tool that provides rapid, high resolution, real-time logging of chlorinated solvent DNAPL source zones. Inspired by the Sudan IV and Oil Red-O dye shake tests, the new DyeLIF optical screening tool works by injecting a hydrophobic dye through a small injection port located several inches below the detection window of a standard laser induced fluorescence (LIF) probe. As the probe is advanced through the subsurface, the injected dye partitions rapidly into any NAPL in contact with the dye. The NAPL-solvated dye is then detected at the sapphire window that is following along behind the dye port. A modified Tar-Specific Green Optical Screening Tool (TarGOST®) LIF system is used to detect the dye-labeled chlorinated solvent DNAPLs as they pass in front of the sapphire window

Approach/Activities. A field verification of DyeLIF was conducted in October of 2013 at a TCE spill site in Lowell, MA. The site's DNAPL footprint occurred in a very small area measuring approximately 100 ft x 50 ft at depths to 80 ft. During a five day test period a total of 28 DyeLIF logs were conducted, with each log reaching depths of ca.70 ft. The five day investigation achieved a total footage for the week of 1,977 ft or 395 ft per day with an average data density achieved with DyeLIF was 0.02-0.03 ft (30 to 50 discrete measurements per foot). Additional CPT Dye-LIF tests were conducted in April, 2014.

As expected, DNAPL signatures were observed to be distributed in a highly heterogeneous fashion, ranging from some major seams of DNAPL signatures over a foot thick to many less than one inch thick. Some geologic horizons were more commonly occupied by DNAPL than others, most likely due to horizontal DNAPL movement driven by geologic facies. Continuous high resolution sampling was conducted at locations co-located with DyeLIF logs. 260 depth discrete horizons at various depths alongside DyeLIF were sampled, with each horizon sampled being sub-sampled into four jars. These 260 horizons will be subjected to Oil Red O shake tests, lab analysis (133 samples), PID screening, particle size analysis, and re-screening with DyeLIF.

Results/Lessons Learned. 100% consistency between ORO, DyeLIF and lab analysis was achieved in samples found to contain > 2.5% DNAPL pore saturation and 98% consistency was found in soil with DNAPL pore saturations of > 0.7%. While the final results have yet to be assessed in detail, it appears that (for this site) the practical field limit of detection (LoD) for Dye-LIF falls somewhere between 1.0% and 0.1 % DNAPL pore saturation. We will present the following at the presentation:

- A brief overview of the DyeLIF system
- How the logs are processed and interpreted
- Graphics comparing the DyeLIF logs with high-resolution validation sampling at co-locations
- A statistical breakdown of the various data sets and how the various techniques compare
- A high-resolution 3-dimensional of the architecture of the DNAPL at the site
- A discussion of overall benefits/limitations of DyeLIF method
- A review of which DNAPL sites will most likely benefit from DyeLIF screening

Magnetic Susceptibility as a Tool for Assessing Bioremediation of Hydrocarbon Contaminated Sites

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Background/Objectives. Contamination of soils and sediments by hydrocarbons remains a global environmental problem threatening freshwater resources and impacting marine ecosystems. Attempts to clean up spills include: siphoning oil off surface waters, pump and treat and excavation of contaminated sediments. However, the sheer volume of these spills suggests that it is almost impossible to completely remove such large quantities of hydrocarbons from the environment through active intervention techniques. As a result, intrinsic bioremediation or natural attenuation is often viewed as an attractive alternative. Current techniques for assessing natural attenuation processes focus mostly on biological degradation of compounds of concern and the evaluation of daughter products or a verification of the presence of microorganisms capable of breaking down the hydrocarbons. These biological and chemical analyses can be time consuming and costly, hence there is a need for non-invasive techniques that can be interfaced with other cleanup efforts in order optimize remediation strategies and reduce cost. In our research we are focusing on optimizing geophysical sensing techniques for fast and efficient localization of hydrocarbon contamination in soil and for providing cost-effective and long-term solutions for monitoring remediation of oil spill field sites.

One such technique that we have been utilizing is the magnetic susceptibility c technique. Although magnetic techniques have historically played an important role at contaminated sites, their main use has been for delineation of subsurface metallic infrastructure such as pipes and buried tanks. Their use for investigating microbial processes has not been fully recognized. Magnetite and greigite are common products of microbial iron and sulfate reduction, respectively, which are strongly ferrimagnetic. Thus, the presence of such minerals allows us to link magnetic anomalies to the presence of oil contamination and natural attenuation.

Approach/Activities. We investigated a site contaminated by crude oil at Bemidji, Minnesota where intrinsic bioremediation is known to occur and iron reduction and methanogenesis are the dominant electron acceptor processes. We characterized the variations in c in contaminated and pristine locations. We performed borehole c logging using a Bartington c probe at the field site and retrieved cores for iron mineralogy using x-ray diffraction (XRD). We also determined the Fe(II) and Fe(III) concentrations from the sediments.

Results/Lessons Learned. Our results show the following: (1) the highest magnitude of c occurs within the hydrocarbon smear zone, within the water table fluctuation zone suggesting that this is the most biologically active zone; (2) c values within the free product plume are higher compared to values within the dissolved product plume; (3) high c coincides with zones of elevated Fe(II) solid concentrations; (4) magnetite was the dominant biomineral. We conclude that c measurements are a: (1) low cost, rapid monitoring tool for assessing the extent of hydrocarbon contamination and (2) a proxy for the presence of intrinsic bioremediation related to iron reduction and bio-mineral formation.

Use of High-Resolution Site Characterization Tools to Efficiently Find and Delineate the Leading Edges of Multiple Groundwater Contaminant Plumes

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Background/Objectives. The U.S. Air Force is conducting Remedial Actions (RAs) at three sites impacted by mixed groundwater contamination (primarily trichloroethene) on the western edge of Rogers Dry Lake at Edwards Air Force Base, California. Site geology consists of unconsolidated heterogeneous alluvial/fluvial deposits that laterally transition into lacustrine deposits. Depth-to-water ranges from 50 to 100 feet (ft) (15 to 30 meters [m]) below ground surface, due to a geologic fault zone in the area. Previous work included the phased installation of monitoring wells to continually refine the lateral and vertical extent of impacts. Groundwater analytical data from recently installed monitoring wells indicated that the plumes had not been fully delineated at the time of RA implementation. High-resolution site characterization (HRSC) tools were selected as an alternative to step-out monitoring well installations to efficiently and cost-effectively find the extent and delineate the leading edges of the contaminant plumes.

Approach/Activities. A tracked DPT rig with percussion hammer system was initially used to drive a Membrane Interface Probe with integrated Hydraulic Profiling Tool (MiHPT) to target depths, generating relative contaminant concentration data and soil hydraulics data (e.g., pore pressure, soil permeability). Due to difficulties advancing the tooling through dense and variably cemented lakebed sediments and the high detection limit of the MIP, the project was completed using a 20-ton, truck-mounted Cone Penetrometer Test (CPT) rig to determine soil characteristics and soil behavior types. Discrete-depth groundwater samples were collected from target intervals determined from the MiHPT/CPT logs and sent off-site for chemical analysis with 24-hour turnaround time. The analytical data generated each day were used to guide the project and determine step-out investigation locations. Depth-to-water was measured in the boreholes to delineate a suspected fault zone. That structural feature was found to affect plume migration and introduced uncertainties that lead to a decision to briefly suspend CPT logging activities in order to collect water table samples within an extensive grid. The data generated allowed for more targeted subsequent CPT pushes, expediting the investigation. Finally, monitoring wells were installed at the leading edges of each plume and sampled.

Results/Lessons Learned. Results from 125 groundwater samples collected from 55 borehole locations added over 50 acres to the previously interpreted combined area of the three plumes. The narrow plumes exhibited distinct southward deflections near the fault zone, which was characterized by a 50-ft hydraulic head loss across approximately 750 ft (230 m) at one of the sites. A high density of hydrostratigraphic data was generated, showing thin higher-permeability transport zones interlayered with lower-permeability clays and silts. Due to aquifer heterogeneity and the presence of the fault zone, traditional site characterization methods would likely have missed some of the permeability structures driving contaminant distribution. The CPT tools were better suited to site conditions than the MiHPT tools, which had difficulty advancing through the lakebed sediments and detecting the low level of contaminants present in groundwater. The HRSC approach allowed for real-time adaption to site conditions, the rapid development of a detailed Conceptual Site Model, and an understanding of the complex geologic controls on plume distribution. This permitted the installation of optimally positioned and screened wells for long-term monitoring and future targeted application of the selected remedies. Benefits of the HRSC approach include reduced risk, uncertainty, life-cycle costs, and resource consumption.

Back to Contents

High-Resolution Site Characterization Using Conventional Technologies to Delineate and Improve the Conceptual Site Model of a TCE Groundwater Plume

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Background/Objectives. The project involves the investigation of a trichloroethene (TCE) plume originating from a former missile site located in a U.S. National Forest. The unconfined aquifer is over 250 feet thick and consists primarily of uniform very fine sand but includes isolated, thin, discontinuous deposits of even finer-grained sand, silt, and clay. The age of the plume (40-50 years) and hydrogeology of the site have resulted in a long, narrow, deep plume. Multiple site investigations over a period of 15 years produced a conceptual site model (CSM) that did not adequately capture the nature and extent of the plume or lead to a complete understanding of fate and transport mechanisms at the site. A new approach was needed to complete delineation and gather information to assess risk and evaluate remedial alternatives.

Approach/Activities. The project team used the Triad and technical project planning (TPP) processes and worked with the regulators to revise investigation objectives. By evaluating temporal trends, concentrations relative to TCE solubility, simple mass calculations, and historic operations, the team demonstrated that a significant non-aqueous phase source was likely not present. The CSM was revised to assume an aqueous-phase or relatively small non-aqueous phase release had created the plume. It was agreed that based on site use, finding the source (if one existed) was not critical to the CSM if the plume is stable or contracting. This shift in focus enabled resources to be devoted to investigating the large dissolved-phase plume. Because of the low TCE concentrations (< 100 µg/L) and depth (> 300 feet), direct-push technologies with real-time data acquisition were not feasible. A dynamic work strategy was developed to perform vertical aquifer profiling (VAP) with rotosonic drilling, collecting discrete groundwater samples every 10 feet and continuously logging soil lithology. Coupled with onsite mobile laboratory support and real-time revision of the 3-dimensional plume model, the team efficiently selected boring and monitoring well locations and depths. This approach saved resources and reduced uncertainty. In addition, the relatively high data density revealed the plume's cross-sectional geometry, allowing meaningful analysis of mass discharge rates. The investigation also includes a study of monitored natural attenuation (MNA) utilizing quantitative polymerase chain reaction (qPCR) analysis and compound-specific isotope analysis (CSIA).

Results/Lessons Learned. The initial phase completed in September 2014 revealed the plume to be over twice as long and over 100 feet deeper than originally projected. A change in plume direction consistent with regional groundwater contours was confirmed. Most importantly, the high-resolution lithologic information and TCE results showed a correlation between higher TCE concentrations and finer-grained soil. The CSM has been revised to assume that low rates of back diffusion from these layers and relatively slow advective flow within them have caused TCE to remain in and near the lower-hydraulic conductivity zones while being flushed from the more conductive very fine sands. One lesson learned was that having two drill rigs on site was problematic. Although having two rigs increased productivity, it resulted in having to make decisions on where to locate one rig's borehole without complete profiling data from the other rig's location. Because of this, several boreholes were drilled in locations that, in retrospect, did not provide useful information for delineation. A second mobilization with a single rig will take place in the spring of 2015 to complete delineation.

High-Resolution Site Characterization and Advanced 2-D/3-D Conceptual Site Model Development for Evaluating Post-Bioremediation Conditions

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Background/Objectives. A high-resolution site characterization (HRSC) program with integrated 2-D/3-D conceptual site model development was completed at an industrial site located in Greensboro, NC to re-assess source area mass distribution and post-remediation site conditions. The site consists of approximately 4.5 acres of land developed with an approximately 20,000 square foot (ft^2) metal building and two concrete loading docks. Subsurface soils consist of approximately 3 to 5 feet of re-worked, red-clay engineered fill beneath the site improvements that overlay a native silty clay that transitions to a micaceous sandy silt with granite bedrock that is encountered from 26 to 33 feet below ground surface (bgs). Shallow groundwater ranges from approximately 14 to 20 feet bgs with an estimated hydraulic conductivity of 2.8 feet per day and a linear groundwater flow velocity estimated at 0.006 feet per day (2.19 feet per year).

In October 1985, an unknown quantity of rinsate water generated during cleaning of a tanker truck was discharged into a drainage swale. Subsequent investigations identified 1,1,1-trichloroethane (TCA), tetrachloroethene (PCE), trichloroethene (TCE), and methylene chloride above regulatory standards. A total of 3.2 million gallons of groundwater were recovered and treated from 1996 to 1998 as an Interim Remedial Measure (IRM) from which 148 pounds of volatile organic compounds were removed. In 2007, 63,000 gallons of Zloy®/ NewmanZone® were delivered to enhance the abiotic/biotic biodegradation processes, and 54 tons of hazardous contaminated soil consisting of 1,1,1-TCA and 1,1-dichloroethane at concentrations exceeding remediation goals was removed from the source area.

Approach/Activities. To re-assess the source area mass distribution and to evaluate post-remediation site conditions following bioremediation injection activities and source removal, a Membrane Interface Probe (MIP) was advanced at locations adjacent to and downgradient of the former source area. Confirmation soil and groundwater samples were collected at targeted discrete intervals to collaborate the MIP results and provide speciation of chemical compounds. In conjunction with the HRSC program, a comprehensive 2-D/3-D Conceptual Site Model (CSM) was developed that included migrating more than 20 years of site investigation and remediation data into EarthSoft's EQuIS and visualizing data in ESRI's ArcGIS and Ctech's Mining Visualization System (MVS) software. This comprehensive CSM included both 2-D/3-D and 4-D (time) visualization as wells as chemical trend analysis for all site wells.

Results/Lessons Learned. High-Resolution Site Characterization in conjunction with the development of a 2-D/3-D CSM provided the project technical team enhanced data density in combination with the ability to evaluate multiple data sets in a spatial and temporal framework. Based on this analysis, it was determined that source removal and in-situ bioremediation had removed 94% of chemical mass and has contributed to a 99% reduction in maximum groundwater concentrations. In addition to the benefits for the technical team, these tools have resulted in development of a Stakeholder-accepted CSM that has been used to streamline remediation lifecycles with more logical, mutually acceptable risk-based business decisions.

High-Resolution Characterization for Determination of ERD of Chlorinated Solvents in Clay Till

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Background/Objectives. Natural attenuation (NA) or enhanced reductive dechlorination (ERD) of chlorinated solvents in clay till and other low permeability geologic media, where flow predominantly takes place in high conductivity conduits as fractures and embedded sandstringers, is highly dependent on the occurrence of biodegradation in the low permeability matrix. Therefore, determination of the effect of or potential for NA and ERD requires a detailed understanding of the redox and biodegradation processes occurring in the low permeability matrix. Both natural and enhanced biodegradation of chlorinated solvents by reductive dechlorination require anaerobic conditions and the presence of specific degraders. The overall objective of the study was to determine the potential for ERD in clayey till matrices. High resolution characterization of the clay till matrix 2 and 4 years after ERD was introduced played a very important role for interpretation of the remediation potential.

Approach/Activities. High resolution characterization of matrix, fracture and sand stringers in clay till cores with respect to chlorinated solvents and degradation products as well as redox conditions was performed at 2 ERD sites. Stable carbon isotope analysis were used to document degradation and to distinguish between degradation and other processes. Molecular biological tools were used to quantify the specific degraders. The sub-sampling strategy was made based on transport and degradation process modelling. Samples were collected with a discretization varying from each 0.5 cm close to sand lenses/fractures up to 5 cm in the clay till matrix.

Results/Lessons Learned. The results yield a detailed picture of the distribution of contaminant, electron donor and specific microbial degraders in sand lenses, stringers, fractures and the clay till matrix. Evidence of presence of specific degraders and for biotic and abiotic degradation was found. High resolution characterization proved to be essential for determination of the ERD potential and effect.

Acknowledgements. The authors would like to acknowledge Orbicon, Capital Region of Denmark and Region of Southern Denmark for site access and data as well as co-funding and the research project ”Innovative Remediation and Assessment Technologies for Contaminated Soil and Groundwater” (REMTEC) for the main funding.

Back to Contents

State of the Practice in Sustainably Optimizing Existing Remediation Systems

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Background/Objectives. The remediation field has matured to the point that there is widespread recognition that optimizing existing remediation systems improves effectiveness, shortens remedy lifetimes, and saves money. In addition, the remedy optimization stage is optimal for integrating sustainability concepts into cleanups. There exist various tools, technologies, and practices that increase the effectiveness of remedies while concurrently incorporating sustainable concepts into cleanups. Furthermore, a movement is underway that is improving the practice of sustainable remediation.

Approach/Activities. Various organizations, including the U.S. Environmental Protection Agency, the Intrastate Technology & Regulatory Council, Department of Defense, ASTM International, Inc., and the Sustainable Remediation Forum, have developed programs and protocol for optimizing remediation systems while also reducing the environmental footprint of cleanups. Through instructional literature and training these organizations are promoting the practice of sustainable remediation. It is an interesting time for the sustainable remediation community as the practice transitions from research and development to implementation.

Results/Lessons Learned. Advances in the State of the Practice have created a subfield of remedy optimization within the overall remediation industry. Now, remediation professionals are pushing the envelope by incorporating sustainable remediation practices into the remedy optimization process. The industry is no longer just sustaining, but thriving through such practices as reusing reclaimed and treated groundwater for industrial uses, thus reducing the use of potable water. Or, using solar or wind power to operate remediation systems and redirecting excess power to the grid, thereby, eliminating the need for energy derived from fossil fuels. Implementing sustainable remediation improves the cleanup's effectiveness while minimizing raw material use, improving energy efficiency, reducing air emissions and greenhouse gases, conserving water, promoting land and ecosystems, and, when possible, improving the economic and social fabric of communities.

While there is often reticence in expending the effort and expense to sustainably optimize remediation systems, experience shows that this approach not only improves effectiveness, but also saves money. However, the approach is not without its challenges, including demonstrating the return on investment and enticing responsible parties that adoption is superior to the status quo.

Transition to Sustainable Biosparging/Bioventing from Air Sparging/SVE at a Petroleum Hydrocarbon-Impacted Site

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Background/Objectives. A natural gas processing site is impacted with TPH and BTEX in both soil and groundwater. The soil contained maximum concentrations of 44 mg/kg gasoline-range organics (GRO) and 9,300 mg/kg diesel-range organics (DRO). Maximum impact was detected in the smear zone. Groundwater was impacted with concentrations up to 1,900 µg/L GRO and 260,000 µg/L DRO. An air sparging (AS)/SVE system was initially implemented to expedite the removal of GRO and light end of DRO in soil and groundwater. The transition to a biosparging/bioventing system focused the removal on the remaining heavy end DRO through a biodegradation mechanism and resulted in the site nearing a no-further-action status.

Approach/Activities. A SVE system was implemented to remove contaminants of concern (COCs) in the vadose zone when the groundwater elevation declined, resulting in exposed smear zone. The SVE system consisted of six SVE wells, one 10-HP blower, and three 2,000-lb GAC vessels for vapor treatment. A second knockout tank was installed before GAC vessel to enhance moisture removal. After 13 months of SVE operation, free product was detected in one SVE well due to induced vacuum pressure. Absorbent socks were installed in the well to remove approximately 6 gallons of free product. A drum of organoclay was used to remove the free product from the SVE waste stream. Two years later, an AS system was implemented to remove COCs in the saturated zone. The AS system consisted of a 10-HP blower, two air sparge wells, and four groundwater monitoring wells. Recently, the cumulative COC removed by SVE reached an asymptotic level. An early breakthrough of the GAC vessels was diagnosed as low carbon-affinity polar compounds generated from DRO degradation. GRO were not detected in groundwater monitoring wells. These observations indicated biodegradation mechanism gradually dominated the COC removal. The AS/SVE system was transitioned to a more sustainable biosparging/bioventing system by optimizing AS flow rate to sustain air required for biosparging in saturated zone and shutting down low concentration SVE wells to allow for the air to migrate through the vadose zone for bioventing.

Results/Lessons Learned. Transition to biosparging/bioventing system from existing AS/SVE system reduces a significant SVE O&M cost, lowers energy requirements, and is more cost effective in removing heavy parts of DRO through the biodegradation mechanism. SVE helped collect trapped free product in the vadose zone. Installation of a drum of organoclay to remove free product eliminated the generation of a hazardous waste stream. Mixing of GAC with oxidant-impregnated zeolite to remove polar compounds extended the life-cycle of the GAC vessels. After operating the SVE system for 2.5 years, the average VOC concentrations were reduced from 175 to 25 ppmv in the vadose zone and 2,600 lbs of VOCs and 6 gallons of free product were removed. After 9 months of AS operation, the groundwater DRO concentrations decreased approximately 70%. Updated site conceptual model is prepared for no further action request.

Using Sustainability Metrics to Improve the Resiliency of an Active Groundwater Remediation System

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Background/Objectives. The Savannah River Site (SRS) began operating a groundwater remediation system consisting of an air stripper and recovery well network in 1985 and has operated it continuously for over 27 years. The system has an average electrical load of 150kW and recovers and treats groundwater contaminated with chlorinated volatile organic compounds (CVOCs) at a rate of 420 gpm. This represents an average of 1,247,000 kWhr of electricity consumed per year and 209,714,000 gallons pumped per year. The influent trichloroethylene (TCE) concentration to the air stripper decreased exponentially from 25,200 µg/L in 1986 to 2,230 µg/L by the end of 2012. This concentration decrease is a common occurrence for groundwater remediation systems that use groundwater pumping. The air stripper at SRS removed 33,231 pounds of TCE during its' first full year of operation and removed 2,092 pounds of TCE during its' 26th year of operation while consuming the same amount of electricity and removing the same amount of water in both years.

Sustainability metrics such as pounds of contaminant removed per kWhr (energy intensity) and pounds of contaminant removed per 1000 gallons pumped (water intensity) provide measures to assess performance and identify opportunities for improvement. Resilient groundwater remediation systems are systems designed in such a way as to easily adapt operations as performance or site conditions change to maintain high levels of efficiency. This paper presents the results of an analysis conducted to assess performance using sustainability metrics and the recommendations that resulted from the analysis.

Approach/Activities. Twenty seven years of operating data for the full scale groundwater remediation system such as contaminant concentration, flow rate, electrical demand, and hours operated were compiled for the sustainability analysis. This data was then used to develop mass removal models for each of the operating groundwater wells and the air stripper. Water intensity and energy intensity were calculated to analyze the environmental burden of the individual components of the groundwater remediation system and identify the ones that were under performing. Recovery wells with poor performance were evaluated to identify strategies to improve performance. Examples include redevelopment, operating at a different flowrate or abandonment and replacement. Operating conditions for the air stripper were also reviewed to identify any opportunities for improving performance.

Results/Lessons Learned. The overall water intensity and energy intensity have increased by 1600% since the initial year of operation indicating it required 16 times more energy and groundwater to remove 1 pound of TCE in the 26th year of operation than it did in the first year of operation. Results for individual wells were used to identify opportunities for modification of the recovery well network that will make the system more resilient and improve efficiency. Additionally changes in operation of the air stripper were recommended to reflect current levels of contamination in the influent. The proposed modifications to the groundwater remediation system will reduce the environmental burden of the A/M groundwater remediation system through improved mass recovery and reduced use of energy and other site resources.

Accelerated Site Closure Achieved after System Optimization

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Background/Objectives. Due to the often complicated technical and regulatory requirements of environmental work, it is easy to get mired in the existing strategies & technology with no end in sight. Two case studies will be presented to illustrate how stagnant long-term remediation projects are being re-evaluated and positioned to accelerate sites towards closure.

Approach/Activities. Site #1 currently functions as a maintenance shop for an undisclosed military installation in the southeast. During soil sampling activities near a fuel dispenser in 1990, a release from the gasoline underground storage tank (UST)/dispenser was confirmed with evidence of impact to soil and groundwater. Remediation via a soil vapor extraction (SVE)/air sparge system was performed for 13 years with diminishing progress toward closure due to residual impacts remaining in groundwater in excess of groundwater standards and the presence of a nearby creek. Challenge: Site remediation efforts were stalled and risk-based closure is not an option. Solution: Collaboration between the client, consultant, and the regulatory agency provided for accelerated site closure that included Mann-Kendall trend analysis, fate and transport modeling via BIOSCREEN to demonstrate that the creek would not be impacted, and a restriction on groundwater use. The "No Further Action" decision was released in the Fall of 2014 approximately one year after beginning "system optimization.

During operations at Site #2, a petroleum release occurred and impacted soil and the shallow groundwater. Contaminants of concern were treated by dual phase extraction (DPE), SVE, and groundwater extraction. Challenge: Site remediation efforts have stalled and risk-based closure is not an option. Solution: Collaboration between the client, consultant, and the regulatory agency provided for accelerated site closure by re-focusing groundwater management on protecting the creek and accelerating groundwater treatment upgradient of the GWPTS using stabilized hydrogen peroxide. Accelerated oxidation of contaminants has been achieved during pilot testing, and higher residual oxygen concentrations have increased the potential for attenuation downstream of the injection zone. Soil excavation in the source area and continued hydrogen peroxide injections are planned while the GWPTS system continues to operate.

Results/Lessons Learned. Review approach with stakeholders on a regular basis considering how technologies and regulations change over time. Avoid becoming complacent when a long-term remediation project seems to be working as planned. Consider the current business climate and the client's ultimate goal when planning for a successful project.

NAVFAC Portfolio Optimization for Sites under the Installation Restoration Program (P-Opt IRP)

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Background/Objectives. The Office of the Secretary of Defense mandates the Response Complete (RC) goals of 90 percent (%) by the Fiscal Year (FY) 2018 and 95% by the FY 2021 on all sites under the Department of Defense Environmental Restoration Program. Approximately 278 active sites within the Department of the Navy (DON) Installation Restoration Program are projected not meeting the 2021 RC goal. The projected RC dates of these sites range between 2021 and 2061 and the estimated cost to complete (CTC) for the long-term operation and management (RAO/LTM) of these sites in present dollar value is $746million (M), which is equivalent to an average annual CTC of $57.4M. This outlook provides a clear need for a portfolio optimization (P-Opt IRP) initiative to shorten the timeframe and CTC in order to meet the RC goals to the extent practicable. The P-Opt IRP initiative aims at improving the resource utilization efficiency through better and more appropriate use of innovative approaches. Subsequently, the initiative also leads to cost saving, lower residual site risk, and better site management.

Approach/Activities. The P-Opt IRP initiative has five implementation milestones: 1) preliminary sites evaluation, 2) forming focused site categories, 3) developing focused teams and common prioritization strategy, 4) detailed optimization, and 5) implementation and feedback. Using deMinimis criteria (2021 RC goal compliance, RAO.LTM duration, total and annual RAO/LTM CTC, and ratio of toal remedial action construction cost the the RAO/LTM CTC), Milestone 1 resulted in 82 sites for optimization. Milestones 2 results in 4 focused sites categories (Pump and Treat and Containment (P&T); In Situ Bioremeantion and Monitored Natural Attenuation (ISB/MNA); Capping and Land Use Control; Non-Bio Treatment; and, Future Remedy). Milestone 3 is currently in progress. Factors considered in the common prioritization strategy are cost efficiency, schedule accelearation, site complexity, and regulatory challenges. Teams consisting of experts from in and outside DON will perform the detailed optimization. In FY2015, the initiative targets completing Milestone 4 for 35 sites which comprise of P&T and ISB/MNA sites.

Results/Lessons Learned. The initiative will generate common-theme and detailed findings and recommendations for each focused site categories. These findings and recommendations will be tailored at the Facility Engineering Command (FEC) level to ensure that they can be practically implemented and progress/results are measurable at the Program level.

Back to Contents

A Rapidly-Deployable Automated Remedial Injection System—Sustainability Elements and Operational Experiences

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Background/Objectives. This presentation will illustrate the design and operation of a mobile, rapidly-deployable, automated injection system capable of delivering a variety of remedial amendments to the subsurface while minimizing electricity use and operator visits.

Approach/Activities. Delivery of remedial amendments in tight soils or bedrock fractures often precludes high-flow injection and promotes uneven distribution and ineffective delivery, resulting in poor treatment. While high-pressure injection may increase the associated injection rates, it also heightens the risk of surface breakout and personnel injury. Gravity-feed, constant-head injections offer a sustainable and lower cost alternative that operates with the existing site conditions to promote effective distribution.

ERM has developed sophisticated systems for the delivery of in situ chemical oxidation or bioaugmentation amendment that incorporate networked elements including remote control, paging alarms and live video, all of which can be remotely viewed in multiple locations. When applicable, these systems have also been equipped with solar panels (to provide up to 100% off-grid power) and rainwater collection systems (to use of alternative water sources). The incorporation and usage of these improved elements greatly reduce the overall O&M cost and associated carbon footprint of operations.

Many sites have constraints on the physical size and duration of remedial operations. Small systems that can be effectively deployed and demobilized quickly to minimize intrusion, allow for repeated injections without leaving equipment on-site in between, and provide an effective means to address this concern.

Systems that combine these elements are capable of both meeting remedial goals in a timely, energy-efficient, cost-effective, and safe manner, while keeping a light and sustainable site footprint.

Results/Lessons Learned. This paper will review the components of system design, sustainability elements, and operational case studies using sodium permanganate and lactate injections at several field locations.

The Role of the Quality Assurance Process in Long-Term Project Optimization

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Background/Objectives. Regulators, responsible parties, and project stakeholders who have responsibility for Superfund, RCRA, SMCRA, Consent Orders and other environmental compliance programs have a long documented history of requiring project control documents specifically focused on project-specific quality assurance systems. Unfortunately, in too many cases, little attention is paid to changes in personnel, analytical methods, field sampling collection techniques, and regulatory program guidance. The disparity among the assumed levels of care in program planning, sample collection, sample analysis and data reporting when compared to actual activities currently in use at environmental project sites nationwide compromises the data upon which protection of public health and the environment is based.

Long-term projects have a tendency to be particularly vulnerable to eroding quality standards as a level of comfort is acquired by both the regulator and regulated community. By focusing on the quality assurance process (e.g. project control documents, field services) better, more useful data can be generated. Data quality suffers due to a lack of attention during long-term projects and as a result, the environment, the public, and project budgets suffer as well.

Approach/Activities. This paper specifically examines aspects of long-term project quality assurance programs, including firsthand experience with documentation and recordkeeping, implementation of corrective actions and follow-up. Certain trends and common themes have been identified for long-term projects including a lack of public interest, eroding technical focus, and evolving regulatory environments. If not properly managed, these trends result in little more than project delays misappropriated resources, and wasted tax dollars. The goal of this paper is to begin a conversation regarding misplaced regulatory concerns and the production of compromised data by the regulated community that leads to poor decision making and the unintended consequence of unacceptably elevating risks to human health and the environment.

Results/Lessons Learned. Both generic and project-specific observations are provided. Historical examples of long-term regulatory driven projects in which stakeholders systematically lost focus on quality systems and how that loss of focus has resulted in poor decisions provides lessons learned. The risk of public health and stakeholder resources are circumstances that must not be repeated. Project management through regulatory intent, as opposed to obligation and “guidance as law” will be an area of particular focus. The evolution of long-term project focus, and how the quality assurance project needs should evolve in parallel as a project progresses over decades will be discussed. Specific recommendations designed to return long-term projects to better quality systems upon which better optimizing decisions can be based will be made.

Rapid, High-Resolution Site Characterization to Optimize Enhanced Bioremediation of a Chlorinated Solvent Plume

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Background/Objectives. A mature, stable plume containing tetrachloroethene (PCE) and trichloroethene (TCE) in upstate New York has been persistent in groundwater at concentrations up to 100 micrograms per liter despite three injections of organic substrate (emulsified vegetable oil [EVO]) over a 4-year period that created a linear permeable reactive barrier (PRB) immediately downgradient of the perceived source area. When the PRB remedy was conceived it was anticipated that the downgradient portion of the plume would diminish due to removal of PCE and TCE in the PRB and the inferred groundwater seepage velocity within a permeable glacial outwash stratigraphic unit. Although PCE and TCE were effectively degraded in the PRB, concentrations were sustained downgradient of the PRB. REMCHLOR modeling was conducted to further evaluate the effects of the PRB and natural attenuation in the downgradient portion of the plume; results indicated that downgradient concentrations would not decrease below the groundwater standard in less than 30 years. Due to these treatment timeframes, the site was further characterized to better identify source areas and the reason(s) for plume persistence. A rapid, high-resolution site characterization was performed to achieve the following objectives: 1) obtain a better understanding of the location(s) of source mass, 2) evaluate the appropriateness and sufficiency of the previously implemented enhanced anaerobic bioremediation (EAB) remedy, 3) determine the cause(s) of the observed plume persistence, and 4) facilitate assessment of the need for additional engineered remediation.

Approach/Activities. A dynamic work plan was prepared that outlined the use of a direct-push probe to rapidly collect closely-spaced soil and groundwater samples at varying depths along multiple transects across the plume with detailed core logging and rapid analysis of samples in a mobile, onsite laboratory to guide the sampling program according to pre-determined decision logic. Field decisions made using near-real time data combined with the decision logic outlined in the work plan allowed sampling locations to be progressively optimized to effectively achieve the objectives to the extent feasible within the allotted 1-week time period.

Results/Lessons Learned. The high-resolution results identified smaller-scale, more localized site features that may exert significant control over contaminant fate and transport and that were not previously recognized based on installation and sampling of conventional monitoring wells and soil borings. These details include variations in soil type and grain size that appear to cause the contaminant concentrations to vary substantially over small distances and to be highly localized. Concentration profiles indicate that PCE/TCE mass is sorbed in fine-grained (silt/clay) material within and underlying the primary transmissive (sandy) zone, indicating that back-diffusion of PCE and TCE into the transmissive zone is contributing to plume persistence. High-resolution sampling results were used to develop a 3-dimensional visualization model to support data analysis, conceptual model refinement, and assessment of the need for additional engineered remediation. Additionally, the analytical Matrix Diffusion Toolkit was applied to estimate how back-diffusion from low-permeability soils will impact plume longevity.

Remediation of Shallow Groundwater Impacted With Chlorinated Ethenes Utilizing an Engineered Wetland

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Background/Objectives. In 1998, an engineered surface water wetland to remediate shallow groundwater impacted with chlorinated ethenes (trichloroethene (TCE) and daughter products) was constructed at a rural site in the Midwest. At the time of construction, the influent TCE concentration was approximately 2,000 ug/l. Natural biological treatment was deemed a low-energy, affordable, in-situ option that could provide efficient long-term treatment, while creating valuable wetland habitat. A National Pollution Discharge Elimination System (NPDES) permit was issued by the state regulatory agency setting forth limits for TCE, 1,1-dichloroethylene (DCE) and vinyl chloride (VC).

Approach/Activities. The treatment wetland was constructed by lowering the existing surface grade. The wetland consists of four cells, each divided by soil berms, with an aggregate surface area of 3.6 acres. Wetland width was dictated by the necessity for plume capture. An excavated trench filled with gravel and cobble sized material was constructed on the up-gradient side of the cells to provide a preferential pathway for groundwater to passively flow into the wetland cells. The main flow path is through two treatment cells, east (1.1 acre) and west (1.46 acre), flanked by east (0.25 acre) and west (0.40 acre) auxiliary cells. Each cell is equipped with a V-notch weir at its outlet. Discharge from the cell weirs is piped to an outflow trench occupying the entire width of the downstream ends of the wetland cells, and subsequently flows through a fifth V-notch weir designated as the NPDES permitted outfall. Outflow is to a natural wetland area connected to the receiving stream.

Operational issues identified during early operation of the system included muskrat infestation, hydraulic short-circuiting and elevated vinyl chloride concentrations. Optimization of the system included:

- Removal of deep trenches and addition of cross berms to eliminate hydraulic short circuits and decrease muskrat habitat
- Installation of a “muskrat exclusion barrier” on the perimeter fence and muskrat trapping
- Installation of recirculation system to address low flow

Results/Lessons Learned. System optimization has resulted in year-round treatment of the chlorinated plume by the engineered wetland. The wetland has been successful in reducing chlorinated ethenes and meeting design goals and permit requirements. Estimated concentration reductions of 76 – 95% are achieved on an annual basis for TCE and 70 – 95% for DCE. Dechlorination is occurring, as evidenced by the presence of daughter products. A recirculation system has been successful in reducing VC to acceptable levels. Removal rates are generally at their maximum in springtime. Overall, the wetlands have been successful in meeting permit requirements and have resulted in a valuable ecological habitat. Diverse and dense vegetation is present. A wide variety of species use the wetlands, including Sandhill crane, Canada geese, red-winged blackbird, painted turtle, turkey vulture, and Monarch and Swallow-tail butterflies.

Ten Year Review of the Application of Modified Active Gas Sampling

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Background/Objectives. In 2004, Dr. Richard Lewis introduced the Modified Active Gas Sampling (MAGS) at Battelle's 4th International Conference. The purpose of this review is to provide a summary of the application of MAGS in the past ten years. We hope that this ten-year review will yield an appreciation of the positive developments and the remaining challenges to ensure the implementation of MAGS in the United States.

Approach/Activities. MAGS is an environmental engineering assessment technique that rapidly detects unsaturated soil source areas impacted by volatile organic compounds. Dr. Richard Lewis and his colleagues developed the MAGS technique in 2002. Since its development, MAGS has been used initial assessment and/or supplemental source assessment at over one hundred sites all over the United States and adopted by the state of Florida in its Drycleaning Solvent Cleanup Program. MAGS involves the extraction and analysis of soil vapor from a piezometer screened through the unsaturated soil column for the purpose of locating unsaturated zone source material. By utilizing a typical regenerative blower fitted to a temporary soil vapor extraction well, a large volume of soil can be assessed with a limited number of samples. While lacking the resolution of traditional soil sampling methods (*e.g.*, discrete soil sampling, low flow active gas sampling, *etc*.), the statistical representativeness (in the sense of sample coverage) of MAGS results versus traditional methods is much greater. Additionally, the results of the assessment provide more useful transport and exposure assessment information over traditional techniques. Lastly, MAGS is effective as both an initial site assessment and remedial assessment tool, in that, MAGS directly yields data required for remedial design.

At many chlorinated solvent sites, aggressive technologies are typically undertaken to address source areas. However, unknown vadose zone sources are often unaddressed resulting in continued mass flux of the source to groundwater, which can lead to groundwater impacts/rebounding above regulatory standards. Such conditions often require long-term monitoring, hindering property transactions and delay closure. Several case studies will be presented in which MAGS is applied following initial active site remediation. Based on our experience, failure of a remedial design to achieve regulatory levels and the occurrence of rebound in groundwater concentrations are commonly the result of multiple (relatively small) release areas that had not been previously discovered with discrete soil sampling. MAGS provides a novel means of pinpointing the potential secondary sources and has been successfully applied to locate unknown source areas at sites that were showing signs of rebound after initial remediation efforts. Several sites have been closed as a result of additional remediation of new/minor sources identified by MAGS.

Results/Lessons Learned. Often closure is not achieved at many sites after the initial aggressive remediation due to the lack of site assessment, particularly the lack of the unknown release sources. The use of MAGS helps to identify additional source areas at sites where groundwater impacts/rebounding above regulatory standards are occurring after initial source remediation efforts.

Complex Site Remedial Management Optimization Utilizing on the Cloud Computing Systems

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Background/Objectives. The National Acadamies reported at least 126,000 sites across the country have residual contamination levels which prevent site closure (NAP 2013). The estimated cost to complete site restoration is $110-$127 billion dollars. Of these just under 10% or roughly 12,000 are estimated to be complex sites due to site heterogeneity and the contaminants present in the subsurface. Many complex sites lack adequate characterization; others cannot be cleaned up to unrestricted use with available technologies (NRC 2013) and are transferred to long term management. Coupled with this is the desire for greener remediation and incorporation of sustainable considerations during site restoration. To support cost effective and sustainable environmental restoration efforts, site owners need better predictive tools with the capability to incorporate management considerations into risk-informed decision making. Physics Based Management Optimization (PBMO) provides one such tool. “Physics Based” indicates incorporation of both flow and transport into the analysis, permitting optimal remedy design and monitoring based upon contaminant fate and transport characteristics. “Management Optimization” indicates ability to incorporate objective functions (management constraints, emissions reductions and sustainability considerations) into the evaluation. PBMO provides the ability to optimize bioremediation design using a half-life/cost function to determine the optimal design half-life and optimization of remedy transition or sequencing from active to passive remediation based upon mass reduction cost efficiency coupled with management requirements. PBMO permits automated evaluation of 100’s to 1000’s of candidate solutions thereby providing greater confidence that an optimal solution has been determined. Recently, PBMO has been implemented on the multi-core grid computing system (PBMO-Grid). The objective of this effort is the extension of PBMO-grid to Cloud computing resources to facilitate application at complex sites.

Approach/Activities. Our paper provides an overview of PBMO, including application case study results and a case study in the computational benefits of implementing cloud-based PBMO-Grid. In the PBMO-Grid case study, we evaluate flow and transport for a typical optimization search for a moderately complicated project against sequential optimization. The optimization effort is based on evaluating 5,000 candidate solutions.

Results/Lessons Learned. PBMO-Grid reduces the CPU time required to solve the optimization problem by more than a factor of 14X compared to sequential optimization. Implementation of PBMO-Grid on the Cloud allows for increased flexibility and adaptation of computational resources which can now support optimal remedy design and long term management strategies for complex soil and groundwater sites. PBMO-Grid can be deployed for deterministic or stochastic optimization (formally computes design risk, predicted degree of success). The numerical models used can either be a single "mega" model (aka a monolith), or a mixture of models and other calculations or expert systems. PBMO-Grid integrates the computational models in a seamless manner, and models run on the Cloud can be implemented in Windows or Linux platforms.

Use of Advanced Techniques to Maximize Amendment Delivery in Challenging Geologies

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Background/Objectives. The former Unocal chemical distribution facility in Wichita, KS, blended and packaged bulk chemicals for industrial customers. As a result of historical operations, tetrachloroethene (PCE) was released to the groundwater at the site. Since 1989, several remedial technologies have been implemented at the site to treat chlorinated solvents in the groundwater. Despite many remedial activities conducted, the contaminated groundwater has migrated approximately ¼ mile from the primary source area to adjacent properties. To mitigate further expansion of the plume and reduce contaminant concentrations, injections of EHC® and EHC® Liquid have been performed to promote in-situ chemical and biological reduction of PCE and its daughter products.

At the site, the contaminated plume is within the alluvium deposits, which consist mainly of unconsolidated clay with thin, discontinuous sand, silt, and gravel lenses. The alluvium deposits are approximately 10-25 feet thick in the contaminant plume. To enhance amendment delivery and increase contact with the contaminants within this challenging geology, several strategies were employed during the injection phase to manage the amendment delivery, including the use of hydraulic profiling tools (HPT).

Approach/Activities. The injections began in July 2014 and included a total of 165 injection points using a direct-push technology (DPT) rig. Prior to implementing the injections in a given treatment area, HPT was employed to determine specific target injection intervals for each of the treatment areas. At each HPT boring location, dissipation tests were conducted to determine the hydrostatic pressure across the potential injection interval. Based on the HPT flow, HPT pressure, and hydrostatic pressure obtained during the dissipation tests, an estimated hydraulic conductivity was calculated. The estimated hydraulic conductivities versus depth were overlayed with the groundwater monitoring information and geology from boring logs to determine the most practical injection intervals.

In addition to using HPT, several other strategies were evaluated during the injection phase on day to day basis and employed, if necessary to minimize pressure buildup, increase product distribution, and minimize surfacing.

Results/Lessons Learned. Based on the HPT results, boring logs, and recent groundwater monitoring information, it was observed that the contaminants were generally located within lower permeability units over a narrow range within the saturated alluvial deposits. Using the HPT results obtained, the injection intervals could generally be limited to 10- to 14-feet rather than the entire 15- to 20-foot saturated zone. As a result of using a smaller injection interval, project costs were minimized.

Source Area Management Using Membrane Interface Probe and Enhanced Anaerobic Bioremediation

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Background/Objectives. The Bountiful/Woods Cross Operable Unit 1 Site (the Site) in Utah is located in southern Davis County Utah, roughly 10 miles north of Salt Lake City, and includes a two-acre source area with trichloroethene (TCE) contamination of subsurface soil and groundwater that originated from leaks, spills, or discharges to the ground. The treatment zone comprises heterogeneous deposits of dense, well-graded sand and gravel, alternating with layers of sandy, silty clay. Characterization work at the site utilized the membrane-interface probe (MIP) to delineate the areas requiring treatment. During MIP work, a contaminant hot spot was identified with concentrations over ten times greater than previously observed concentrations at the site. A grid of injection wells was installed to treat TCE in the source area using enhanced anaerobic bioremediation (EAB), and additional injection wells were installed in the vicinity of the hot spot to attempt to enhance delivery of amendment. While EAB has been effective in achieving significant contaminant mass reduction in the majority of the source area, the primary hot spot continues to exhibit elevated concentrations, and an additional hot spot was identified through groundwater monitoring. To better define the extent and magnitude of contamination at the hot spots, a TRIAD approach using MIP was employed, followed by installation of new injection wells.

Approach/Activities. A MIP investigation using a TRIAD approach was performed to delineate the areas of TCE contamination generally exceeding 1 ppm, and up to approximately 100 ppm total aliphatic hydrocarbons, within the source area of the Site. Verified by contaminant screening during well installation and subsequent groundwater sampling, the MIP results were used to guide installation of a series of additional monitoring and injection wells that provide targeted treatment of the appropriate locations and depths. Subsequently, periodic injections of an organic substrate were performed to promote reductive dechlorination of TCE. Periodic groundwater monitoring activities were conducted to evaluate EAB performance.

Results/Lessons Learned. The presentation will include a discussion of the use of MIP to aid efficient and effective contaminant delineation and subsequent remedial action. Specifically, reevaluation of the conceptual site model was performed during MIP analysis and implementation of the remedy to facilitate more strategic and effective site remediation. Promising groundwater monitoring results, which indicated significant contaminant mass reductions via reductive dechlorination of TCE, and important lessons learned regarding source area management will be presented.

Back to Contents

Managing Emerging Contaminant Liabilities: To Sample or Not To Sample?

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Background/Objectives. The identification of chemicals of emerging concern (CECs) at established remediation sites can have a significant effect on real or perceived liabilities associated with these sites. Application of a robust decision-making process ensures that likely contaminants are properly identified, but also avoids unnecessary sampling time and expense. Early characterization phases at newly identified hazardous waste sites often have little available information, necessitating a broad (e.g., "shotgun") approach to sampling for environmental contaminants. On the other hand, established remediation programs typically have a wealth of knowledge about hazardous materials used, housekeeping practices, circumstances of release, and distribution of known site co-contaminants. Within this framework of knowledge, valuable information can be gleaned regarding the likelihood of a given CEC being present and even at what levels it might occur. Additionally, key chemical characteristics of the specific CEC, such as solubility, vapor pressure, and sorption coefficient, govern the media likely to be impacted, and therefore can help focus a given sampling effort and avoid sampling of media less likely to be impacted. The application of a well-founded approach to CEC sampling can streamline the assessment process and avoid unnecessary sampling activities.

Approach/Activities. The conceptual site model forms the foundation for assessment of whether CECs are likely to be present, using information related to historical site activities, release mechanisms, timing of potential usage, and hydrogeologic characteristics. This information is supplemented with an assessment of the probable history and usage of the specific CEC at the site, which is often not directly known but must be inferred from historical CEC production or usage data and observations from comparable sites. Because some contaminant occurrence was actually driven by regulations, such as PFOS in chromium plating mist suppression foam, knowledge of the timing for regulations related to the CEC or industry can be used to determine the likelihood of occurrence at a given site. A decision process will be presented which allows a rational and well-considered approach to be followed in determining when sampling is warranted and when it is unlikely to lead to useful information. This process will be demonstrated using 1,4-dioxane and perfluorinated compounds, two CECs of particular interest at present. Examples of where this approach has accurately predicted occurrence and where the analytical findings were in conflict with the anticipated results will be presented to explore the universality of this type of approach to sampling decisions.

Results/Lessons Learned. Robust assessment of site activities, possible release mechanisms, CEC fate and transport, and industry knowledge of the manufacture and usage of CECs can form the basis for a logical and informed decision-making process regarding the merits of sampling. This decision analysis approach can be applied by stakeholders to drive efficient characterization programs with a high likelihood of success.

The Role of Risk Assessment in Sustainable Remediation: A Global Perspective

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Background/Objectives. The practice of sustainable remediation as described in various global SURF and NICOLE frameworks is considered good practice, is consistent with existing risk-informed contaminated land management, and should be recommended as a basis for future practice on the management of soil, sediment and groundwater contamination. Common to each of the frameworks is acknowledgement that some of the greatest sustainability gains can occur early in the life cycle of a project before the technical approach to remediation at a site is evaluated including the development of risk-based and achievable remedial goals. The development of achievable, risk based remedial goals allows for a more thorough evaluation of sustainable remediation technologies while assuring that the three pillars of sustainability (social, economic and environmental) are included as part of the remedy selection.

Approach/Activities. The application of sustainability principles through the life cycle of several projects are explored with a particular focus on the role of risk assessment and the integration of risk assessment in sustainable decision making. Case studies are presented from the US, UK, Europe and Asia where site specific risk assessment has resulted in a significant impact on the overall sustainability of a project and conclude with a number of recommendations for the continued and further integration of sustainability with risk informed contaminated land management.

Results/Lessons Learned. Incorporating risk assessment early in the project life cycle, with the approval of all stakeholders (regulators, responsible parties and local communities) provided for the development of achievable remedial goals. This allowed for a more thorough review of applicable remediation strategies and the ultimate selection of sustainable remediation based on meeting social, economic and environmental criteria.

Advances in Groundwater Plume Stability and Plume Diagnostic Evaluations

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Background/Objectives. Evaluation of the relative stability of a groundwater contaminant plume is generating increasing attention as many domestic and international stakeholders are realizing the applicability of plume stability as part of the environmental evaluation and/or remedial planning process of a site. This is especially important in the development of a long-term risk management strategy for a site. A plume stability evaluation allows the stakeholder to assess whether a contaminant plume is stable, decreasing, or increasing for a variety of metrics (i.e., area, concentration, mass, center of mass, and spread of mass). This allows better evaluation of whether additional remedial action is necessary, if risk-based closure of a site is applicable, or whether natural attenuation processes may be occurring at a site. The Ricker Method® for plume stability analysis[1] is a unique method of evaluating plume stability that overcomes limitations posed by conventional well-by-well analysis techniques.

Approach/Activities. Outputs from the Ricker Method® can be used as a basis for primary analysis and other plume diagnostic tools that allow the user to further evaluate and communicate groundwater plume dynamics. This method has been used as a basis for the cessation of remediation systems, identification of commingled plumes, identification of potential unrealized source areas, and providing additional lines of evidence for natural attenuation; examples of which will be presented. This session will also present certain aspects of a proprietary analysis tool called Remediation System Benefit Analysis (RSBA®). RSBA® is an interpretation of the relative benefit of a remediation system based on graphical data outputs created from the Ricker Method® evaluation and additional data inputs. In effect, what RSBA® does is evaluate the efficiency of an active groundwater remediation system that removes contaminant mass from groundwater (e.g., pump and treat). The tool evaluates whether an active system may be considered efficient or inefficient based on an evaluation of contaminant mass removed via the system and the relative stability of a groundwater plume.

Results/Lessons Learned. The Ricker Method® has been successfully used as part of long-term risk management strategies to help stakeholders analyze unique groundwater plume characteristics including area, average concentration, and mass indicator, and describe the behavior of that plume as decreasing, increasing, or stable. Further, using the supporting plume diagnostic tools, we have been able to distinguish commingled plumes, demonstrate MNA progression, identify unknown source areas, define specific molar based signatures for chlorinated compounds, reduce monitoring requirements, and close sites.

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[1] [1] Ricker, J.A. 2008. A Practical Method to Evaluate Ground Water Contaminant Plume Stability. Groundwater Monitoring & Remediation 28, no. 4: 85–94.

Use of Quantum GIS to Manage Risk and Advance Complex Site Technical Understanding and Analysis

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Background/Objectives. The Air Force Civil Engineer Center (AFCEC) Technical Support Branch, in an effort to manage risk, consistently optimizes environmental site characterization and remediation to accelerate closure and reduce long term liabilities. AFCEC is focusing on many challenging sites in the USAF portfolio to develop risk management strategies addressing those with complex hydrogeology or site conditions; recalcitrant or highly mobile contaminants; high or disproportionate risk; and those with anticipated long-term or high cost remediation. The volume of data associated with these sites span decades of sample collection and is truly “Big Data” routinely exceeding multi-million records. NewFields Government Services, LLC (NGS) provides multi-dimensional, quantum geographic information systems (QGIS) tools supported by PostSQL to rapidly mine, visualize, and make readily available all data to date across multiple installations. These efforts often require networking of multiple database platforms of data and text to facilitate the unique, in-depth technical analysis required at these sites.

Approach/Activities. The project supports site technical analysis and development of remediation and exit strategies for sites and installations across the US. First, all data, including electronic chemical data, lithological data, geobase and infrastructure data, and relevant site and regional environmental data is collected and compiled into the environmental database via a GIS and/or QGIS platform. QGIS provides a technical platform for geostatistical/statistical, time series, and spatial analysis working from the empirical data and NGS uses customized programming to create a secure and flexible framework that sustains charting tools, cross section functionality, and other applications that can be tailored to the specific project needs. Once compiled, NGS analysts digest site data and support AFCEC by bringing the complete QGIS and functional tools, which are utilized “live” in the team working group meetings to allow rapid analysis and development of recommendations for key decision points. If desired, elements of the GIS can be used in a web-based format or translated to applications to enhance the project communications. As an example, using a combination of the tools, the team examined the empirical data to look at patterns of chlorinated solvent impacts, migration, and degradation as well as cross sectional data highlighting connectivity patterns that were not initially apparent to discern additional source areas. The team further assessed geochemical zones affecting attenuation rates, the presence and patterns of daughter products and performed statistical evaluation of the well network across multiple depths and site areas to better correlate the current data and interpretations. The QGIS and associated tools have helped bring the data to the forefront making it readily available in multiple formats to the team.

Results/Lessons Learned. Through efficient data mining and visualization, we have continued to leverage the vast quantity and value of USAF data. By utilizing a QGIS platform with customizable functional tools, the data is now accessible to allow the team to understand and communicate the big picture to all decision makers while developing effective, sustainable remedial strategies.

Use of Monte Carlo Analysis to Identify and Mitigate Risk

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Background/Objectives. There are numerous risk drivers on a typical remediation project; at the core, these risks are rooted in uncertainty. Uncertainty can be in terms of costs and schedule. Conceptual model uncertainty and design variables also represent sources of uncertainty that need to be considered in managing remediation projects. A Monte Carlo analysis is a good tool to identify risks and evaluate risk mitigation opportunities.

Approach/Activities. This presentation will provide an introduction to Monte Carlo analysis. It will then identify some of the most common significant risk sources in traditional remediation projects and describe how a Monte Carlo analysis can be used to assess risks. Examples of where a Monte Carlo analysis was used to estimate risks and support decision making will be provided for the following scenarios: 1) technology comparison based on cost uncertainty, 2) design variable uncertainty, 3) value of information to help answer a question if additional data should be collected, and 4) how a Monte Carlo analysis can be used within a structure of decision tree management tools. Traditional Monte Carlo assessment tools will be presented along with their attributes, relative costs, and training requirements for practitioners.

Results/Lessons Learned. Once risk is estimated via Monte Carlo analysis, mitigation measures can be considered to determine if risks can be minimized. The tool can also be used to estimate the risk of a mitigation measure so a decision maker can determine if the cost of mitigation provides an acceptable return on investment. A Monte Carlo analysis is a useful and simple means to convey complicated risk uncertainties to stakeholders in an easy-to-understand graphic.

Back to Contents

Nitrate: Manage Risk by Understanding the Dynamic Nitrogen Conceptual Site Model

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Background/Objectives. Nitrate has become an increased regulatory concern due to gradual deterioration of surface and ground water quality related to persistent and widespread fertilizer application. Given the increased attention to regional escalation of groundwater nitrate concentrations and associated impacts to community water systems, stronger requirements for remediation of point-source nitrate plumes are being enforced by oversight agencies to decrease the overall nitrogen flux into already stressed aquifers. For example, the California Department of Public Health has established a “trigger” concentration of half the maximum contaminant level (MCL) of 10 milligrams per liter (mg/L) that requires water distributors to initiate corrective actions to reduce nitrate concentrations in the water supply. Understanding how the complete nitrogen cycle can influence sustained nitrate impacts is critical to developing a robust conceptual site model and effectively managing overall site liability. Nitrate impacts to groundwater are often merely a symptom of a sustained source which includes a number of various nitrogen forms, such as ammonia and urea, analogous to how non-aqueous phase liquid can serve as a long-term source of volatile organic compounds contamination. At sites containing other contaminants with more historic regulatory attention (e.g., chlorinated solvents), residual nitrate remaining following remediation can prohibit site closure.

Approach/Activities. Three case studies will demonstrate multiple nitrogen risk management strategies that can be used to achieve success. The first will highlight active treatment to promote denitrification using carbon substrate. The second will demonstrate the effective use of source identification forensic tools such as compound-specific isotope analysis (CSIA) and additional analytical suites to distinguish between multiple sources of nitrogen including synthetic or natural fertilizer, domestic wastewater and septic discharges, explosives, and motor oil and lubricating compounds. The third will demonstrate a combined remedial approach which consisted of both air sparging and carbon injections to promote in-situ nitrification of the residual ammonia source and subsequent denitrification of the produced nitrate.

Results/Lessons Learned. Implementation of the three described case studies illustrate the importance of understanding the volume of nitrogen source mass and its original form in order to develop a complete nitrogen conceptual site model prior to selecting or implementing a remedial strategy. To date, considerable literature has focused on various ex-situ treatments for nitrogen waste. For in-situ denitrification, success is largely based on effective delivery of the carbon source to the targeted treatment interval, and requires an understanding of changes in aquifer redox conditions and their bearing on nitrogen transformation and persistence. CSIA can be a powerful tool combined with other analyses to demonstrate not only source, but also active natural attenuation processes that contribute to closure objectives. In light of emerging regulations surrounding nitrate contamination and increased focus on multiple nitrogen source materials, development of an effective nitrogen conceptual model, an adaptive investigation approach, and targeted active remediation are all key facets of achieving treatment goals and reducing remediation liability.

Health Risk Assessment and Risk Management on a Contaminated Groundwater Site in Taiwan

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Background/Objectives. Revising EPA methodologies from the U.S the Taiwanese EPA has started to incorporate many models for their health risk assessments (HRA). In Taiwan, HRA concepts, such as the baseline risk assessment and the development of risk-based preliminary remedial goals, are used as one of the evaluation tools to set up alternative remedial goals and to appropriate remediation technologies at sites. Therefore, the aim of this study is to evaluate a contaminated groundwater site by HRA, and based on the assessment results to apply suitable risk managements for avoiding contamination sources, containment and removing contaminations.

Approach/Activities. In this study, HRA is applied to a contaminated groundwater site in northern Taiwan. Dichloromethane, Benzene and Toluene are the contaminants of concern (COCs) at this site. Groundwater modeling software was used to simulate the extent of contamination and to define the scope of this assessment. Questionnaires are also used to survey the locals near the process zone to pinpoint the potential risk factors for contamination, and the localized parameters for risk assessment can be obtained as well.

Results/Lessons Learned. Workers at process zones are the primary group of exposure, usually in relation to their cleaning duties using the groundwater source. Based on questionnaires data, the main exposure pathways of workers are inhalation and dermal via contaminated groundwater. Carcinogenic and non-carcinogenic risks from studied area are identified acceptable by the Monte Carlo method. The results at 95% confidence are 1.08E-11~2.88E-8 and 3.86E-4~1.31E-1, for carcinogenic and non-carcinogenic risks respectively. Therefore, the uncertainty results could identify specific exposers who should be protected from contaminated site. Besides, decision maker set up the reasonable remediation actions based on risk analysis. The follow-up risk managements, such as replacements of double-layer and FRP-coating sumps and renews of grounded wastewater pipelines, have been done in this site to avoid the pollution sources. In addition, continuously monitoring on groundwater is used to prevent contaminations. Moreover, the contamination areas are well-defined, it helps us decide suitable remediation technologies to control and remove contaminants. In this case, in situ chemical oxidation for hot spots and air-sparging with soil vapor extraction for boundary regions would be suggested to apply in the site.

Back to Contents

State of the Union: Privatization of Contaminated Property Remediation Oversight—A Survey of State Site Remediation Programs

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Background/Objectives. Several states have developed professional licensure programs in an effort to streamline and partially or fully privatize contaminated site remediation work. These professional licenses have been authorized by state legislatures primarily as an effort to streamline the state site remediation program and facilitate and accelerate economic development and/or recovery. The level of responsibility and authority delegated by the state regulatory agency to the professional varies. Further, the framework of each state program varies such that the degree of independent decision making and for which areas of site remediation work ranges widely. Accordingly, the exercise of independent judgment applies to a narrow set of criteria in some states and is very broad in others. This paper intends to provide an update on the status of these programs and how they currently operate across the United States.

Approach/Activities. A review of the status of privatization/semi-privatization will be performed by evaluating all 50 state environmental cleanup regulatory programs. Detailed program information is available for all states including those with privatized elements. Interviews with state program regulators were conducted as available. This paper will describe the role of the licensed professional within the framework of each program with particular focus on three elements: (1) the use of the Conceptual Site Model (CSM) approach and how it applies to the development of cleanup targets and independent decision making; (2) program elements such as the delineation of the extent of contamination and the development and application of site-specific or programmatic cleanup/remediation goals; and (3) the site close out protocol (NFA, RAO, etc.). Available data regarding the number of cleanups completed and the timeframes for such actions before and after professionals were included in the program will be provided. Professional associations representing the interests of these professionals are clearly part of the stakeholder process for site remediation program development and execution. Interviews with state/regional professional association leadership regarding these three elements were conducted and provide insight for how the privatized programs operate.

Results/Lessons Learned. The current state of (semi) privatization of state site remediation programs varies widely across the nation. Several states require professionals to be directly involved with site cleanup programs and at least three require full licensure and complete oversight of site remediation activities. Others include professionals in aspects of the process but do not authorize professionals to exercise major site cleanup decisions. States with licensed professionals accomplish more site remediation activities, more site closures, and do so faster than those without. Privatized programs are continually evolving to accomplish site remediation, particularly with respect to the use of the CSM and application of cleanup goals to achieve site closure.

Evaluation of Licensed Remediation Professional Programs: A Comparison of Programs in Three States

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Background/Objectives. Several northeastern states have established licensing programs for environmental professionals providing assessment and remediation services at contaminated sites. These "privatized" programs place the responsibility for managing site cleanups under the auspices of a private licensed individual rather than a government agency. These innovative programs have been praised by some, but criticized by others. A clearer understanding of the benefits, problems, and pitfalls of these programs can help regulators, legislators, and advocacy groups reach rational decisions as to whether or not some variation of one or more of these programs would be appropriate for their specific states.

Approach/Activities. This study compares the attributes of three leading professional licensing programs: the Licensed Site Professional (LSP) program in Massachusetts, the Licensed Environmental Professional (LEP) program in Connecticut, and the Licensed Site Remediation Professional (LSRP) program in New Jersey. Program factors covered include the basis for making decisions regarding the extent of contamination, risk, and the need for remediation; the role of professional judgment in decision-making; and regulatory timeframes. Program governance factors will also be covered, including the size and make-up of the governing boards of registration; common complaints against licensed professionals, and sanctions applied to individuals; and the frequency with which decisions by the licensed professionals are overturned by a regulatory agency. A summary of the ground rules for each program will be presented, and a generic site addressed through each of the programs in order to compare the relative cost, time to completion, protectiveness of the selected remedy, and continuing obligations following the completion of active remediation. A comparison to a non-privatized (state oversight) program will also be presented.

Results/Lessons Learned. Relative measurements of the cost, speed and thoroughness of each privatized state program will be presented along with actual numbers of cases closed before and after the shift to a privatized system. An analysis of the problems encountered under each program will be used to highlight issues of special concern.

Five Relationship Models for Licensed Professional and Person Responsible for Conducting Remediation

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Background/Objectives. In an effort to decrease the time taken to remediate contaminated sites (due to redevelopment pressure, a desire to decrease public health and environmental risks, or both), several northeastern state legislatures created licensed professional programs. When implemented, these programs increase the private-sector role in the investigation and remediation of sites where releases of hazardous materials have occurred. This increased private role reduced, or shifted, the review and approval role of state environmental regulatory agencies and altered the relationships among licensed professionals, their remediating-party clients, and the state environmental agencies.

The objectives of this analysis are to: (a) summarize key relationship models that have evolved under environmental licensing programs in two states with robust programs (Massachusetts and New Jersey); (b) Describe those factors in each state program that influence which of the models are most prevalent; and (c) analyze which of the models are most beneficial to the timely remediation and repositioning of sites.

Approach/Activities. To facilitate detailed examination of the new licensed professional/ responsible party relationship under these state programs, five models will be defined: (a) traditional consultant; (b) advisory licensed professional; (c) third party licensed professional as "regulator/agent of the state"; (d) third party licensed professional as "consultant"; and (e) program manager.

Additionally, the key factors in each of the state programs that influence which model or models dominate include: (a) reporting obligations under state statute; (b) age, evolution , and success of each state program; (c) applicability of risk based decision making; and (d) personal liability considerations.

Results/Lessons Learned. The Massachusetts program is well established and served as the model for the New Jersey program. New Jersey, however, has never been a state to merely adopt another government entity's program in its entirety and instead chose to provide additional requirements not found in the Massachusetts statute and omitted other program elements. How these differences in program design and implementation play out "on and in the ground" will be examined, contrasted, and debated.

Forging a New World Order: Challenges and Lessons Learned in Development of a Licensed Site Remediation Professionals Program

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Background/Objectives. Most state remediation oversight programs have evolved as varying forms of command and control government. New Jersey's site remediation program was a prime example before its Legislature enacted the Site Remediation Reform Act in 2009. Moving from an administrative program based on highly prescriptive requirements and oversight toward one in which third-party, private-sector licensed professionals have responsibility for remediation decision-making presents many challenges – political, institutional, and legal challenges among them. This presentation will review these challenges faced by state legislators, regulators and the professional community as they forged a new Licensed Site Remediation Professional (LSRP) program, discuss how these challenges were addressed and identify lessons learned.

Approach/Activities. The presentation will review the political, institutional and legal challenges confronted in the development of the New Jersey LSRP program. The politics and agency considerations that led to the program briefly will be examined. In light of New Jersey's entrenched approach toward site remediation and "Spill Act" liability for hazardous substances, a particular focus will brought to the statutory and regulatory impediments and changes that had to be confronted in order to allow and implement the LSRP program. Changes in technical regulations, new licensing program considerations and the code of conduct, as well as accommodating due diligence and "all appropriate inquiry" by environmental professionals will be examined. A brief review of differences to other state licensed professional program will be included.

Results/Lessons Learned. The Site Remediation Reform Act and its LSRP Program were aptly called a "New World Order" by regulators and practicing professionals in New Jersey. At this early stage of its development, the new program is largely viewed as a success by an overwhelming majority of stakeholders. The state has more contaminated sites under active remediation than ever before. A focus has been brought to evaluating and protecting "receptors" unlike any efforts before enactment of the new law. Remediation is performed at a faster pace. The presentation will identify successes of the program, lessons learned that will translate to other jurisdictions considering development of a licensed professionals program and suggestions for improvement.

The Importance of an Independent Board in Licensed Site Remediation Professional Programs: The New Jersey Experience

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Background/Objectives. This presentation will focus on the importance of incorporating an independent licensing board into a comprehensive Licensed Site Remediation Professional program.

The New Jersey experience in changing a rigorous command and control regulatory environmental program for remediating hazardous sites into one totally reliant upon the judgment of private Licensed Site professionals is noteworthy and informative. New Jersey's regulatory hazardous site cleanup program was mired in bureaucratic inertia. Site remediation backlogs grew to the point of being unacceptable. Legislative fixes were imposed. However, programmatic changes to the status quo needed to be equitable for all concerned, including the Licensed Site Remediation professional. This was accomplished by legislatively creating an independent licensing board which was exclusively responsible for overseeing and regulating the licensed professional. As the regulatory agency had a history of being capricious, the Board assured the licensed professionals that there would be an independent auditor and judge of their performance.

The legislatively mandated role of the Board, its power and authorities, will be examined. The purpose of this presentation is to familiarize the audience with the significant transition of a strong governmental command and control program to one totally dependent on private Licensed Site Remediation Professionals who are empowered to use their professional judgment and the important role played by the independent licensing board.

Approach/Activities. The need to accommodate the use of professional judgment in lieu of a "one size fits all" regulatory approach became apparent. Previously, the regulators were in sole command of investigations and remediation. The expertise and experience of the environmental professional was often discounted. By incorporating seasoned, experienced, skilled professionals into a robust stakeholder process that include a broad spectrum of interests, a viable, credible, enhanced statewide site remediation program emerged.

Results/Lessons Learned. As governmental budgets become increasingly tighter, this new regulatory paradigm will be increasingly considered and employed. The value of a robust stakeholder involvement in crafting the program from start to finish cannot be overstated. Without such involvement, an independent board might not exist and the success of the program imperiled. The importance of including the regulatory agency, the public and the consulting community in the formulation of this program will be discussed. The conversion of the remedial program is having significant success, resulting in quicker, less costly, and more effective remediations.

Back to Contents

Turning a Brownfield Site into a Health Center

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Background/Objectives. A Community Health Center is constructing a clinic on a brownfields site in the Greater Boston Area. A requirement of the project and agency's landlord was the remediation of the site to closure under the Massachusetts Contingency Plan (MCP). Remediation is occurring in conjunction with the building construction. The objective of the remediation is to achieve a "Permanent Solution" with conditions under the MCP.

The contaminants of concern at the Site are chlorinated volatile organic compounds (cVOCs) and extractable petroleum hydrocarbons (EPH), including several polycyclic aromatic hydrocarbon (PAH) compounds, and metals. The PAHs and metals are associated with coal ash-containing urban fill.

Approach/Activities. Based on pilot testing results, GZA is implementing a three-part remedial action. High Vacuum Extraction (HVE) will be used to mitigate elevated cVOCs concentrations in groundwater in the source area to below upper concentration levels (UCLs) to allow for permanent closure of the site with an activity and use limitation (AUL). HVE installation will begin in October 2014 and operation is expected to last one to two years. Enhanced reductive dechlorination (ERD) will be used to treat the dissolved phase plume down gradient of the source area. Vapor intrusion will be mitigated by installing a sub slab membrane system (SSMS) under the slab of the new building. This membrane system was installed during the summer of 2014.

GZA also provided licensed site professional (LSP) and remedial services, geotechnical engineering and field oversight, asbestos and hazardous materials survey and abatement oversight, and construction phase health and safety monitoring. Remediation is occurring in conjunction with the building construction.

Results/Lessons Learned. This project has involved work with many different design disciplines and contractors, including stakeholders, the agency's landlord, architects, general contractors, civil engineers, and HVAC engineers. Scheduling and coordination are key factors to a successful brownfields remediation in conjunction with site redevelopment. The building will receive LEED certification. The Health Center plans to apply for Brownfield funding.

By May 2015, GZA anticipates having several months of monitoring data for the HVE system. Depending on the HVE results, the ERD part of the three-part remedial action may be undergoing implementation at that time.

Back to Contents

Do GSR Frameworks Adequately Represent Ecosystem Services and Natural Resources?

Panel Discussion Tuesday/Track E

Moderator
Rick Wice (TetraTech)

Panelists
Brenda Bachman (U.S. Army Corps of Engineers)
Pankaj Lal, Ph.D. (Montclair State University)
Carlos Pachon (U.S. EPA)
Harry Stone (Battelle)
Jonathon Weier (CH2M Hill)

Many green and sustainable remediation (GSR) frameworks, approaches, and tools incorporate environmental impacts of remediation, such as emissions of greenhouse gases and criteria pollutants and consumption of resources. However ecosystem services and natural resources often are ignored. Land covers such as forested uplands, grasslands, shrublands, and fresh and saltwater wetlands are natural resources that offer numerous benefits such as flood control, habitats that enhance biodiversity, carbon sequestration, and water purification. In some cases, site restoration activities may alter these land covers, resulting in the destruction of ecosystems and loss of natural resources. In addition, long-term maintenance requirements may preclude ecological restoration for long periods or permanently. Conversely, the implementation of other remedies may enhance ecological restoration. The panel will address the following questions:

- ► What methodologies currently exist to evaluate the impacts that remediation activities would have on land covers and resulting impacts on ecosystem services and natural resources?
- ► Are these existing methodologies being used by practitioners on a routine basis and if not, why not?
- ► Are new approaches or modifications to existing approaches needed to facilitate the consideration of these impacts, and what might those approaches be?
- ► Would these efforts ultimately improve decision making and remedy implementation and enhance the net environmental benefit of remediation?

Back to Contents

The Growing Impact of ASTM's New Standard Guide for Greener Cleanups

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Deborah Goldblum (U.S. EPA, Philadelphia, Pennsylvania, USA)
John Simon (Gnarus Advisors LLC, Arlington, Virginia, USA)

Background/Objectives. ASTM finalized a new Standard Guide for Greener Cleanups in November 2013 as ASTM E2893-13. Federal and State agencies are beginning to adapt this standard guide into training and project funding requirements. This presentation provides an overview of the new ASTM standard guide, outlines where it is being adapted, and discusses how best to implement the guide.

Approach/Activities. Since ASTM International Committee E50.04, Task Group for Standard Guide for Greener Cleanup, developed ASTM E2893-13 in November 2013, the Committee has reached out to State and Federal agencies with training courses and presentations. EPA has provided on-line training with over 300 attendees. In addition, the Committee has continued to enhance the Standard Guide, particularly expanding the list of best management practices (BMPs) which will be rolled out by early 2015.

Results/Lessons Learned. Agencies are beginning to recommend or even require incorporation of ASTM Standard Guide for Greener Cleanups (E2893-13) into criteria for awarding projects and grants. The Massachusetts Department of Environmental Protection has instituted a policy which advocates use of ASTM Standard Guide for Greener Cleanups (E2893-13). Other states and EPA regions are instituting similar language into their standards and contracts. This presentation will provide an updated assessment of state, federal, and private industry implementation of the standard guide. The number of reports uploaded to the ASTM E2893-13 will be noted, along with other data that indicate the trends for acceptance of this new standard guide. The presentation will also summarize the documented benefits of implementing the standard guide.

Synergy between Optimization, Green and Sustainable Remediation, and Green Remediation Practices across Federal Agencies

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Amy Hawkins (Navy Facilities Engineering Command, Port Hueneme, CA)
Kirby Biggs and Carlos Pachon (U.S. Environmental Protection Agency, Washington D.C.)
Deborah Goldblum (U.S. Environmental Protection Agency, Philadelphia, PA)

Background/Objectives: Federal Agencies have been proactive in developing and implementing a variety of remedial optimization, green and sustainable remediation (GSR), and green remediation (GR) initiatives in order to save resources and reduce environmental footprints. Development of management practices, sometimes call best management practices, has often been part of this process. Although there are differences between each Federal Agency initiative's management practices, there is considerable similarity between the combined set of each Federal Agency's management practices across optimization, GSR, and GR. The differences between the management practices within each initiative are often linked to the goal(s) and the specifics of the related optimization, GSR, and/or GR Federal Agency policy(s) and strategies. The objectives of this presentation are to summarize the different Federal Agency remediation optimization initiatives, strategies, and policies and the management practices associated with the same, and to present the larger body of management practices that are common across the optimization, GSR, and GR initiatives.

Approach/Activities: The management practices of the different remedial optimization, GSR, or GR initiatives of US Environmental Protection Agency, the Army, the US Army Corps of Engineers, the Air Force, the Navy, and Department of Energy were evaluated for similarities and differences in the management practices between optimization, GSR, and GR initiatives and related policies and strategies. A combined set of management practices was found to be common over the optimization, GSR, and GR initiatives.

Results/Lessons Learned: When the management practices across the different Federal Agency remedial optimization, GSR, and GR agencies are combined, a common set of management practices results. Where there is no formal optimization policy or initiative, the management practices for Agencies with a GSR policy were found to include management practices that other Agencies included in their optimization initiatives. The results argue for a more comprehensive set of management practices that could be applied across the optimization, GSR, and GR spectrum that would maximize resource savings and footprint reduction. The presentation proposes a general approach to achieving application of this broader set of management practices.

How Can a Green Remediation Project Benefit by Incorporation of Sustainability?

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Background/Objectives. Green remediation (GR) considers all environmental effects of remedy implementation and incorporates practices to maximize the net environmental benefit of the cleanup actions. These green options are most often incorporated into an already-selected remedy, but need not necessarily wait for this stage of the project. In comparison, sustainable remediation (SR) strives to balance environmental, economic, and social concerns–the triple bottom line (TBL)–throughout the life cycle of the remediation project. If we take another step and monetize the socio-economic benefits of GR practices, we can extrapolate environmental indicators to global-scale impacts. Here we incorporate cost-benefit analysis methodology into a GR project, starting from its footprint analysis, to demonstrate the social and economic benefits that can be realized by monetizing environmental effects such as greenhouse gas emissions (GHG). The results support additional value of GR (for a cost-averse audience), and lead the way to further project improvements (for a TBL-averse audience).

Approach/Activities. The case study site is a manufacturing facility with chlorinated solvent contaminated groundwater beneath an active factory building. As the groundwater pump-and-treat (P&T) system reached its asymptotic removal limit, it was gradually replaced with *in situ* anaerobic bioremediation through systematic injection of aqueous food-grade carbon substrate. The transformed treatment strategy improved removal of the contaminants and reduced the environmental impact of the remediation system as quantified by field logs, utility bills, invoices, and operation and maintenance records. GHG emissions for P&T versus bioremediation were summed as carbon dioxide equivalents (CO_2e) from drilling, transportation, electricity use, etc. In turn, the CO_2e contributions to global climate change and projected damage to health and quality of life were quantified as costs, based on the economic researches of others, including the US Government. In this way, the carbon footprint of the remediation project was converted into monetized global impacts. The project's water footprint was also evaluated, but the current state of economic research limited our ability to monetize the impacts of water depletion.

Results/Lessons Learned. This evaluation predicted costs for long-term global damages from implementation of the two alternative remedial strategies. The results allowed for a direct comparison of the two remedial approaches; provided a single, universally recognized unit–cost–for disparate metrics; and demonstrated a method to quantify the more elusive socio-economic effects of a remediation project. The calculations also revealed a possible numerical decision point for selecting one remedial approach over another: when the market cost plus environmental damages (= social cost) of the new approach become less than the social cost from making no changes. Consideration of monetized socio-economic impacts demonstrated a mechanism to incorporate the TBL without compromising the environmental cleanup, and thus help to move the state of practice toward more sustainable remediation, so that further positive impacts can be incorporated into remediation projects.

Socioeconomic and Environmental Considerations for Optimising Remedial Design of a Mixed-Use Contaminated Site in India

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Background/Objectives. Twenty-seven (27) hazardous waste dumpsites (predominantly hexa-valent chromium-contaminated) were identified along the highway- in areas that were mainly industrial, though other uses like small commercial establishments, services, hostels, residences, agricultural fields also occurred along the 18 km long corridor. Early in the process it was recognised that the remediation could potentially cause significant negative socioeconomic and environmental impacts in the affected area. As a result a programme of extensive stakeholder engagement was undertaken that included iterative discussions with the regulator, client and local population with the objective of minimising the overall negative impacts during implementation of remediation while aiming for net long term environmental and socioeconomic benefits.

Approach/Activities. Consultations with potentially impacted persons on these sites were undertaken to seek their inputs, support and expressly stated consent for the implementation of the remediation plan as this would result in small to significant temporary disturbance in their activities- livelihoods of employees in the small shops, industrial units, *etc*. (most make US$2 to US$4 daily). Stakeholder consultations brought out that the concern for remediation was matched with that of minimising lost-days of work and production; the danger of closure of small business and the resultant unemployment /livelihood loss due to the length of temporary closure.

What had started as an (arguably) simpler exercise of assessing Social and Environmental Impacts of remediation actions to be mitigated and managed through an ESMP (Environmental and Social Impacts Management Plan) became integrated with the technical design development process. The aim was to include these additional constraints and considerations to try and minimise the impacted area, period of disturbance/relocation, in several cases by breaking work up into phases, providing alternate access through additional civil works, logistical and transition support for lost-days of work and relocation, among other strategies.

Preliminary signed consent for remediation work to go ahead has been provided by all but one site. Currently, the design documents and ESMP are going through the regulatory review process. This will be followed by finalization of the bid documents.

Results/Lessons Learned.
Socioeconomic concerns, if integrated in the technical design process make the remedial planning process more sustainable. Stakeholder involvement (consultation and disclosure) from the early stages of assessment and design have resulted in a greater buy-in and support of the remediation plan and thus has a higher chance of successful implementation. This process will set precedence for the forthcoming remediation of other historical contaminated sites across the country.

SURF USA's Case Study Initiative Identifies Sustainable Remediation Trends

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Background/Objectives. The Sustainable Remediation Forum (SURF; USA) established a technical initiative to collect case studies demonstrating successful sustainable remediation project implementation. Through this Case Study Initiative, SURF is actively gathering case study summaries from SURF members and others, including international remediation organizations. The case studies demonstrate various best management practices exemplifying the environmental, economic, and social aspects of sustainable remediation projects. This robust collection of information provides real world examples in a concise standardized format accessible for remediation professionals globally through SURF's website.

There are numerous drivers and incentives providing regulatory, public relation, and economic reasons for utilizing sustainable remediation principles. Examples of regulatory drivers exist in the EPA's programs and cleanups conducted in New York State, which has sustainability requirements contained within its green remediation policy. Furthermore, there are social and economic incentives, including reducing costs, potential carbon credits, and wetland and natural resource mitigation banking opportunities. Finally, the public relations benefit of increased corporate social responsibility related to implementing sustainable remediation projects is an important incentive. The Case Study Initiative is designed to capture these drivers.

Approach/Activities. The Case Study Initiative Team is evaluating a compilation of case studies to identify common themes to input into a database of information that will include best management practices and economic and social drivers for sustainable remediation projects. The database will enable critical trends to be culled, summarized, and presented for the benefit of the sustainable remediation community.

Results/Lessons Learned. The SURF Case Study Initiative provides a consistent process for reporting the results of sustainable remediation projects. Through this initiative SURF is actively compiling an informational database from sustainable remediation case studies. The Case Study Initiative Team will summarize the case study evaluation and identify trends of the most common best management practices and drivers.

The project findings will demonstrate the optimum best management practices for environmental footprint reduction and improved social and economic metrics. Based on an initial evaluation of when best management practices are implemented, the greatest opportunities for integrating the economic and social aspects of sustainable remediation is during the project planning stage, whereas, for the environmental aspects, the optimum stage is during the project design.

Back to Contents

SVE Success: Sustainable Goals and Performance from Design to Completion

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Background/Objectives. A full scale soil vapor extraction (SVE) system was designed and installed at the Klockner Site, Operable Unit 3 (OU-3) of the Rockaway Borough Wellfield Superfund site in New Jersey, to remediate the soil in the vadose zone that is impacted by chlorinated volatile organic compounds (CVOC). The system was installed in the interior and exterior parking and storage area of an active manufacturing facility. The full scale design incorporated sustainable remediation practices through design and construction, as encouraged by the US Environmental Protection Agency (EPA). The SVE system extracted sufficient VOC mass from the subsurface to successfully meet the remedial action objectives established in the Record of Decision (ROD).

Approach/Activities. The design examined alternatives to increase the efficiency of the system, and reduce the overall project footprint while remaining cost effective and optimizing remedial efficiency. Several sustainable practices, focusing on minimizing energy consumption and waste generation, reduced the carbon footprint of the project as well as the overall construction cost and schedule. TRC designed the SVE system to operate in a cyclical sequence of rotating zones to optimize the recovery efficiency, ultimately selecting a blower with 1/3 of the capacity needed to operate all wells simultaneously. The piping design was optimized to reduce the piping runs and friction losses. All interior piping was installed above ground, eliminating concrete cutting, minimizing waste production and facility disruptions at a lower cost, energy, and air quality impact.

For exterior piping installation, native soil was reused as backfill and bedding material to the fullest extent possible, to reduce generation of waste and importation of fill. Excavated asphalt was segregated and recycled and curb stone was segregated and reused. Oversized, granular re-activated carbon (GAC) vessels were used to optimize reuse and minimize GAC change-out. Renewable energy credits (REC) from wind power providers were also purchased to off-set the electrical consumption from fossil fuel sources. RECs represent the environmental attributes of power generated from renewable electric plants with no emission of greenhouse gases. The estimated annual environmental benefit is equivalent to the carbon sequestered by 2,210 tree seedlings grown over 10 years or by removing 18 passenger vehicles from the road. The EPA Spreadsheet for Environmental Footprint Analysis (SEFA) was used to quantify and determine the overall reduction in environmental footprint from each sustainable technique.

Results/Lessons Learned. By incorporating sustainable practices into the design phase of the SVE system, TRC was able to design and implement a successful and efficient system that optimally benefitted from sustainability principles. The operational results have shown the system has performed as efficiently as anticipated, removing over 21 lbs (~10 kg) of VOC mass from the subsurface within a relatively short duration. The analytical results of confirmatory post-treatment, soil samples revealed that VOC concentrations within the treatment area decreased below the ROD Remediation Goals and that soil remediation at the site is complete.

Making Thermal Remediation More Sustainable: A Detailed Analysis

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Background/Objectives. In situ thermal remediation (ISTR) technologies such as in situ thermal desorption, electrical resistivity heating and steam enhanced extraction have proven to be efficient and rapid methods for cleanup of a variety of highly contaminated source zones including chlorinated sites and sites contaminated with oils and tars. Also it has been shown that thermal approaches can have lower environmental impacts than conventional source zone technologies such as excavation and off-site treatment. While avoiding the adverse impacts of excavation, in situ thermal remediation methods require a significant amount of energy as well as material use for on-site installations and equipment. This presentation will convey options that can improve the sustainability of thermal remediation projects. Recommendations will be based on results from detailed “cradle-to-grave” life cycle assessments conducted for several thermal methods as well as results from sites where sustainable approaches has been implemented.

Approach/Activities. A detailed life cycle assessment (LCA) was utilized to identify the most important environmental impacts of an in situ thermal project. The environmental exchanges during the life-cycle of the thermal remediation (use of finite resources, emissions to air, soil and water) were evaluated in terms of their corresponding environmental impacts, including global warming, ozone formation, acidification, eutrophication, respiratory impacts, human- and ecotoxicity and resource use. A thorough data collection phase using real project data served as the basis for the LCA, which covered all parts of the remediation projects, i.e. the wellfield materials and establishment, the capping materials, the air and water treatment systems, the electricity use and the transportation of materials and personnel. Based on the outcome of the LCA, some field modifications were made to minimize the environmental footprint. These modifications include cycling the energy input required for soil heating over the day to optimize the power usage; pre-heat process streams using waste energy; and utilizing recovered contaminants from the subsurface to run fuel consuming equipment such as thermal accelerators and steam boilers.

Results/Lessons Learned. The presentation will highlight the findings from the LCA, present field test data from implementing the recommendations from the LCA, and focus on how thermal remediation projects are continually developing in a more sustainable direction.

Best Management Practices: ISCO and ERD

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Background/Objectives. In situ chemical oxidation (ISCO) and enhanced reductive dechlorination (ERD) are among the most frequently selected remedial alternatives for addressing chlorinated solvent impacted groundwater sites. While there is a considerable experience base with these technologies built upon over the past 15 years, they are still less mature in terms of design practices and standards compared to conventional environmental systems (e.g., pump and treat systems, water and wastewater treatment systems, and landfill covers). Therefore, design information, formats, and standards are generally not as readily available and consistent. There is also substantial room for improvement in the optimal design of these in situ remediation systems including efforts to incorporate green and sustainable remediation (GSR) best management practices (BMPs).

Approach/Activities. GSR BMPs for ISCO and ERD were developed through the examination of case study information, project experience, and a literature review. The objective was to develop GSR BMPs that could be used by project managers and design engineers to help to reduce the overall environmental footprint for these in situ remediation systems. This information was compiled in a consistent format so that it can be readily incorporated into design documents, Feasibility Studies, and/or other CERCLA documentation. In addition, proactive management of potential performance risks plays an important role in the successful design and implementation of these two technologies. For this reason, information was also summarized on lessons learned and potential performance issues than can be anticipated and addressed early in the design phase.

Results/Lessons Learned. GSR BMPs for improving the sustainability of ISCO and ERD remedial systems will be presented. The GSR BMP categories include: 1) materials management and waste minimization; 2) energy usage; 3) transportation; 4) alternative fuels; 5) air emission control measures; 6) optimized equipment use; 7) monitoring program optimization; 8) water resource conservation; 9) land management and ecosystem protection; 10) worker safety considerations; and 11) community considerations.

Back to Contents

Future Land Use and Sustainable Remediation at the Sydney Tar Ponds: A Case Study and Lessons Learned on Adaptive Remedial Design

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Background/Objectives. The Sydney Tar Ponds Remediation Project is the result of nearly 100 years of steel production in Sydney, Nova Scotia, leaving a legacy of contaminated soils, sediments and groundwater, contaminated with PAHs, VOCs, PHCs, PCBs and heavy metals at two major sites: the Tar Ponds, a 34 hectare marine site; and, the Coke Ovens, a 68 hectare land based site. Given the urban setting, the remediation program presents an opportunity for sustainable remediation, reclaiming an industrial brownfield, and creating a unique solution to concerns and contaminants commonly encountered on many railroad-related projects.

The vision for the remediation of these sites has its roots dating back over 30 years and has encompassed aspects of Green and Sustainable Remediation. With the remedial engineering design completed in 2009 all twelve contracts were completed in August 2013; by this time the reality of a sustainable community based solution for brownfield development at these sites came clearly into focus. This reality, coupled with strong community support for successful remedial implementation to date, has created momentum with respect to this vision for urban renewal that extends beyond the remedial construction phase.

The Project Proponent, the Sydney Tar Ponds Agency, has leveraged recommendations from the Environmental Assessment to develop a Future Land Use Plan for the sites. Supported by Community engagement the task of integrating the design and implementation of the remedial works with the Future Land Use Plan has begun. The Project's, through implementation of the Future Land Use Plan will build upon sustainable remediation features in the remedial design and provide the necessary base foundation to enable future brownfield development to occur.

Approach/Activities. The primary remedial solution for the Tar Ponds site is Solidification/Stabilization (S/S) of approximately 700,000 tonnes of coal tar contaminated sediment within the marine influenced site. The remedial solution features Green and Sustainable Remediation aspects supporting a recreational and park-type future land use. This has culminated in a Future Land Use Plan encompassing a Commons Area, walking trails, a look-out over Sydney Harbour, and passive recreational infrastructure that are coordinated with the remedial design and integrated with the surrounding area, including the Atlantic Ocean.

The remedial solution of the Coke Oven site includes subsurface infrastructure such as groundwater collection pipes and vertical cutoff walls. The entire site will be covered with a soil cover. This remedial solution includes similar sustainable remediation aspects to the Tar Ponds site. In addition, the Coke Oven site bisects two residential communities within Sydney and as such the intent is to connect these areas via surface streets and promote light commercial development while preserving some areas as green-belt.

Results/Lessons Learned. This paper will provide a review of sustainable remediation aspects of one of Canada's largest remediation projects as a case study on the implementation of Green and Sustainable Remediation on the Tar Ponds and Coke Ovens sites. The focus of the presentation will lend itself to common attributes shared with sediment, urban renewal and

Application of Green and Sustainable Remediation Means and Methods in the Remedial Closure of a Former Lead Smelter Site

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Background/Objectives. Green and sustainable remediation (GSR) means and methods were incorporated in the remedial closure of a former mid-continent lead smelter site situated along the banks of the Mississippi River. The former plant area is situated on an upland plateau and was demolished in place in the early 1960s. Metals-impacted soils, building debris, and aluminum dross were present in the site's upland areas. A 13-acre slag pile, metals-impacted sediments, and localized impacted groundwater were present in the site's lowland areas.

Approach/Activities. Site remediation activities were conducted in four phases. Phase I lowland remediation activities conducted in the spring 2013 entailed excavation of lead impacted sediments, development of an upland on-site clay borrow pit, placement of 28,000 CY of lead impacted sediments and bricks on the slag pile, and backfilling of the excavation with 600 tons of crushed limestone to effectuate passive groundwater treatment. Phase II upland preparation remediation activities conducted in fall 2013 entailed the importation of 13,000 CY dredge spoils from a nearby state park and the clearing and chipping of trees that generated 12,000 CY of wood chips. Phase III upland remediation and slag pile capping conducted in the summer and fall 2014 entailed the removal and recycling of 360 tons of scrap metal; placement of 107,000 CY of lead impacted upland soils and bricks on the slag pile; employment of wood chips for construction roads and erosional control berms; placement of 30,000 CY of clay on the slag pile as the first two, 8-inch lifts of the cap's two-foot low permeability layer. Phase IV final site restoration activities will be conducted in the summer of 2015 will entail placement of the final 8-inch clay cap lift, placement of dredge spoils on the slag pile as beneficial reuse as the cap's top soil layer, incorporation of native plants for wetlands restoration, planting flowering prairie grasses for the slag pile cap's low-maintenance vegetation layer, and scattered use of tree root balls and wood chips for upland habitat restoration purposes.

Results/Lessons Learned. GSR means and methods employed during the successful remediation of this former smelter legacy site included use of crushed limestone for passive groundwater treatment; recovery and recycling of scrap metal; use of an on-site clay borrow pit for the site cap's low permeability soil layer; beneficial re-use of dredge spoils for the site cap's top soil layer; use of wood chips for construction roads; use of wood chips for erosion control berms; use flowering prairie grasses for a low-maintenance site cap vegetative layer; and use of native plants, tree root balls and wood chips for habitat restoration purposes. The GSR actions yielded savings of $1 million (20 percent of the project cost) to this fund limited, environmental bankruptcy trust site. The GSR remediation of the former smelter site accomplished an environmentally friendly remediation effort, provided benefits to the neighboring community, and achieved cost savings in the overall remedial effort.

Sustainable Thermally Enhanced Bioremediation at a Methylene Chloride Site in the UK

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Jay Dablow (Environmental Resources Management, Irvine, CA)

Background/Objectives. Following accidental release to ground of about 15,000kg of methylene chloride, due to pipework failure at an active manufacturing facility, ERM was commissioned to rapidly design and implement a remediation solution to expedite recovery of the solvents. Sustainability has been a key consideration throughout the project, including at the site investigation stage, where High Resolution Site Characterization techniques were used to quickly determine the extent and magnitude of methylene chloride within the underlying heterogeneous alluvial aquifer. The presence of Dense Non-Aqueous Phase Liquid was identified within the alluvial deposits, which was expected to inhibit contaminant biodegradation.

A Quantitative Risk Assessment (QRA) showed that in the absence of such degradation processes, a risk existed to a downgradient surface water course. Conversely, the same QRA identified that if biological processes were active, then this risk would be mitigated. The objectives of the remediation were:

- to recover as much of the solvent mass as technically possible; and
- to encourage attenuation of any residual impacts via biodegradation.

Approach/Activities. A remedial options appraisal was undertaken using a holistic sustainability approach, where environmental, social and economic indicators were evaluated to determine the most sustainable option. The results showed steam enhanced vapor extraction to be the most technically appropriate, rapid and sustainable solution within the project boundaries.

Whilst this technology is relatively energy intensive, it has previously been shown to have a lower carbon footprint than longer term alternatives, such as pump and treat. ERM also identified opportunities to reduce energy use and associated environmental footprint, including procurement of process equipment to lower carbon use and by adapting the portable steam boiler to run on natural gas or propane rather than electricity.

Results/Lessons Learned. The treatment area impacted by methylene chloride was heated in zones. During heating of the first area, it was identified, contrary to expectations at the start of the project, that biotic and possibly abiotic degradation were the dominant contaminant mass reduction mechanisms; rather than, as is typical for in-situ thermal projects, mass transfer via volatilization. Given these lessons learned, the target temperatures in other parts of the treatment area were subsequently lowered to temperatures more suitable for in situ biotic and abiotic degradation reactions to occur. This change in the mass reduction mechanism from predominantly removal to in-situ destruction significantly reduced the carbon footprint and the energy usage of the works.

The project is on-going and these results will be quantified in this paper. This will include an assessment of the success of the approach together with quantification of the mass removal via different pathways and the projects carbon footprint.

Sustainable Remediation and Its Influence on "Next Generation" LNAPL Recovery and Management

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Matthew Zenker Ph.D., P.E., BCEE (AECOM, Raleigh North Carolina, USA)

Background/Objectives. Virtually every segment of modern society has begun a quest for achieving 'sustainability.' Agriculture, manufacturing, construction, transportation, and even the average person in his/her everyday life is looking at energy consumption, carbon footprints, and their burdens on ever dwindling natural resources. Since 2006 when the Sustainable Remediation Forum (SURF) was formed, the remediation industry has also recognized and responded to both obligations and opportunities to further consider the social, economic, and environmental impacts of remedial decision making and to reduce ancillary environmental impacts. State and Federal green and sustainable remediation (GSR) regulations and guidance have also been developed (e.g. ITRC, WISRR, NYSDEC DER-31, ASTsWMO, etc.).
During this same period, the science and understanding of Light Non-aqueous Liquid (LNAPL) mobility and recoverability have also evolved dramatically. And more recently significant scientific advances have been made related to the mechanisms and rates of natural degradation of LNAPL (i.e. Natural Source Zone Depletion (NSDD)). Notably these advances in LNAPL science and NSZD are consistent with the tenants of Risk Based Corrective Action (RBCA). But despite these advances, risks associated with LNAPL and sites with mobile and/or recoverable LNAPL will still warrant its recovery under certain site-specific conditions which is also consistent with RBCA. Despite the significant evolution of Sustainable Remediation it has yet to significantly influence LNAPL recovery and management techniques but certainly should.

Approach/Activities. This presentation will explore the potential influence of sustainability on what could also be referred to as "Next Generation" LNAPL recovery and management techniques. For example:

- how best can hydraulic recovery be made more sustainable?
- what role should time/duration play in selecting recovery techniques (i.e. should a more sustainable but slower technique be chosen over a faster one with a larger footprint)?
- what sustainability metrics should be weighed more heavily in selecting a sustainable LNAPL recovery method?
- Is surfactant enhanced LNAPL recovery more sustainable?
- What if the equivalent energy required for LNAPL recovery (expressed as gallons of LNAPL) greatly exceeded the volume of LNAPL recovered? And is that Sustainable?

Results/Lessons Learned. A Sustainable LNAPL Management Approach was applied to several sites including exploring a new Sustainable LNAPL metric expressed as LNAPL Recovery Intensity and evaluating the LNAPL Recovery Green House Gas Intensity. The LNAPL Recovery Intensity is expressed as the equivalent gallons of LNAPL required to recover a gallon of LNAPL. The results of these evaluations and associated lessons learned are presented and discussed.

Back to Contents

Incorporating Sustainability Concepts into Effective Site Remediation Strategies

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Overview. Success of all remedial techniques require effective delivery of the remedial agent/process to the contaminant mass, wherever that contaminant mass is located. Thus, the crux of all remediation--facilitating effective contact--remains a multidisciplinary and complex consideration in the implementation of any remedial strategy. This crux applies to all remediation whether the remedial agent/process involves solid (fracture emplaced media such as ZVI particles), liquid (injection of various substrates, stabilizers, bioaugmentation amendments, reactants, multi-phase extraction) or vapor (hydrogen, oxygen, hydrocarbons, bioventing, sparging or extraction) processes. To facilitate destruction the remedial process must contact the target contaminant(s).

Approach/Activities. Contact is not a straightforward process as it largely controlled by a variety of direct and indirect factors including:

- site conditions—geology, hydrogeology, conductivity contrasts, heterogeneities,
- external constraints—labor, budget and cost, site access,
- physical constraints—transport processes (advection, dispersion and diffusion), pore diameters, connectivity, capillary forces, fabric, kinetic,
- biological constraints—availability of food source, indigenous populations and maintenance of growth conditions, as well as
- mechanical limitations—limitation in the remedial process (injection rate, pore pressure, equipment reliability and uptime).

This paper with discuss the nature of the various constraints with attention to the manner in which they constrain remediation strategies and propose several delivery techniques that complement natural conditions and promote remediation that is both effective and sustainable. These innovative approaches focus upon low energy input and passive systems that minimize the amount of infrastructure and associated project costs for execution.

Results/Lessons Learned. Case study information will be presented from project sites to illustrate remedial techniques including: constant head injection; pulsed targeted injection; fracture emplacement, soil mixing and slow release strategies.

Sustainable Treatment Using C3™ Refrigerated Condensation

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Background/Objectives. A technical evaluation of treating contaminated off-gas using C3™ refrigerated condensation at the Huntsman Chemical Company Australia Pty Limited (HCCA) former chemical manufacturing facility, Victoria. The remediation approach has proven to be an innovative, efficient and sustainable method for treating VOCs in off-gas vapour streams and represents the first implementation of the C3™ technology into the Australian market.

Dominant groundwater contaminants of concern were isopropyl benzene, alpha methyl styrene, cyclohexane and benzene.

Approach/Activities. C3™ refrigerated condensation is a proprietary technology developed by the US-based GEO Environmental Remediation Company (GEO) and supplied in Australia by Environmental Remediation Resources (ERR). The C3™ technology involves three steps to remove volatile organic compounds (VOCs) from the vapour phase; compression, cooling and condensation. The C3™ technology is not limited by VOC concentration, is capable of up to 99.9% removal of contaminants from the off-gas stream and removed the need for supplementary fuel or power.

Results/Lessons Learned. Operation of the C3™ technology achieved recovery of more than 5,200 L of recovered (condensed) VOCs over a 6-month treatment period before LNAPL had been removed to the extent practicable. Ongoing monitoring is assessing any risk of future rebound (none measured so far) and the treatment program is shifting from “active” to “passive” forms of treatment.

The advantage of the C3™ technology over alternative approaches is that it was not limited by the concentrations of VOCs and therefore able to substantially reduce treatment times compared to traditional treatment systems that require dilution to achieve destruction efficiencies. The environmental footprint for C3™ refrigerated condensation was significantly less than alternative treatment systems. In all aspects, i.e. greenhouse emissions (specifically electrical and gas use), waste management/disposal (landfill) and recycle/reuse, the C3™ technology has an advantage.

The lower establishment cost, reduced treatment time, lower energy consumption, smaller quantity of “waste” to be disposed and lower O&M costs resulted in a reduced cost to HCCA compared with alternative treatment approaches. Being able to demonstrate better sustainability (or triple bottom line) credentials made the project easier to approve within HCCA. By achieving its treatment objective more quickly HCCA has benefitted the environment, community, regulator (Environment Protection Authority) and industry.

The C3™ refrigerated condensation technology was proven to be an innovative, efficient and a sustainable method for treating VOCs in off-gas vapour streams at the former HCCA chemical manufacturing facility when compared to other treatment technologies (soil vapour extraction or multiphase extraction combined with granulated activated carbon or thermal/electrical destruction). A further advantage of the C3™ technology is that it is able to convert a hazardous waste into a potential resource.

Incorporating Sustainability Evaluation into a Feasibility Study for a 1,4-Dioxane-Contaminated Site in South Carolina

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Background/Objectives. Parsons is currently overseeing environmental activities at a project site in eastern South Carolina. The site formerly housed a cleaning operation for fibers manufacturing components from a nearby facility. The cleaning operation was discontinued in 1991, and the site has been unused since that time. An on-going voluntary environmental assessment program was initiated to evaluate possible groundwater impacts from past operations, and analytical results indicate that 1,4-dioxane is the main constituent-of-concern. Several chlorinated solvents were also detected in relatively low concentrations. In March 2007, an on-site remediation effort was conducted that included the installation of a phytoremediation system. The goal of the system was to accelerate attenuation to shorten the time it would take for all constituents to meet state groundwater protection standards. Plant tissue samples have also been collected from the installed and surrounding native trees in an attempt to bound the groundwater plume and determine the effect that phytoremediation has had on the site groundwater conditions. In August 2013, the site was entered into the South Carolina Voluntary Cleanup Program and a Voluntary Cleanup Contract (VCC) was signed. The VCC requires the preparation of a feasibility study (FS) to determine if additional corrective action is required at the site and to identify potential remedial technologies and corrective measures alternatives that can be implemented. The project team is currently completing the FS.

Approach/Activities. As part of the FS, the volumes/areas requiring additional remedial action will be determined, and potential remedial technologies (including expansion of the current phytoremediation system) will be evaluated. To incorporate sustainability as a balancing criterion, Parsons is in the process of conducting a sustainability evaluation using the life cycle assessment (LCA) tool SimaPro (version 8.0.1) to compare the environmental impacts of the various remedial alternatives that have been suggested for use at the site. The LCA system boundary is from cradle to grave, including all raw materials and energy sources started in the earth and ended back in the earth. On-site activities are modeled using data from the pilot phytoremediation system. Upstream and downstream processes are modeled using known inputs and outputs or state-of-the-art research studies, and where data is not available, the Ecoinvent database and the US-EI database are used. For processes for which no existing database provides information, an economic input and output method is used to obtain approximate inventory using cost data. For impact assessment, the ReCiPe method is used. To assist in interpretation, all impacts are normalized to person equivalent. Both the mid-point and end-point indicators are presented to assist in interpretation by various types of stakeholders.

Results/Lessons Learned. The results of the LCA will be presented. The remedial alternatives will be given an overall sustainability ranking based on the end-point ReCiPe indicator. The performance of the remedial alternatives will also be compared in each impact category using the mid-point indicators. Based on the analysis, the project team will identify the most sustainable alternatives and will use the results to develop an overall remedial path forward for the site. The LCA will also identify the major contributors of environmental impacts by the selected remedy, thus allowing the project team to optimize the remedy to reduce its environmental footprint.

ISCO & Enhanced In Situ Biodegradation (EISB) Of Dissolved Benzene Plume in a Fractured Rock Aquifer

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Background/Objectives. The site, which is located in Hobart, Tasmania (Australia), has an extended history of groundwater contamination and also remediation activities. Remediation and monitoring were conducted since 2000, when light non aqueous phase liquid (LNAPL) impacts were first identified. Despite these activities, LNAPL continued to persist both at the site and up to 200m off-site underneath neighbouring residences and a primary school.

The objectives of the study were to assess, based on risk exposure basis the most efficient remediation options for LNAPL and then to implement the selected remediation technologies. The selection criteria were developed and field pilot trials conducted to test the options selected based on their “theoretical” technical merits. The primary objective of the remediation works was to achieve nominated, risk-based remediation goals (RGs) within a reasonable timeframe with the primary school exposure to vapour risk being a priority.

Approach/Activities. Based on a comprehensive technology review; including the ITRC green and sustainable remediation (GSR) principles, GHD nominated in situ chemical oxidation (ISCO) remediation based on high-pH activated persulphate which has an effective ability, to oxidise benzene. Of particular importance of selecting this technology was that, the oxidant by products would migrate down gradient and provide impetus for aerobic and anaerobic bioremediation of the off-site benzene plume.

The groundwater remediation activities consisted of the following key tasks:

a) Completion of a bromide tracer test, to provide a better understanding of travel times in the complex fractured rock aquifer to inform the injection rate;
b) Design and Construction of a dedicated site specific ISCO system;
c) Supervise the construction and testing and final sign off; and
d) Conduct performance monitoring using derived RGs as a KPI benchmark; the RGs were presented and agreed to with the State EPA.

The remediation system operated over 4 months. During this period, 12.5 tonne of persulphate and ~ 10,500 L of 48% Na(OH) were mixed with it and injected into two main treatment areas through the existing well network. The distribution of oxidant in the subsurface was enhanced by using recirculation wells, where oxidant was injected up gradient while groundwater was being extracted from down gradient wells to enhance the flow of products.

Results/Lessons Learned. The monitoring of wells (i.e. located between the injection and extraction wells, that is, centrally located within the recirculation cell) indicated a 70%-80% reduction in benzene concentrations in the key source zone, and achievement of on-site health-based RGs. Also, the sulphate concentrations in a key down gradient and off site monitoring well confirmed the breakthrough of sulphate in this well approximately 100 m down gradient of the main ISCO treatment area.

The ISCO treatment has resulted in significant reductions in benzene source concentrations, and the breakthrough of sulphate detected in down gradient off site wells indicated that conditions are being established for ongoing remediation of the off-site benzene plume via EISB especially on the Primary School crawl space, where the vapour intrusion risk was eliminated. Amongst other lessons learned are rate and concentration of products injected, rate of groundwater extraction, and community consultation.

Back to Contents

Advancing the Sustainability Evaluation Process for Remedial Activities

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Background/Objectives. Over the past decade, the remediation industry has developed a variety of guidance documents and calculation tools to evaluate the sustainability of remedial activities. These instruments are constantly being reexamined and revised to better encompass the triple bottom line (TBL), i.e., environmental, social, and economic. Current established tools mostly focus on determining the environmental impacts from remedial activities. Socio-economic impacts quantified in these tools are limited to cost benefit analysis of project implementation, accident risk, and global impacts that have socio-economic consequences (e.g., contribution to climate change). However, new methodologies are being developed to evaluate directly the socio-economic impacts of remedial activities. These methodologies are also being established as stand-alone tools. One disadvantage of separate tools is that they do not incorporate impacts from the interconnectedness among the three pillars of the TBL. As the remediation industry advances its understanding of sustainability, it is important to acknowledge this interconnectedness and incorporate this factor into the revised tools. The objective of this paper is to make the case for developing a mechanism that incorporates this synergistic effect.

Approach/Activities. A literature review was performed, which focused on a variety of sustainability assessment approaches from disciplines outside the remediation sector, including sociology, economics, natural disasters, and public health. These approaches addressed the interrelations among the three pillars of the TBL. The results of the literature review were considered for use by remediation industry in reassessing the process and methodology behind sustainability assessment tools.

Results/Lessons Learned. The literature review suggests that the sum of separate environmental, social, and economic assessments does not equal the whole (i.e., sustainability). Rather it equates to more than a simple sum of the impacts due to the synergistic effect among the inter-linkages between the TBL objectives. An integrated assessment identifies and incorporates these inter-linkages in its analysis. In addition, the literature suggests that by conducting an integrated assessment the unavoidable trade-offs are fully exposed. An example of a trade-off is “overly promote the prevailing economic agenda and thereby undermine 30 years’ worth of hard-won environmental policy gains” (Pope et al., 2004). The most efficient approach would incorporate methodologies quantifying the inter-linkages into an existing footprint tool. This presentation provides suggestions for a path forward to assist the remediation industry in advancing in this direction. For example, inter-linkages can be addressed by incorporating social cost of environmental metrics, community impact survey results, risk perception, hedonic valuation, contingent valuation, return on investment, etc.
Pope et. al. Conceptualising Sustainability Assessment. Environmental Impact Assessment Review. 2004. Issue 24. Pages 595-616.

Life Cycle Assessment, Footprint Analysis, Decision Analysis, and Best Management Practices: A Utilization Roadmap

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Background/Objectives. Since the beginning of the sustainable remediation movement, the industry has worked to identify and develop tools to be used in improving the sustainability of site cleanups. Since 2007, there has been significant focus on the development of multi-criteria decision analysis (MCDA) models, footprint assessment tools, best management practices (BMPs) compilations, and utilization of traditional life cycle assessment (LCA) tools. While all these tools have helped practitioners improve the sustainability of site cleanups, specific tools are generally applied because they are the only tool with which the project team is familiar. Knowledge of all the tools available provides an opportunity to apply the best tool for the questions that need to be answered and better understand sustainability opportunities in remediation projects.

Approach/Activities. This presentation will survey the attributes of LCA, footprint analysis, MCDA tools, as well as BMPs across several attributes to provide an objective comparison of the application value for each tool. The attributes will include cost, schedule to implement, training for practitioners, results provided, decision making input, and stakeholder understanding. With this information, a decision flow chart will be provided that users can utilize to walk through a decision-making process of when the specific tools should be considered for use in making site cleanups more sustainable.

Results/Lessons Learned. Awareness of sustainability improvement tools can result in developing more sustainable remedies. A decision flow chart that utilizes a simple “if-then” questions can help practitioners be more aware of different sustainability improvement tools and help them identify the best tool(s) for sustainability decision making

Green and Sustainable Sediment Remediation and Evaluating Sediment Sites Using SiteWise™ Version 3.1

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Background/Objectives. Navy Optimization Policy requires a Green and Sustainable Remediation (GSR) evaluation using SiteWise™ for all sites during the feasibility study phase of work. However, most examples and resources focus only on the optimization of groundwater or upland sites. There exists little guidance on the consideration of GSR and best management practices for remedial alternatives for sediment sites. This necessitates a comprehensive document discussing the application of GSR guidance on sediment sites. Furthermore, although SiteWise™ Version 3.0 was developed in 2013 as a lifecycle assessment-based spreadsheet tool for evaluating the environmental impact of the remediation of terrestrial sites, Version 3.0 does not include materials and equipment specific to the remediation of contaminated sediments. Although SiteWise™ Version 3.0 can be used for sediment sites, it requires a higher level of research and knowledge on the part of the user to perform this analysis and would also create a lack of consistency with how the analysis is performed. To improve the ease and consistency of performing a GSR analysis for sediments sites, an updated tool that includes calculations specific to sediment remediation activities is needed.

Approach/Activities. Battelle is developing a Sustainable Sediment Remediation White Paper bridging the gap between Navy GSR Guidance and Navy Sediment Guidance. This document will discuss policy background and sustainability considerations for sediment remedial alternatives, as well as the methods of incorporating GSR into the sediment remedy selection framework and the role of SiteWise™ in this process. GSR best management practices will be developed for dredging, capping, and monitored natural recovery for easy incorporation into Feasibility Studies or other CERCLA documentation. SiteWise™ Version 3.1 will be developed to account for the specialized materials, equipment, and activities associated with sediment remediation in GSR evaluation. These activities include dredging and cap placement, dewatering and disposal, in situ amendments, and performance monitoring for sediment and pore water for both near shore and open water sites. Furthermore, the SiteWise™ User Guide will be updated with guidance for the application of the new calculations modules and functionality. Several case studies will be reviewed with examples of the application of Navy GSR Guidance for both near shore and open-water sediment sites. It is expected that this work will be completed prior to the conference and the results will be presented.

Results/Lessons Learned. The updated Navy Guidance will facilitate the consideration of GSR strategies for sediment sites. The updated SiteWise™ tool and User Guide will improve consistency of GSR evaluations. The inclusion of activities specific to sediment remediation in SiteWise™ Version 3.1 will simplify its use for sediment sites. The resulting increased transparency of GSR evaluation for sediment sites will improve the reliability of SiteWise™ in its incorporation in the Sediment Remedy Selection Framework. Sustainability considerations for typical sediment remedial alternatives will be presented, along with best management practices, components of the updated functionality of SiteWise™, and case studies for the application of SiteWise™ Version 3.1 for both near shore and open water sediment sites.

Source Characterization and Green Remediation at Petroleum Impacted Sites

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Background/Objective. At petroleum impacted sites, petroleum hydrocarbons are arguably the most pervasive contaminants in the environment. As with other contaminants, investigation and remediation typically involve large footprints and often generate secondary pollution. To reduce the footprint, measures in consideration include updated conceptual site model (CSM), sound remedial strategy and optimal engineering design. However, to make these measures effective, one of the key components of CSM development is source characterization. The conventional approach for source characterization at petroleum impacted sites has relied on the typical components of petroleum hydrocarbons (e.g., total petroleum hydrocarbons, BTEX and oxygenates). However, the standard laboratory analyses used in this approach do not measure most source diagnostic compounds (e.g., paraffins, nathphenes and biomarkers). As a result, investigations and cleanups may have large spatial and environmental footprints that could otherwise be reduced through a more targeted and effective characterization. The objective of this paper is to demonstrate use of environmental forensics (EF) techniques to reduce footprints associated with site investigation and remediation through more vigorous source characterization at petroleum impacted sites.

Approach/Activities. EF is a discipline that focuses on characterization of contaminant sources such as petroleum and various related products. Use of EF enhances characterization of petroleum sources, which in turn helps to better understand potential release migration pathways. With assessment or understanding of post release alterations, potential migration pathways may be prioritized for focused investigation and remediation. More focused investigation and remediation is crucial in reducing the spatial and environmental footprints of a cleanup and will also aid in reducing other secondary impacts (e.g., site disturbance, energy and fuel consumption, equipment use) during the project life cycle.

Results/Lessons Learned. This paper presents two case studies to demonstrate the results of application of environmental forensics to reduce footprints of remediation through more thorough and specific source characterization. The first case study presented is associated with a release of petroleum product(s) at a site with documented historical releases. Differentiation of current from historical releases assisted with expedited remediation by limiting cleanup to the area that was impacted only by current release(s). The second case study is on an occurrence of crude oil in a former refinery, which neighbors an active petroleum terminal. Using petroleum biomarkers, sources of crude oil were determined and release migration pathways were identified, which lead to optimizing the site's remedial design. In these case studies, a more focused characterization strategy resulted in a more effective remedy with a smaller environmental footprint and time scale for site closure.

Quantifying the Full (Remediation + Spilled Hydrocarbons) Greenhouse Gas Emissions for Petroleum Release Sites

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Background/Objectives. One of the primary objectives in a green cleanup is to minimize air pollutants and greenhouse gas emissions. The remedial components that are often considered relevant to this core element are the type/quantity of materials and fuels used for remediation. Typically not considered in a quantitative footprint analysis are the greenhouse gas emissions from the contaminant itself. Yet for a petroleum release site, the spilled hydrocarbons represent a greenhouse gas source that may ultimately enter the atmosphere and contribute to larger scale climate change. A footprint analysis that incorporates the spilled hydrocarbon emissions source, and accounts for whether the remediation will decrease these emissions, would provide a more complete picture of the full environmental footprint of site operations. This presentation will present a footprint analysis from this perspective.

Approach/Activities. Remediation of an example petroleum release site will be considered. The estimated long term greenhouse gas emissions from the contaminant will be based on a mass estimate of hydrocarbons in place and the ratio of long term CH_4 to CO_2 emissions due to biodegradation of hydrocarbons. This will comprise the baseline greenhouse gas footprint of the pollutant. Sitewise^{TM} tool for green and sustainable remediation will then be used to estimate the greenhouse gas emissions for five approaches to remediating the contaminant (to the extent practicable). Whether the remediation decreases long term emissions from the pollutant will be incorporated to the estimate, with reductions counting as a credit versus the baseline. With this approach, the full greenhouse gas emissions of the site (i.e., spilled hydrocarbons plus remediation) can be considered.

Results/Lessons Learned. The five examples will cover a range of remedial options often considered for petroleum site cleanup. The first two examples will be those for which remediation could actually decrease the emissions from spilled hydrocarbons. One example is based on an assumption that reusing recovered hydrocarbons for some type of beneficial use means removing them from the greenhouse gas footprint of the contaminated site. This assumption is consistent with the ASTM Guide for Greener Cleanups (2013), which lists reusing or recycling recovered product as a best management practice. The second example is changing the form of subsurface emitted gases from a mixture of CO_2 and CH_4 to only CO_2. For comparison, three additional examples will be presented: remediation by excavation, remediation by LNAPL recovery without recycling of recovered product, and natural source zone depletion. The total greenhouse gas emissions footprint for a hypothetical petroleum site that employs these technologies will be presented. The total footprint includes not just emissions from remediation but also emissions from the contaminant itself. As will be demonstrated, this approach to footprint analysis provides a more complete context for remedial alternatives evaluation.

Back to Contents

Using Current GSR Tools to Evaluate Horizontal Remediation Wells in Site Remedy Selection

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Background/Objectives. Horizontal wells and horizontal directional drilling (or HDD) are becoming more common as a remedy for contaminated sites. With proper well design and installation, horizontal wells have proven to be very effective in treating large soil or groundwater volumes using sustainable treatment methods such as biosparging, air sparging or oxygen injection, and injection or recirculation of biological substrates.

HDD technology has been in mainstream remediation use for nearly 15 years. However, although many of the benefits for this technology are well known from an anecdotal standpoint, it has been difficult to derive direct comparisons between horizontal wells and other cleanup technologies. With the development of several sustainability tools that facilitate comparisons of remedy construction technologies, the ability to make such comparisons has now been simplified, however horizontal wells are not typically included in these applications. As a result, the technology is often not considered in the remedy selection process, even if the approach may be otherwise viable or preferred at a particular site.

Approach/Activities. Current GSR tools have fairly wide latitude in specifying parameters for various aspects of each phase of a cleanup activity. Proper adjustment of these parameters enables the researcher to simulate the use of horizontal wells in the remedy selection process, even if selection of the technology may not be directly accessible through the tool’s menu structure. However, such adjustments also requires intimate knowledge of the HDD technology itself. For consultants unfamiliar with the process and equipment, the research required to begin evaluation of HDD using these tools can be cumbersome.

Results/Lessons Learned. Consideration of HDD as a GSR technology involves not only the direct site and community impacts during the construction activity, but influences the long term O&M costs and effects, even for identical treatment approaches (e.g., injected bioaugmentation substrates) using different access technologies (e.g., vertical direct push vs. HDD). A thorough evaluation of the technology includes both aspects.

This presentation provides insight into the use of current GSR tools as a means to compare HDD remedies with other current technologies for remedy selection. By providing the range of tool parameter adjustments that should be made, attendees can learn to quickly set up their preferred tools to make these comparisons.

Horizontal remediation wells often compare favorably to competing technologies for site cleanup when analyzed in a GSR context. Enabling these comparisons using the most frequently-used sustainability tools provides a more quantified view of these benefits and assists consultants and site owners in making more informed decisions about remedy selection.

How Life Cycle Assessment Can Identify Environmental Burdens and Support Sustainable Decision Making

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Background/Objectives. There are a number of tools used to improve sustainability decision making for remediation projects. The most commonly utilized tools for quantifying environmental impacts are footprint analysis tools and life cycle assessment (LCA) tools. Footprint analysis tools are in the public domain and the learning curve to effectively utilize them is not steep. In contrast, LCA tools are generally expensive and the learning curve is steep. For this reason, footprint analysis tools are utilized more often than LCA tools to estimate environmental impacts of remediation projects. While costs and learning curve are lower for footprint analysis tools, the level of information provided with respect to environmental burdens is also less robust. This presentation will highlight the type of information afforded by a LCA that cannot be identified using footprint analysis tools. With this information, practitioners can decide if the additional costs and learning curve are worth the price of the additional information gained from LCA.

Approach/Activities. This presentation will overview the environmental impacts that can be considered by using LCA. Topics such as burden shifting and optimization/substitution opportunities will also be discussed. Insights gained from past LCAs, including those published in literature as well as individual case studies will be presented. The results provided will focus on the incremental information afforded by LCA and the cost associated with gaining those insights, as compared to a footprint analysis.

Results/Lessons Learned. Sustainability practitioners generally understand that footprint analysis tools are less costly and easier to learn, as compared to LCA footprint tools. With this presentation, they will also become acquainted with the incremental information that can be gained by completing an LCA so they can make a determination if the environmental questions they are asking would be better answered by a LCA or footprint analysis tool.

Life Cycle Assessment (LCA) for Green and Sustainable Remediation

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Background/Objectives. Many governmental bodies, regulatory agencies and industries are seeking to understand big-picture costs and consider multiple benefits when making decisions. This is driving increased awareness of life cycle impacts and tradeoffs for projects, products and services. Life Cycle Assessment (LCA) is one analytical tool that can be leveraged to implement internal sustainability programs, decision making or pursue project credentials under such frameworks as LEED®, ISI Envision and Green and Sustainable Remediation guidelines. LCA is a “cradle-to-grave” assessment method that considers how energy and materials are utilized across the interdependent stages of a product’s life from raw material extraction through end of life.

Approach/Activities. Managing environmental performance can be enhanced through targeting contributing factors that add to greenhouse gas, pollutants, embodied energy and water footprints. LCA methodology was assessed to compare remediation case study findings where LCA demonstrated environmental tradeoffs and estimated impact reductions.

Results/Lessons Learned. One LCA case study highlights a soil remediation project where lead stabilization and off-site disposal were implemented. Two levels of assessment were completed using the software tools Sitewise® and Gabi® to build life cycle inventory and impact assessment models. The approach yielded insights about soil management and removals and tradeoffs associated with soil remediation scenarios.

Back to Contents

Green and Sustainable Remediation in Practice: International Perspectives and Local Contexts

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Background/Objectives. In recent years, there is an emerging “green and sustainable remediation” (GSR) movement. It is drawing increasing attention from both the government and the industry, because this GSR movement is promising in accelerating process in addressing the contaminated land issue, by overcoming regulatory barriers, encouraging technological innovation, and balancing life cycle environmental stewardship with economic vitality and social well-being. However, there is still a lack of consensus on the practical meaning of GSR, both due to divergent views in the international community and variability of local contexts.

Approach/Activities. This study uses a combination of case studies, questionnaire survey data analysis, and qualitative interview. Several remediation cases in the US and the UK are examined in regards to the sustainability implications embedded in their planning, designing, and implementation activities. Data obtained from an international questionnaire survey, with responses from over two hundred remediation practitioners, were analyzed. And data from a qualitative interview with tens of remediation practitioners in the US, the UK, and China was also used.

Results/Lessons Learned. The present study provides a comprehensive analysis of green and sustainable remediation in practice. The assessment will include not only perceived results, as indicated by professional practitioners’ perception of how green and/or sustainable remediation is adopted in their projects, but also measured results, as demonstrated by real actions in case studies.

Green and Sustainable Remediation Development in Taiwan: Framework, Tools and Case Studies

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Background/Objectives. In 1980s, various types of soil and groundwater contaminated sites were found. In order to manage and supervise growing numbers of site investigation and cleanup activities of subsurface environment, the Soil and Groundwater Remediation Act was enacted in 2000. Since then, contaminated site investigation and remediation have develop a comprehensive management system. However, cleaning up contamination and preparing impacted land for reuse requires substantial energy, water, and other natural resources. The environmental regulator and remediation industry have recognized the potential high environmental footprints and social and economic impacts during the course of cleanup. Consequently, different issues have been rethought to incorporate sustainable concepts into the remedial process. Therefore, the overall remediation practices can maximize the overall environmental, societal, and economic benefits, which is the central spirit of green and sustainable remediation (GSR).

Approach/Activities. In 2012, Taiwan Environmental Protection Administration (TEPA) initiated a framework and executive flowchart for promoting GSR and cooperated with SuRF-Taiwan to organize the first Sustainable Remediation Forum. For the past two years, TEPA and SuRF-Taiwan have jointly worked on GSR development in Taiwan. This paper describes the development of the GSR framework, executive flowchart and summarizes the methodologies used in GSR assessment. Under the GSR framework, TEPA has developed various tools to encourage site managers to adopt GSR during the site cleanup process, including a remedy selection decision MCA tool, an environmental footprint analysis tool, a BMPs screening list, a social questionnaire sample and an economic impact analysis tool. In 2014, three demonstration sites implemented sustainable principles throughout the cleanup activities. Results of the GSR assessment will also be presented in this paper. Through environmental footprint assessment and human health risk assessment, remedy alternatives comparison and subsequent BMPs planning were conducted for the demonstration sites.

Results/Lessons Learned. Although TEPA has been promoting the GSR concept for two years. GSR application is still in an infant stage. For some of the small scale contaminated sites, a full scale GSR assessment which includes remedy comparison and quantitative analysis may be too complicated to conduct,. Hence TEPA will set up a tiered appraisal system based on the type of site to simplify the required assessment for some sites. The feasibility of the MCA decision supporting tools also needs to be affirmed. Since the promotion of the GSR concept in Taiwan is more of a top-down approach supported by the Taiwan EPA, an explicit and systematic approach for GSR assessment is very critical, thus TEPA is also considering launching a GSR certification program and appraisal measures are under development.

Sustainable Remediation: Which Approach Shall I Use?

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Background/Objectives. Sustainability in remediation of contaminated sites is a recent concept that aims at having a holist approach capable to assess the global impacts of remediation at the enviromental, economic and social levels. Unfortunately, a common defintion and guidelines shared at international level are still lacking. This work is the state of the art on the subject and reports about the available approaches and tools.

Approach/Activities.
In 2008, US EPA defined "green remediation" as the practice of considering all environmental effects of remedy implementation and incorporating options to maximize net environmental benefit of cleanup actions. A green remediation approach is usually based on the environmental footprint analysis (EFA) or a life cycle assessment (LCA). In the EFA, five core elements have to be evaluated: energy requirements, air emissions, water requirements and associated impacts on water resources, impacts on land and ecosystems, material consumption and waste generation. Few tools are available for the task, such as SEFA (Spreadsheets for Environmental Footprint Analysis, by EPA), SRT (Sustainable Remediation Tool, developed for AFCEE) and SiteWise (by the Navy, Army Corps of Engineers and Battelle). LCA methods may assist in considering the total environmental impact of the remediation project from cradle to grave. Traditional impact categories in LCA methods include those at the global level, such as climate change and ozone depletion, and those at the regional level, such as acidification, photochemical smog formation, ecotoxicity and toxicity. SimaPro is the most used tool for LCA, though not specific for cleanup purposes.

The Sustainable Remediation Forum (SURF) - Italy defined a sustainable remediation as "the process for remediation and management of contaminated sites, aimed at identifying the best solution when considering environmental, social and economic factors, through a balanced decision process agreed by stakeholders”. Compared to green remediation, economic and social issues have also to be considered. As far as costs are concerned, the Remedial Action Cost Engineering Requirements (RACER) System is a PC-based tool suitable for cost estimates for environmental remediation. The UK (1999) guideline "Cost-benefit analysis for remediation of land contamination" provides a framework for a combined cost-effectiveness analysis (CEA) and multi-criteria analysis (MCA), or a cost-benefit analysis (CBA). REC (Risk reduction, Environmental merit and Costs) combines three tools to estimate risk reduction, environmental merit and costs of remediation alternatives. No tools are available to quantify social benefit, which might include commercial, health or education services, increase in local occupation or real estate values.

Results/Lessons Learned. Although a universally shared concept of sustainable remediation is still lacking, a few tools have been developed or adapted from other fields in order to estimate environmetal impacts and benefit and costs at a reasonable level. On the contrary, it is still unclear how to deal with the social component.

GoldSET$^{©}$ CN: A Project Life-Cycle Approach to Operationalizing Sustainability in the Field of Contaminated Site Remediation

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The integration of sustainability in site remediation projects has gained considerable momentum in the last decade. It has been demonstrated that the early consideration of sustainability indicators, alongside technical factors, can influence positively the performance of a project through better control over project schedule, faster permitting process, cost reduction through optimization, and ultimately enhancing the corporate image through improved relationship with key stakeholders.

In 2007, CN mandated Golder to develop a customized version of GoldSET©, a sustainability decision support tool that evaluates the strengths and weaknesses of remedial options with respect to environmental, social and economic dimensions. This approach has now been used on more than 25 contaminated CN sites across Canada and the United States.

As in any field, the benefits of considering sustainability issues are greater when performed at the onset of a project, during the early planning and design phases. That being said, if sustainability considerations are not monitored across the entire project life-cycle, their effect on actual project performance cannot be verified. In 2012, CN mandated Golder to develop a Monitoring and Evaluation (M&E) tool which would optimize and standardize the way that sustainability indicators are tracked across the project life-cycle. The GoldSET CN M&E web-based application was launched in June 2014. It provides managers and engineers with the means to monitor and control sustainability impacts throughout project execution. The aggregated data can then be used to engage stakeholders, improve management, improve future decisions and for corporate sustainability reporting.

This presentation will first provide an overview of the drivers and challenges associates with integration of sustainability in site remediation activities, and look at what SuRF Canada and other groups are doing in this field. It will then illustrate how CN has succeeded in operationalizing sustainability within their contaminated site management program through the use of the GoldSET –CN tools. The step by step process by which sustainability metrics are integrated and then monitored across the project life-cycle will be illustrated through a case study.

International Perspectives on GSR:
State of the Practice, Challenges and Opportunities

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Background/Objectives. We will highlight established and emerging examples of Green and Sustainable Remediation (GSR) frameworks and applications around the world, and how sustainability assessment and management in land remediation can contribute to sustainable development, climate change adaptation and community resiliency. A variety of international and national resources and regional initiatives can support this effort. The timing is optimal given the recent international climate change agreements and the significant decrease in technology costs including renewable energy.

Approach/Activities. We will report on the advance of sustainable remediation in the international community, international drivers for sustainability, and communication among international organizations. We will also present selected GSR case studies on Brownfield redevelopment, increased cost-effectiveness, environmental & social improvement.

We will summarize U.S Executive Orders and international reports to create land management programs in developing countries and how GSR can be incorporated in these nascent programs. We will highlight technical and financial tools that can be used especially to demonstrate monetary benefit to site owners and local stakeholders. We will explore public/private partnerships that can provide both revenue and resiliency to help meet basic human needs.

Results/Lessons Learned. Our presentation will conclude with recommendations on how the current state of the practice, case studies, tools and bench mark reports can be used as a springboard for increased application worldwide.

Back to Contents

Case Study: Negotiations with the Environmental Agency for the Use of Monitored Natural Attenuation at a Pharmaceutical Manufacturing Facility in Brazil

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Background/Objectives. Volatile Organic Compound (VOC) impacted groundwater at a pharmaceutical manufacturing facility site in Brazil is migrating off-site. Remediation activities are designed to control the migration of VOCs to one of the two rivers bordering the site and to reduce the mass of contaminants in the hotspot. Groundwater, through the existing monitoring wells, has been monitored since 2005. The major Compounds of Concern (COC) are trichloroethene (TCE), cis+trans-1,2-dichloroethene (1,2-DCE), 1,1-dichloroethene (1,1-DCE), vinyl chloride (VC), toluene, ketones (methyl isobutyl ketone and acetone), methanol and total petroleum hydrocarbons (TPH).

Approach/Activities. Three major source areas have been identified. Areas 1 and 2 are located on the site and Area 3 is located at the property boundary and, partly off-site. 1,2-DCE (cis+trans), VC and toluene have detected in groundwater samples collected from on- and off-site wells at concentrations above the state environmental agency (SEA) intervention values. A hydraulic containment was requested by the SEA and a Recirculating Well Technology (RWT) system was installed to both contain the plume migration and to remediate the source area at Area 3.

A Human Health Risk Assessment (HHRA) was conducted to calculate the Site Specific Target Levels (SSTL) and a Natural Attenuation Evaluation was performed to estimate the rate of COC removal in the source areas and evaluate the expected timeframe for remediation of groundwater, i.e. to achieve the SSTLs.

Results/Lessons Learned. The Natural Attenuation Evaluation concluded that reductive dechlorination is occurring on and off site. Toluene, alcohols and ketones, and TPH are co-located with the chlorinated ethenes and are serving as carbon substrates and sources of electron donor for reductive dechlorination. In the absence of these compounds, naturally occurring organic carbon is supporting the dechlorination process. Preliminary decay rates were calculated for VC in Areas 2 and 3. The decay rates were used to estimate the time required to achieve the SSTL for VC. In Area 2, the time required to achieve the SSTL for VC ranged from 6 years to 28 years. In Area 3, the time required to achieve the SSTL was calculated to be 10 years for PM-31 (off site).

As a result of this study, continued monitoring for natural attenuation parameters is recommended for Area 1. Because the timeframe to achieve the VC SSTL in portions of Area 2 was expected to be long and to address the SEA's reluctance in accepting MNA as an alternative for this area, the existing RWT system was extended to Area 2 to enhance the removal of the VOCs and reduce the mass loading of VOCs from Area 2 to Area 3. In Area 3, the RWT system is working to both remove and contain the migration of VOCs.

A Biostimulation Program Applied at a DNAPL-Contaminated Site in an Urban Setting

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Background/Objectives. Bioremediation was evaluated as a second-stage component of a remedial strategy for a site located at an urban area in Brazil. The conceived remediation system was implemented in 2009 and consisted of a mixed solution of an intercepting trench and a coupled plastic diaphragm wall that allow the removal and migration control of the plume dissolved phase. This approach was considered the most suitable alternative, due to the proximity of the site to residential areas. For the biostimulation pilot system, environmental molecular diagnostics were used to evaluate the extent of natural and stimulated biodegradation of the dissolved chlorinated organic plume that has overtaken the control system. The method identified specific degraders of importance such as *Dehalococcoides* spp., a key reductive dechlorinator and the only bacteria capable of utilizing VC as growth-supporting electron acceptor.

Approach/Activities. The soil has low permeability and was mostly contaminated with chlorinated ethanes (1,1,2 trichloroethane and 1,2 dichloroethane), with a DNAPL free-phase vertically limited to a shallow and continuous shale layer. The trench system was deployed upstream of the diaphragm wall and nearer the existing secondary source zone, to allow efficient extraction of free phase as well as the recirculation of nutrients to be injected upstream from the free-phase product.

Bio-Trap® In Situ Microcosm (ISM) studies were performed in five monitoring wells to evaluate biodegradation of contaminants under existing natural site conditions and to investigate the effectiveness of biostimulation with electron donor addition. The ISM assemblies consisted of a control unit which simulated Monitored Natural Attenuation conditions and two Biostimulation units which were amended with EVO and molasses as electron donors. After a 114-day incubation period, the ISM assemblies were recovered for lab analysis of contaminant concentrations, geochemical parameters and a quantitative polymerase chain reaction (qPCR) enumeration of dechlorinating bacteria (Dehalococcoides spp. and Dehalobacter ssp.) and its associated dehalogenase genes.

Results/Lessons Learned. *Dehalococcoides* spp. populations, as well as vinyl chloride reductase genes, were detected at relatively high concentrations (> 10^4 cells/bead) at three monitoring wells evaluated and spanned orders of magnitude, indicating that biodegradation potential differs for various locations across the site. Ethene and ethane production was detected at extremely high concentrations at wells in the vicinity of the free-phase product although bacteria growth was inhibited in these cases, probably due to low pH (below 6.0) and the toxic environment. Results demonstrated that electron donor addition did not stimulate further growth of *Dehalococcoides* spp for wells with high gene counts (bvcA and vcrA) in MNA units. Based on these results, a biostimulation pilot study program is being implemented at the site to provide optimized operating parameters to a potential large scale remediation plan.

High-Resolution Site Characterization (HRSC) in South Africa: Challenges, Successes and Lessons Learned

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Background/Objectives. Inadequate characterization of contaminated sites often leads to the development of poorly constructed conceptual site models and consequently, the design and implementation of inappropriate risk management strategies. As a result, the required remedial objectives are not achieved or are inefficient in addressing the identified risks. Unfortunately, it is all too common to find remedial intervention strategies that run for lengthy periods of time at great cost while generating little environmental benefit due to inadequate characterization of site conditions. It is becoming widely recognized that high resolution site characterization (HRSC) can provide the necessary level of information to allow for development of rigorous conceptual site models, which can be used to develop and implement appropriate risk management solutions for environmental problems.

At the outset, the HRSC approach generally has comparatively higher costs than traditional state-of-the-practice assessment methods. However, the project lifecycle costs can be substantially reduced due to development of optimal risk management strategies. In developing countries where there is a lack of legislation relating to soil and groundwater contamination or, a lack of enforcement of legislation which is present, the long-term liabilities related to contaminated sites are often not immediately apparent to the parties responsible for the sites. This often creates a reticence to employ HRSC techniques due to their increased cost, especially when much of the technology must be imported on a project specific basis from either Europe or the United States.

Approach/Activities. The Authors provide information from several case studies conducted in South Africa where HRSC techniques have been employed to gain a greater understanding of subsurface conditions. Techniques employed have included surface-based geophysical techniques such as electrical resistivity tomography (ERT) and multi-channel analysis of seismic waves (MASW), passive soil gas surveys, deployment of Flexible Underground Technologies (FLUTe®) liners, diamond core drilling, fluid electrical conductivity profiling, downhole geophysical logging tools, the Waterloo Advanced Profiling System (APS), and the use of field laboratories. Several of the techniques required importing equipment and personnel from Europe or the US, and in several case studies, were a first to be employed in South Africa, or the continent of Africa for that matter.

Results/Lessons Learned. The Authors present data obtained using the HRSC techniques from the case studies and elaborate on how the information obtained was used to drive effective decision making in terms of managing long term environmental risks at the various sites, which has been positively embraced by local clients. The authors also highlight key challenges in conducting HRSC investigations in an emerging market context in terms of lack of available HRSC technologies, limitations related to the technical capacity of local suppliers, and changes in environmental legislation, which create uncertainty in terms of scoping investigations appropriately in order to achieve site closure and regulatory approval.

Earthworms Improve Heavy Hydrocarbon Degradation in Soil

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Background/Objectives. Remediation of soil contaminated with heavy hydrocarbons (HH) from crude oil is a widespread challenge. Recalcitrant HH are difficult to degrade and costly to eliminate from soils. Earthworms stimulate the rapid breakdown of organic materials through a combination of mechanical activity, input of enzymes and mucus, and the stimulation of microbial activity. Studies have indicated that earthworms may promote degradation of petroleum hydrocarbons, and our previous research with the common composting worm *Eisenia fetida* found that earthworms increased degradation in artificial soil contaminated with crude oil, relative to additions of organic matter alone, or no treatment. The research presented here expands these studies into natural soil contaminated with crude oil (a remediation site) using two species of earthworms, *Eisenia fetida* and *Aporrectodea caliginosa*, both common in soils throughout the U.S. The working hypothesis was that the activity would be as high or higher in a natural soil with a microbial community adapted after long-term exposure to crude oil. Our main objectives were to confirm the previously observed degradation activity in a more relevant test by using soil from an active remediation site, and evaluate additional species of worms in a lab setting, including testing tolerance of *E. fetida* and *A. caliginosa* to the natural remediation site soil, and the potential for reproduction of the earthworms in the test soil.

Approach/Activities. Lab scale experiments were used to evaluate heavy hydrocarbon degradation over time in natural and artificial soil, with and without the composting worm *E. fetida*. Worms received organic feed (carrot pulp and coffee grounds) weekly, and controls included a feed alone, and a no treatment control. Initially, toxicity tests for the remediation site soils were run on three species of worms using a standard published method. To compare the performance of a natural soil microbial community to that of a lab-prepared sandy loam soil, treatments using a defined soil with added crude oil were compared to the defined soil with crude oil and 10% natural remediation site soil as an inoculum. To test the natural soil at 100%, *A. caliginosa* and *E. fetida* were used, and hydrocarbon levels overtime were compared between treatments. All contaminated soils were prepared to contain about 30,000 milligrams per kilogram (mg/kg) of total petroleum hydrocarbons (TPH) based on toxicity tests. TPH levels were monitored over time using gas chromatography with a flame ionization detector (GC-FID).

Results/Lessons Learned. Earthworms tolerated heavy crude oil up to levels relevant for remediation (2-5% w/w), and toxicity increased with the volatile hydrocarbon content of the oil. The treatments with the highest rates of degradation included earthworms and remediation site soil. We hypothesize improved degradation is a function of the microbial composition of the soil, and indicates that performance in natural soils should be better than observed for artificial soils. In the first degradation experiment (10% natural soil inoculum), petroleum concentrations declined significantly ($p<0.01$) in the presence of *E. fetida* compared to controls. After 342 days, concentrations declined by 56% without the microbial inoculum and 63% with the microbial inoculum. Heavier and more complex hydrocarbons were more resistant to degradation. In the second experiment, after 292 days petroleum concentrations in natural soil with earthworms declined approximately 93.5%, significantly more than the reduction observed in the controls (added feed, no worms declined 75%; volatilization alone declined 44%). The results of these experiments show that earthworms accelerate degradation of crude oil and are a promising candidate for the enhancement of crude oil bioremediation (vermiremediation).

Bioremediation of Petroleum Hydrocarbon-Contaminated Soil following Ozone Pre-treatment

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Background/Objectives. Bioremediation of petroleum hydrocarbons represents a cost-effective approach to restore soil at contaminated sites. The heavy fraction of total petroleum hydrocarbons (TPH) is particularly challenging for bioremediation. The rates and extent of TPH biodegradation are strongly dependent on the soil properties, the availability of O2 and nutrients, and the microbial community present. The chemical structure of heavy hydrocarbons also plays a role in bioremediation. Many heavy hydrocarbons have large, complex structures with low solubility and high viscosity; thus, these hydrocarbons are often poorly amenable to microbial degradation.
We evaluated bioremediation of a contaminated soil containing heavy hydrocarbons using an approach that simulates conditions used in land-farming. Furthermore, we investigated bioremediation following an ozone gas pretreatment as a means to partially remove heavy hydrocarbons and/or transform these hydrocarbons to less complex, more biodegradable forms.

Approach/Activities. We carried out a series of bench-scale studies in glass pans containing 1.5 kg soil/pan. All pans were humidified and tilled twice weekly. We provided macronutrients (source of N and P) and micronutrients (trace minerals and vitamins) for the biostimulation scheme. We subjected the contaminated soil to gas-phase ozone treatment (2300 ppmv of humidified gas) for 2 hours, then we biostimulated with nutrients.

Results/Lessons Learned. We initially evaluated the biodegradability of the heavy hydrocarbons in the contaminated soil using a modified 5-day, time-course biochemical oxygen demand (BOD5) test. Consumption of O2 in the BOD bottles proceeded after ≤ 1 day, leading to a final BOD5 of 15000 mg/kg soil. The BOD5 data were indicative of a robust indigenous TPH-degrading microbial community. We measured TPH weekly using gas chromatography. Within 57 days of bioremediation, TPH decreased from 15000 mg/kg soil to >2000 mg/kg soil. This represents an 87% TPH reduction from time 0. Enhanced natural attenuation (humidity and tilling) has also proven to be effective in TPH removal, albeit at slower rates than biostimulation. Our chemical analyses thus far show the strong potential of bioremediation of heavy-hydrocarbons in this soil. We are in the process of enriching these data with microbial community analyses using high-throughput sequencing and quantitative PCR. Furthermore, we will present our results on the effect of ozonation on the contaminated soil as a means to further improve time-frames of bioremediation.

Back to Contents

In Situ Remediation in Brazil

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Background/Objectives. In situ remediation in developing countries presents a unique set of challenges, nevertheless as awareness develops in these countries about the risks associated with soil and groundwater contamination and the need to safeguard drinking water supplies, remediation is required.

CRA performed remedial activities at two sites in Brazil. The first site had metals (lead and silver) present in groundwater which was migrating downgradient towards a river that was used as a drinking water source. The second site had cumene present at LNAPL quantities in groundwater. The site was located on the bank of a creek that was a tributary to a river that was a major drinking water source for a nearby city.

Approach/Activities. For both sites an assessment of remedial options was performed followed by laboratory treatability studies to test the selected technologies. Technologies selected and tested needed to overcome the following issues:

- Likelihood of acceptance of the technology by Brazilian regulators
- Availability of treatment products in Brazil
- Presence of amendments/products on the list of chemicals accepted for injection in Brazil by Brazilian Environmental and Renewable Resource Institute (IBAMA)

For the first Site in situ chemical reduction of metals was selected and implemented. For the second Site surfactant enhanced removal of cumene was selected and implemented as a pilot test.

Results/Lessons Learned. The methods used to overcome the regulatory issues described above will be discussed. Both sites have been treated, however, some issues remain to be resolved.

First Site: In situ chemical reduction treatment was successful, however, some issues with sampling methodology complicated the interpretation of the results. Second Site: Reductions in cumene concentrations were observed in the treatment area, however, an increase in cumene concentration was observed in downgradient wells.

Overall Lesson Learned: Implementation of in situ remedies in Brazil must include and understanding of standard operating procedures and regulatory preferences in this country.

Remedial Actions in Colombia: Challenges and Progress to Date

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Background/Objectives. The country of Colombia occupies 440,800 square miles (1.142 million km²) of land surface and has a human population of *ca*. 48,000,000. Colombia is the second most biologically diverse country in the world (Brazil is first, but it occupies ca. 7-times the land mass). With an estimated 314 ecosystems, Colombia supports the highest the number of bird species and it harbors an estimated 45,000 plant species (equivalent to 10 or 20% of total global species). Importantly, it houses the largest number of endemisms (species that are not found naturally anywhere else in the world).

An estimated 10% of all life species of the Earth live in Colombia. Given this great diversity, it is a difficult to establish holistic regulations that are protective of human health and the environmental. Moreover, Colombia is an emerging economy with its growth driven largely by oil and gas exploration/production and natural resource mining, both of which can be destructive and damaging to the environment when poorly implemented. Hence, there is a critical need to effectively manage inevitable growth and economic development with the protection of precious and indispensable natural resources.

Approach/Activities. Working with myriad international consultancies, local academics and regulatory experts, we have developed strategies and implemented remedial actions for some of first (soil and) groundwater remediation projects undertaken in Colombia. The projects were conducted in remote, ecologically sensitive, rural and urban settings, and they included: i) combined excavation, ISCR and ISCO approaches for recalcitrant organochlorine pesticides in soil and groundwater, ii) ISCO for MGP and creosote type wastes, iii) Advanced ISCR with methane control for the treatment of chlorinated solvents in urban settings, iv) stabilization of heavy metals (mercury) associated with industrial operations, and v) “Emergency Response” efforts associated with illegal mining activities. In addition, we have conducted conventional aerobic bioremediation of soils impacted by petroleum hydrocarbons. Each of these projects have met with significant challenges associated with: i) importation and basic logistics, ii) lack of implementation experience, iii) limited availability of specialized equipment, and iv) a general absence of clear guidelines governing performance monitoring and remedial action objectives.

Results/Lessons Learned. This presentation will summarize the challenges encountered from the conceptual design stage (proposals and procurement) to work plan development (site characterization and technology selection) to field-scale validation (pilot testing and performance monitoring) to full-scale field implementation (regulatory approvals and site closures). We will also present lessons learned from technology implementation in emerging countries with limited resources. Some of these lessons can potentially be used to improve efficacy of similar operations - even those conducted by others with more project experiences.

Comparative Pilot-Scale Evaluation and Cost Benefit Analyses of ISCR, ISCO and ERD for Treatment of CVOCs at a Site in Brazil

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Background/Objectives. Groundwater at an automotive industry located in Sao Jose dos Campos, Sao Paulo State, Brazil was impacted by Chlorinated Volatile Organic Compounds (CVOCs) including PCE, TCE, 1,2-DCE, VC, 1,1,1-TCA, 1,1-DCA and 1,1-DCE. In addition, portions of the plume area also contained hexavalent chromium. Groundwater is located at 16.5 m bgs in a sandy lithology. The impacted area was estimated at 2,500 m^2 with an average plume thickness of 4.5 to 6.0 m. The primary remedial goal was to prevent further migration of impacts into the neighboring Serimbura Tributary Creek, which was the main receptor identified. Baseline geochemical conditions appeared unfavorable for natural attenuation / reductive dechlorination considering oxidizing conditions (ORP values between +100 to +300 mV, DO between 1.0 to 3.0 mg/L), acidic groundwater (pH between 4.5 to 6.0), low levels of TOC and high levels of competing electron acceptors in the form of nitrate.

Approach/Activities. A pilot scale field effort was undertaken to evaluate four different remedial substrates: EHC® and EHC -L® for in situ chemical reduction (ISCR), emulsified vegetable oil (EVO) for anaerobic bioremediation, and sodium persulfate (Klozur®) activated with Fe-EDTA® for chemical oxidation. Each test area included the injection of substrates into three direct push injection points installed directly upstream of a performance evaluation well. The goal of the side-by-side pilot tests was to identify the most efficient approach to enable achievement of the remedial goals in terms of cost and treatment performance. The pilot study results were complimented by data from hydraulic and tracer testing, as well as mathematical modeling of flow and transport, in support of the development of a cost-benefit analyses and full-scale remediation plan.

Results/Lessons Learned. Six monitoring campaigns were performed over ten months in the four areas of pilot tests. Analytical results showed that, of the three techniques used, which shows better result was the In Situ Chemical Reduction (ISCR), considering cost-benefit, the effectiveness and reaction time.

Evaluation of the Combined Use of MNA and Active P&T System at a Chemical Facility in Brazil

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Background/Objectives. The combined use of MNA approach and a groundwater recovery system was successfully applied at a chemical facility located in the state of São Paulo, Brazil. There were four separate groundwater contamination plumes identified at the site, and the purpose of this approach was to demonstrate to the environmental agency that no other remedial measures were needed at the time. This presentation will cover the field activities performed, the main results obtained and the interaction with the local environmental agency during the entire process.

The facility in question had been under active remediation for one year when the MNA approach was proposed, following concerns from the environmental agency that the proposed remedial measure would not be sufficient. The remedial action at the time was a groundwater extraction system. The then existing groundwater extraction system was designed to remove volatile organic compounds/semi volatile organic compounds (VOC/SVOC) mass from the four identified groundwater plumes at the site. The main objective of this project was to clearly show that microbial activities were taking place within the plumes.

Approach/Activities. Groundwater monitoring wells, recovery wells and the WWTU aeration tank were sampled for MNA parameters and aerobic and microbial activity. MNA parameters were measured in accordance with the Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water (US EPA, September 1998) and microbial activity was measured in accordance with EPA method 9215B. In parallel, a Pump and Treat system was in operation at the site. The results of the sampling were used to determine that MNA could be successfully proposed to the environmental agency.

Results/Lessons Learned. The natural attenuation monitoring results indicated that the existing plumes were being actively biodegraded and treated via in-situ mechanisms in the subsurface formation beneath the Site. Both the bacterial and geochemical data within the plumes indicated that viable bacterial population were present in the subsurface and changes in the groundwater geochemistry through these plumes indicated that biodegradation was occurring. In the case of the chlorinated plume, the bacterial and geochemical data was further supported by the groundwater VOC data which indicated that sequential reductive dechlorination was actively occurring in the subsurface.

Evidence of Vinyl Chloride Degradation at an Industrial Site Using Molecular Diagnostics

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Background/Objectives. Molecular biological tools were used to evaluate the extent of natural and stimulated biodegradation of a shrinking vinyl chloride (VC) plume underneath an industrial site in Brazil. Biostimulation was considered following a risk-based remediation approach developed as a design tool to support the decision-making process and re-examine remediation goals at the industrial site. This strategy is becoming a common practice in Brazil, as enforced by most environmental agencies and regulators. Risk analysis results indicated that vinyl chloride was responsible for the highest calculated risk values at the site. The method identified specific degraders of importance such as *Dehalococcoides* spp., a key reductive dechlorinator and the only bacteria capable of utilizing VC as growth-supporting electron acceptor.

Approach/Activities. The dissolved plume is currently being achieved by a hydraulic pump-and-treat system to provide source control and DNAPL mass recovery. The major contaminants include vinyl chloride (VC) and 1,1 dichloroethane (1,1 DCA) with concentrations ranging from 0.01 to 3 mg/L. There is no contaminant free-phase at the site and the dissolved plume is being vertically retained by the bedrock formation at approximately 30-35m of depth. Bio-Trap® In Situ Microcosm (ISM) studies were performed in six monitoring wells to evaluate biodegradation of vinyl chloride under existing site conditions and to investigate the effectiveness of biostimulation with electron donor addition. The ISM assemblies consisted of a control unit which simulated Monitored Natural Attenuation (MNA) conditions and a second unit which was amended with lactate as an electron donor. After a 75-day incubation period, the ISM assemblies were recovered for lab analysis of contaminant concentrations, geochemical parameters and a quantitative polymerase chain reaction (qPCR) enumeration of *Dehalococcoides* spp. and its associated dehalogenase genes.

Results/Lessons Learned. *Dehalococcoides* spp. populations, as well as vinyl chloride reductase genes, were detected at relatively high concentrations (> 104 cells/bead) at half the monitoring wells evaluated and spanned orders of magnitude, indicating that biodegradation potential differs for various locations across the site. Ethene production was observed in 80% of field samples with the highest *Dehalococcoides* spp. populations, concurrent with a one order of magnitude decrease in vinyl chloride concentrations during the incubation period. For wells with moderate dehalogenase genes, results clearly demonstrated that electron donor addition could stimulate further growth of Dehalococcoides spp. Conversely, at locations with naturally elevated gene counts (bvcA and vcrA), the biostimulated samples had no further effects in VC degradation as compared with MNA samples due to the fact that halorespiring populations were already high. In fact, elevated methane concentrations were verified in most samples (>1 mg/L), indicative of reducing conditions. The pH values at the site were between 6.1 and 6.7, a little below the pH range for optimum growth of Dehalococcoides spp., between 6.8 and 7.5. Based on these results, a biostimulation pilot study program is being implemented at the site to provide optimized operating parameters to a potential large scale remediation plan.

Back to Contents

Nanoparticles for the Treatment of Effluents Contaminated with Chlorinated Organic Compounds: An Overview

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Background/Objectives. The organochlorines compounds are part of persistent organic compounds, due of their physical chemical properties, degradation is slow and tends to accumulate in fatty tissues of various animals throughout the food chain. One way to enhance the removal of chlorinated compounds is using nano-materials. The latter are characterized by their low size, ranging from 1 to 100 nanometers. Because of their small size, their properties are different compared to their millimeters counterparts, such as more surface contact and increased reactivity. Nanomaterials are the core of a promising technology that can be used to accelerate and improve the transformation and detoxification of chlorinated organic compounds (COCs). The objective of this review is cover topics such as efficient nanomaterials for COCs treatment, supports and stabilizers that improve the process, interactions of nanomaterials with the microorganisms involved, and emerging fields.

Approach/Activities. We have reviewed significant subjects such as efficient nanomaterials for COCs treatment, use of supports and stabilizers that improve the process, interactions of nanomaterials with the microorganisms involved, and emerging fields.

Results/Lessons Learned. The most common material used for treatment of waters polluted with COCs has been zero-valent iron (ZVI) because of its efficiency and low cost. However, there are concerns on the stability and long term durability of ZVI *NP*. For this reason there are some works with other materials such as Pd, Zn or Ni and with combination of materials in the fabrication of NP. The bimetallic NPs allow for a lower cost of production, since one of the materials could be the most economic but not the most efficient whereas the second metal, the most expensive, provides a higher degradation capability. Alloyed and core-and-shell types of bimetallic NP have been tested. The process with NP can be made more efficient by using a support that prevents the aggregation of NP during reaction and in some cases can facilitate the recovery of the NP afterwards. Currently, the application of NP in bioreactors and *in situ* treatments is gaining momentum. Another significant issue especially for hybrid treatments is the interaction between NP and the microbial community harbored in bioreactors and devices, ranging from toxicity issues to biosynthesis of NP. There has been an attempt to incorporate metal NP onto the microbial cells for COC treatment, although more research is needed because some adverse effect has been detected. Furthermore, there is increased interest on biosynthesis of NP with microorganisms in order to have true “nanoparticleized biomass” with increased degradation capability of pollutants. Among important emerging fields we can highlight the studies on health and environmental impact as well as life cycle analysis of the NP fabrication and application. We have found that in spite of its importance the research on this area is scarce and has to be increased to avoid future, unpleasant surprises in the use of NP.

Back to Contents

Remediation for Mercury Stabilization by In Situ Chemical Reduction (ISCR) in Groundwater (Brazil Site)

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Background/Objectives. An active Paper Plant, located in the São Paulo State (Brazil), has its groundwater impacted by Mercury, with concentrations up to 895 µg/L. A remediation process is taking place aiming the protection of the River, located downstream the site. The plume of contaminant extends through an area of 9000m²(124 m x 111 m), with 8 m deep (from 5,00 to 13,00 meters above ground). The predominant lithology is composed of sandy sediments and it is estimated that the linear groundwater flow velocity is 0,077 m/s.

Approach/Activities. The remedial approach involves stabilization of Mercury *in situ* via injection of EHC-Hg® amendments, which is composed of ZVI (Zero Valence Iron), and a source of Sulfide and Phosphorus to promote precipitation of Mercury as HgS.

In December of 2011, a pilot test was conducted in an area measuring 36 m^2 and. The injection was performed in the vicinity of a monitoring well, whose baseline for Mercury concentration was 420 µg/L. After 194 days from the injection, the results showed a reduction of almost 92% of Mercury. Geochemical data showed an increase of pH and a decrease of ORP to around -285 mV, confirming that favorable conditions for mercury stabilization as sulfide salts had been attained.

Given the results of the pilot test, an intervention plan was designed aiming the reduction of Mercury Mass (Hg^{2+}) in groundwater.52 tons of EHC-HG® were estimated to be needed for reaching the goal. This product is supposed to be injected through 262 injection points distributed along the plume and extremities. The injection is to be executed in 4 steps. Calculations shows a 2.5m radius of influence for each injection point. This calculation is confirmed by soil samples collected equidistantly between two injection points.

Results/Lessons Learned. After the EHC-Hg® injection, groundwater was monitored in the surrounding monitoring wells to assess the performance of the remediation. The analysis was conducted between the steps of injection of remedial product. A systematic reduction of mercury concentration was noticed in the area. A splitting of the plume into two parts and the reduction of more than 80% of the initial area of 9000 m^2 of Mercury plume were observed.

No concentrations beyond the previously established 10 ppm of Mercury was observed in the wells located downstream the Electrolysis area, which implies in no risk of the plume reaching the River.

In Situ Bioremediation to Protect a Residential Area

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Background/Objectives. An area of approximately 25 hectares in the south region of Brazil was contaminated in the past by aromatic compounds, due to accidental spills from the industrial wastewater pipes. The contaminants of environmental relevance, benzene and naphthalene, reached the free aquifer, at a depth of more than 15 meters, and reached a residential area located out of the site. Aiming to eliminate any potential future risk to the external receptors, two systems were deployed: one for the hydraulic confinement of the plume and the other to stimulate the in situ biodegradation of the environmentally relevant compounds.

Approach/Activities. Before decided to use in situ biodegradation process, a detailed site characterization was conducted to provide balanced information on the chemical nature of contamination, the hydrogeochemical properties of the contaminated site and its microbiological characteristics. Biodegradation of the environmentally relevant compounds were tested in bench-scale studies, pointing out that the aerobic stimulation of the natural attenuation process would promote significant time reduction in the degradation of these compounds. A mathematical model of dispersion of nutrients and electron acceptors in the aquifer was used to design the engineering concept adopted. A bioremediation system composed of 12 wells distributed in the residential area was installed and operated for 18 months, with daily injections of aqueous solution of nutrients and electron acceptors.

Results/Lessons Learned. The efficiency of biological degradation was proven in monitoring campaigns carried out after the startup of the system operation. There was a reduction of more than 95% in the concentration of contaminants in the residential area after 18 months of operation, which was consistent with the estimated results that underpinned the conception of the remediation project. The operational and environmental data obtained so far point to the end of the remediation process within the original deadline.

Full-Scale Demonstration of Enhanced In Situ Bioremediation (EISB) with a Focus on Chloroform at a Field Site in Brazil

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Background/Objectives. Enhanced In Situ Bioremediation (EISB) applications based on anaerobic degradation processes have been established to great effect at contaminated sites in North America and Europe, but it is growing in other regions and emerging countries. The Latin American region is one such case in point, where public awareness of the importance of risks posed by contaminated sites develops each year. This abstract details one of the first known applications of EISB using electron donors to achieve anaerobic reductive dechlorination of a mixed plume of chlorinated compounds, with an emphasis on chloroform, at a field site in Brazil. The anaerobic degradation of chloroform is of particular interest due to its toxicity and noted recalcitrance in the subsurface soil. Chloroform (CF) is also a potent inhibitor of many vital microbial processes.

Approach/Activities. The project started with bench testing of field samples, which then led to a Pilot Phase (Pilot) testing the efficacy of milk whey and molasses as electron donors in the degradation of carbon tetrachloride and chloroform plume in an upper aquifer consisting of colluvial-alluvial materials deposited over crystalline basement rock. The pilot results indicated in-situ reductive dechlorination of CF, CT and other chlorinated compounds. Once the Pilot Phase (from December 2007 to March 2010) was concluded, Phase I and II (Full Scale) of the system using molasses was installed as two parallel biobarriers, perpendicular to the direction of the plume, and were placed at the center and downgradient edge of the plume. Donor addition (molasses) then proceeded for three years.

During both Pilot and Full Scale, system performance was evaluated using four lines of evidence: (a) declining concentrations of constituents of concern with generation of degradation products; (b) geochemical analysis to verify reducing conditions; (c) microbial community investigation using Denaturing Gradient Gel Electrophoresis (DGGE) and Polymerase Chain Reaction (PCR); and (d) Compound Specific Isotope Analysis (CSIA). The remedy effectiveness was also evaluated using conventional hydrogeological tools; tracer tests, slug tests and water level measurements. Stochastic modeling using PREMChlor (Probabilistic Remediation Evaluation Model for Chlorinated Solvents) was used to test the ability of analytical modeling to predict the observed system performance.

Results/Lessons Learned. The lines of evidence approach used various techniques which either did not exist in Brazil at the time or had not been used before to assess the performance of a remediation system, such as CSIA, DGGE and PCR. The data collected to date indicates that EISB was effective at treating these volatile organic compounds, with both biotic and abiotic degradation occurring. Probabalistic modeling using PREMChlor was partly able to capture the full range of observed plume response to treatment.

Back to Contents

Bioremediation of Hexavalent Chromium: A Few Significant Site Histories in Italy

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Background/Objectives. In situ bioremediation has a significant role in the remediation techniques for its general sustainability in terms of environmental impact and costs. However, while organics can be mineralized, inorganics can only change their oxidation state, hopefully reducing their toxicity and mobility in the environment.

The most common forms chromium in soils are Cr(III) and Cr(VI) species. Cr(VI) is water soluble and is highly toxic to all forms of living organisms, while Cr(III) sorbs or precipitates under common environmental conditions and is less harmful. Innovative and promising clean up technologies for Cr(VI) have been tested mostly at lab- and pilot-scale; among these, bio-induced reduction, bio-reduction and bioimmobilization.

In Lombardy (Italy), about 25% of the sites ranked in the Regional Plan of Contaminated Sites are affected by Cr(VI) in groundwater and/or soil. Therefore innovative sustainable remediation techniques are under investigation, with pilot- or full-scale applications reported in this paper.

Approach/Activities. Site n. 1 is a chromium plating factory, where Cr(VI) has affected soils down to 20 m b.g.s. (values up to 2000 mg/kg) and groundwater (values up to 200 mg/l) in the phreatic sandy-gravel aquifer (groundwater level at about 17 m b.g.s., hydraulic gradient of 0.15-0.3%). About 28000 l of MRC® and 3D-Me® products were injected at two different depth intervals (14-19 m b.g.s. and 20-25 m b.g.s.). Few months after injection, Cr(VI) concentrations in groundwater were about 100 µg/l, resulting in removals between 59% and 99%.

Site n. 2 is a weapons factory, where values of Cr(VI) in soils and groundwater were up to 5000 mg/kg and 600 µg/l, respectively. Lithology is quite heterogeneous. MRC® and 3D-Me® (2100 kg of both products) were injected in two trenches, resulting in concentrations of about 150 µg/l at the groundwater point of compliance.

EHC-M® was used for full scale remediation at site n. 3 (former chromium plating factory). Groundwater, in the semi-confined silty sand aquifer, was affected by Cr(VI), with values up to 200 mg/l in the plume 30 m long. Direct push injection (90 kg EHC-M) were carried out in the unsaturated soil and groundwater at the pollution source area. Redox potential and Cr(VI) decreased to values of -300 mV and <5 mg/l respectively.

At site n. 4, the phreatic aquifer (a mix of conglomerate, gravel and sand, with hydraulic gradient of 0.2-0.3%) was affected by Cr(VI) with values up to 20 mg/l, in a plume 260 m wide and 2.6 km long. A patented product (based on macronutrients for bacteria biostimulation) was injected 40 m far from the pollution source. After 40 d, values <5 mg/l were found in the monitoring wells 50 m and 300 m downgradient of the source area.

Site n. 5 (former chromium plating factory) is a very small area (150 m^2), where Cr(VI) in groundwater had values up to 540 mg/l. The patented product used for site n. 4 was injected downgradient of the source, resulting in concentrations of <5-100 mg/l at the two monitoring wells 90 m and 200 m downgradient of the source.

Results/Lessons Learned. The experience performed at the sites pointed out that Cr(VI) groundwater pollution cannot be solved unless the unsaturated zone is treated as well. Soil heterogeneity is a critical issue and mixtures usually have to be injected at different depths. Iron, manganese and sulphate side-contamination can result in groundwater after injections. In order to reduce costs, whey will be used for the second remediation step at site n. 1.

Back to Contents

Application of Molecular Biology for the Understanding, Engineering and Modeling of Chlorinated Solvent Bioremediation

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Background/Objectives. The successful bioremediation of chlorinated compound contaminated soil and groundwater relies on the appropriate physical chemical conditions as well as active microorganisms. Recent research has provided insight into the physiological requirements that the bacteria specifically responsible for chlorinated compound degradation require. Among them, compounds produced by other members of the microbial community (*e.g.*, acetate produced by *Clostridia*) appeared to be critical. Therefore, the microbial ecology of chlorinated compound degradation during soil and groundwater bioremediation can explain in part the success or failure of the applied technology.

Approach/Activities. Metagenomic approaches can help elucidate the relationships between different members of the microbial community, especially when some of the members are dependent on others for their substrates. In the case of the anaerobic degradation of chlorinated compounds by reductive dechlorination, some of the responsible bacteria (*e.g.*, *Dehalococcoides* sp.) require hydrogen and small organic acids such as acetate in addition to the chlorinated compounds, which serve as electron acceptors. Hydrogen and acetate are produced by fermentative bacteria degrading more complex organic compounds. We used next generation sequencing, quantitative PCR as well as molecular labeling to demonstrate the interrelationship of these different community members during the monitoring of successful bioremediation of chlorinated compounds, and investigated both laboratory- and field-scale sites.

Results/Lessons Learned. The calculated rates from these laboratory and field sites have been correlated to measurements of the relative gene abundance and qPCR values of specific genes, especially those for the degradation of less chlorinated intermediates. Characterization of the microbial community and their genes involved in the dechlorination food web could both demonstrate that the degradation is occurring and provide some insight into the relative speed of the degradation.

In Situ Microcosms for Evaluation of Sulfate Enhanced Bioremediation

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Background/Objectives. This paper summarizes the field implementation and results of a field treatability study performed to evaluate the anaerobic bioremediation of petroleum hydrocarbons at a site located in the Southeastern US.

The subject site's groundwater plume consists of dissolved-phase petroleum hydrocarbons and low-level, non-contiguous chlorinated solvents. Past work has accomplished LNAPL removal with no LNAPL detected since 2009. Hydrocarbon constituents of concern (CoCs) include BTEX and TMBs indicative of residual gasoline that accumulated in permeable sands at the water table ranging from 9 to 32 feet below ground surface. Following investigation and evaluation of the 10+ acre area of dissolved-phase impacts, geochemical conditions noted oxygen and nitrate depletion and limited evidence of iron and manganese reduction. Background ppm concentrations of sulfate existed, but within the dissolved-phase plume sulfate concentrations were less than background.

A remedial program of sulfate amendments was initiated in 2013 with three applications to-date. Additional applications are pending an evaluation of amendments to the sulfate solution to ensure residual CoC targets are effectively remediated to regulatory program goals.

Approach/Activities. The addition of sulfate to an anaerobic petroleum-impacted aquifer can stimulate benzene degrading and sulfate reducing microorganisms. At many sites, a common technological challenge is maintaining sufficient nutrient concentrations to support biomass growth as well as contaminant metabolism. The addition of nutrients can facilitate the remediation process.

Evaluation of corrective actions designed to enhance biodegradation of petroleum hydrocarbons include chemical, geochemical, and microbiological lines of evidence. Monitoring and analysis of trends in dissolved contaminate concentrations are routinely used to document contaminant loss and provide an indicator of enhanced biodegradation. However, the potentially most direct line of evidence to evaluate the ability of a remediation technology to stimulate biodegradation is to quantify the specific genes encoding enzymes responsible for biodegradation of the contaminants of concern.

To evaluate sulfate-enhanced bioremediation, Bio-Trap® and Bio-Stim® In Situ Microcosms were tailored to provide microbial, chemical, and geochemical data. Bio-Trap® samplers are passive sampling tools that collect microbes over time for the purpose of better understanding biodegradation potential. Bio-Stim® units provide means to evaluate groundwater geochemistry and potential amendments, in this case, additional electron acceptor (sulfate) and micro/macro-nutrients. Three separate units were placed in on-site monitoring wells consisting of:

1. Bio-Trap® Control Unit containing no additional electron acceptor or amendments and representing MNA or existing site conditions
2. Bio-Stim® Unit containing sulfate
3. Bio-Stim® Unit containing sulfate and nutrients

Results/Lessons Learned. Field implementation activities will be completed in October 2014. This paper will provide the results of analytical and microbial testing data. A summary of the lessons learned during the field implementation will also be provided.

Development of a Systematic Data Evaluation Procedure for a Bioventing System to Support Site Closure

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Background/Objectives. Aerating soils to stimulate in situ biological activity (bioventing) has been employed at multiple sites for reduction of aerobically-degradable volatile organic compounds (VOCs). This form of bioremediation is sustainable, low energy, and requires low maintenance. For this site, the system is being operated as a polisher to previously conducted thermal remediation.

The site historically consists of a sand and gravel pit in which illegal dumping of industrial waste occurred. A bioventing system began operation in 2011. Quarterly respirometry tests are conducted to evaluate oxygen utilization and system efficiency. The absence of oxygen utilization is the typical criteria to support system shut down. However, utilization data and site data do not always correlate. This paper examines ways to review various site data to effectively evaluate system performance, when the standard evaluation process falls short, to support moving the site towards closure.

Approach/Activities. Quarterly respirometry testing has been conducted since 2011 on selected piezometers. Ideally, over time as aerobically-degradable VOC concentrations decrease, it is expected that oxygen will not be utilized due to the lack of fuel (VOCs) for the microbial population. Bi-weekly soil-gas monitoring should show sustained high oxygen, low carbon dioxide, and low VOC concentrations over time. This scenario has been observed in several of the piezometers at the site. However, in several locations, the picture has not been as clear, requiring the development of a data review process to evaluate what is truly occurring at those locations.

For this next level evaluation, a flow chart was developed to evaluate respirometry, soil-gas, groundwater, and historic soil data through a step-by-step process. The purpose of the review process is to first evaluate if aerobic biodegradation is occurring at a location, followed by an evaluation of the presence of aerobically biodegradable VOCs in the soil-gas. Groundwater data are then reviewed to evaluate groundwater VOC concentration trends (aerobically- vs. anaerobically-degradable) in the area. Finally, historic soil data at that location are reviewed to compare with the soil-gas and groundwater data. All of the data are then reviewed to evaluate the potential need for anaerobic bioremediation following shutdown of the bioventing system.

Results/Lessons Learned. The results of the multi-stage data review allow independent evaluation of various areas and provide a process for determining what is occurring at each location. This process is instrumental to supporting system shut down in locations when the primary respirometry data review fails to provide a clear line of evidence. Relying on just respirometry data may result in excess operation of the bioventing system, causing a delay in moving the project towards site closure.

Low-Tech In Situ Screening Approach for Biostimulant Selection

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Background/Objectives. Biostimulant selection for in situ biological remediation projects is often based on pilot study results, with practitioners using numerous screening approaches for remedial additives such as electron donors, electron acceptors, and inorganic nutrients. A low-technology, in situ screening approach is presented employing Passive Release Sock (PRS) technology for the selection and efficacy evaluation of solid-phase biostimulants.

Approach/Activities. PRSs, composed of a filter fabric that contains biostimulants, are deployed into groundwater monitoring wells to evaluate additive effectiveness for enhancing the biological degradation of targeted contaminants. Upon PRS deployment into a monitoring well, biostimulant is released upon hydration and the additive propagates through the well bore and into the formation by hydrodynamic dispersion.

Screening remedial additives using PRS technology is a three-step process consisting of: 1) No-purge, pre-deployment groundwater sampling to establish baseline conditions at PRS deployment wells; 2) Deployment of PRSs containing biostimulant into the screened interval of the wells; and 3) Multiple rounds of no-purge groundwater sampling of deployment wells, with PRS replacements once additives are spent, to evaluate biostimulant performance. No purge sampling is performed given that both conventional three-well volume purging and low-flow sampling is anticipated to collect aliquots of formation water that have not been in direct contact with biostimulant, thereby increasing the likelihood of false negatives. Replacement of PRS is a function of biostimulant solubility and formation seepage velocity, with PRSs containing more soluble additives deployed in formations with faster velocities replaced more frequently than PRSs containing less soluble additives deployed in formations with slower velocities.

Results/Lessons Learned. Based on the results of dozens of biostimulant screening studies utilizing PRS technology from the USA and internationally, PRS screening study results are sound, predictive tools of biostimulant efficacy on a go-no go basis providing multiple lines of evidence that are temporally-based; however, these studies are not entirely scalable given they are carried out in well bores, not formation matrices. Three bioremediation case studies employing PRS technology will be presented, two from chlorinated volatile organic compound sites and one from a petroleum hydrocarbon site, in which PRSs were used to evaluate biostimulant efficacy.

A Novel Method to Assess Bioremediation Potential of Petroleum Hydrocarbons or Herbicides in Calcareous Cold Soils

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Background/Objectives. In the clay rich, calcareous soils of Western Canada, assessing the potential activity of microorganisms to degrade hydrocarbons can be challenging. Standard assays such as most-probable number rely on the culturing of microorganisms and the addition of radioactive labelled hydrocarbons hampers the ability of experimenters to manipulate the soil after incubation. As part of the Sustainable In Situ Remediation Cooperative Alliance (SIRCA), a novel approach using cavity ring-down spectrometers to assess the isotopic ratios of released CO_2 following amendment with a ^{13}C enriched compound such as benzene, phenanthrene or glyphosate. However, due to the pH of typical soils in Western Canada, i.e. > pH 7.4, released CO_2 from target compound mineralization can be immobilized on the soil surface. The goal of this project was to develop a method to assess degradative potential that was also suited to subsequent molecular analysis.

Approach/Activities. ^{13}C-labelled benzene or phenanthrene was added as the model of petroleum hydrocarbons and ^{13}C-labelled glyphosate as a model herbicide. Using sealed 160ml serum bottles, a 1M NaOH trap acted to draw released from the 5g surface soil. Subsamples of this NaOH and the soil samples reacted with 1M HCl and released CO_2 determined by GC/TCD. The concentrations of CO_2 in these gas samples were either diluted with CO_2 zero air or enhanced by the addition of 1.01% CO_2 so that the CO_2 concentration was in the optimal level (500 ppmv) for the Picarro G1101-i Isotopic Carbon Dioxide Analyzer.

Results/Lessons Learned. Over a 7-day incubation, ^{13}C-CO_2 from the degradation of labelled phenanthrene was observed, accounting for approximately 8% of total ^{13}C-CO_2 detected by day 7. The result for the remaining ^{13}C-CO_2 in the acidified soil also supported the increasing degradation of labelled phenanthrene during the incubation. However, typical field application rates of glyphosate are too low for accurate detection of degradation products such as CO_2 using this experimental procedure. Refinements to the technique are expected to allow characterization of herbicides as well as other contaminants.

Back to Contents

Use of Modern Molecular Technologies for Evaluating Electron Acceptors for Anaerobic Bioremediation of Petroleum Hydrocarbons

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Background/Objectives. Enhanced aerobic bioremediation technologies such as air sparging, oxygen injection, oxygen diffusion or the use of oxygen releasing compounds are commonly used to accelerate naturally occurring degradation of petroleum hydrocarbons (PHCs) and recalcitrant fuel oxygenates such as MTBE and TBA by indigenous microorganisms in the subsurface. However, these indigenous microorganisms do not function well in the high contaminant concentrations of the source area. Therefore, oxygen addition technologies have to overcome the anaerobic conditions firstly by meeting chemical and oxygen demand of the source area and often due to the presence of iron.

An evolution in the remediation of petroleum hydrocarbons has occurred that employs a sulfate-enhanced in situ remediation strategy. Sulfate reduction and methanogenic conditions appear to dominate natural degradation processes at most sites. These processes will cease in the presence of added oxygen. On the other hand, rejuvenating depleted sulfate, anaerobic groundwater bacteria may continue to use PHCs, MTBE and TBA for carbon and energy and thus mineralize them to carbon dioxide and water.

This paper summarizes the field implementation and results of a field treatability study performed to evaluate sulfate enhanced bioremediation PHCs using modern molecular technologies. The objective of this paper is to compare three approaches for the remediation of PHCs under anaerobic conditions: monitored natural attenuation (MNA), sulfate addition and sulfate / nutrient addition.

Approach/Activities. The use of modern molecular technologies allows for the direct monitoring of a site's indigenous microbial population. These techniques can be used to provide a significant insight into current bioremediation activities and provide strong direction in regards to electron acceptor selection and proposed remediation activities at a site. These insights can result in more efficient and effective remediation activities, greater bioremediation success, and an overall reduction in project lifecycle costs.

Results/Lessons Learned. This paper will provide the results of molecular testing and present an evaluation of the effectiveness of anaerobic bioremediation of PHCs. A summary of the lessons learned for deploying in situ traps to evaluate MNA, sulfate enhanced bioremediation and sulfate/nutrient enhanced bioremediation will be provided.

Utilizing Respirometry to Assess the Potential for Bioremediation

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Background/Objectives. Bacterial remediation of contaminated soil is a common practice in the United States. There have been many claims that soils augmented with commercial bacterial products improve degradation rates over in situ bacterial culture, but there is also evidence suggesting that naturally occurring bacteria are better acclimated and do not require augmentation. Respirometry testing is a technique whereby the respiration rate of bacteria is measured in a controlled environment. A respirometry study was designed to evaluate whether commercial bioaugmentation products have a significant advantage over indigenous bacteria. The oxygen uptake of bacteria naturally found in soil was compared to a soil augmented with a commercially available bacterial product with both soils receiving the same dosage of contaminant, in the form of hydrocarbons. If commercial bacterial products were to have an advantage over the in situ bacterial culture, then greater oxygen uptake would be observed in soil receiving the bacterial product compared to the soil containing just the in situ culture.

Approach/Activities. For this laboratory study, a commercial closed system RSA PF-8000 respirometer with specialized soil columns was utilized. This respirometer responds to pressure changes by delivering oxygen as it is consumed by the bacteria in the columns. A total of four soil columns were set up with each column receiving the same amount of soil and contaminant. Two columns received the same addition of the commercial bacterial product with the other two columns serving as controls containing just the in situ culture. The study was run for approximately two weeks with the oxygen uptake being monitored continuously in all columns. In addition to monitoring the oxygen uptake in the columns, final testing was conducted on the columns for Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), and bacterial plate counts.

Results/Lessons Learned. The columns that received the addition of the commercial bacterial product showed greater oxygen uptake initially compared to the in situ columns. However, at the conclusion of the study, cumulative oxygen uptake was comparable between all columns. In addition, the final COD and BOD values were comparable at 1254 mg/L and 1246 mg/L and 23 mg/L and 21 mg/L, respectively. The results of this study show that the use of commercial bacterial products can potentially aid in increasing the rate of biodegradation of contaminants in soil initially, but when given enough time, the in situ culture alone will give comparable results. However, the soil used for this study was humic and thus had a high initial bacterial count. Soils with higher clay content would be expected to have lower initial bacterial counts and bioaugmentation may have a greater effect. Also, for this study, the commercial bacterial product was only dosed once, but repeated dosing may maintain the higher rate that was observed earlier in the study. Therefore, time available for bioremediation and the type of soil to be bioremediated are critical factors to consider when evaluating whether or not the use of bioaugmentation products would be advantageous for bioremediation of contaminated soils.

Comparison of Chlorinated Ethene Degradation Rates and Geochemical Conditions at 40 Enhanced Reductive Dechlorination Sites

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Background/Objectives. Electron donor addition is a proven and effective in situ technology for stimulating enhanced reductive dechlorination (ERD) of chlorinated ethenes. Typically, large amounts of organic carbon are injected to generate methanogenic conditions, with additional injections often performed to sustain methane production. Adding large amounts of organic substrate increases costs and also increases the potential for secondary water quality impacts (SWQIs) to downgradient receptors.

Approach/Activities. In this work, we calculate zero- and first-order degradation rates for chlorinated ethene species (i.e., PCE, TCE, DCE, and VC) and total organic chlorine (TOCl) using data collected from injection area wells at over 40 different ERD sites. These rates are then compared with data for various geochemical parameters (e.g., iron, sulfate, methane, TOC), to identify relationships between chlorinated ethene degradation rates and site geochemical conditions. Questions addressed include:

- What are typical dechlorination rates at ERD sites?
- Are very reducing (i.e., methanogenic) conditions required for effective dechlorination?
- Does dechlorination continue following TOC depletion?
- Does dechlorination cease once methane production stops?

Results/Lessons Learned. Preliminary results of our analysis include the following:

- Chlorinated ethene degradation was better fit with a first-order relationship than a zero-order relationship.
- Degradation rates generally decreased with decreasing order of chlorination. Median first-order degradation rates for PCE, TCE, cis-DCE, and VC were 0.0087 d^{-1}, 0.0065 d^{-1}, 0.0052 d^{-1}, and 0.0044 d^{-1}, respectively.
- The median first-order degradation rate for TOCl was 0.0042 d^{-1}. TOCl degradation rates were more closely correlated with methane production rates than iron production rates.

Encountering Microbial Issues While Implementing Aerobic Bioremediation

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Background/Objectives. Aerobic bioremediation was implemented as a polishing remedy at five gasoline service station sites affected by low concentrations of petroleum hydrocarbons and methyl tertiary butyl ether (MTBE), and more significant levels of the daughter product, Tertiary Butyl Alcohol (TBA). The use of enhanced aerobic bioremediation for treatment of MTBE/TBA is established. At each site where the aquifer oxidation-reduction potential (ORP) was sub-optimal; a fast release oxygen amendment was added along with a slower release material to rapidly raise and maintain the aquifer ORP condition. In all but one site, the approach led to a site closure. The remaining site is the subject of this presentation.

Approach/Activities. Each site was assessed through groundwater monitoring events at baseline (pre-application) and at regular two month intervals (post-amendment application). The monitoring program was designed to document changes in contaminant mass, shifts in geochemistry/field parameters, and detect associated microbial populations/gene functions. These data were used in the initial design as well as to assist the project team in understanding the extent of aerobic conditions produced in the treatment area and to guide adjustments, as needed. The use of molecular biological tools (MBT's) was pivotal in identifying less favorable shifts in microbiological populations and helped track attempted corrections when alternative amendment strategies were employed.

Results/Lessons Learned. An initial amendment injection event at the subject site failed to show treatment progress and unusual fluctuations in carbon dioxide (CO2) and methane were observed between monitoring events. Geochemistry and field parameters failed to identify the cause of the sluggish performance, suggesting a microbial issue might explain the data. Total microbial populations, fuel oxygenate degraders, methanogens (anaerobic bacteria that generate methane), and methanotrophs (aerobic bacteria that degrade methane and produce CO2) were evaluated. The data showed unusually high densities of methanogens and methanotrophs, not often found together, creating a cycle of CO2 and methane production and utilization. In effect, the methanotrophs had suppressed other microbial populations, scavenging the oxygen, and preventing more significant degradation of COCs.

A second injection event was completed with a higher loading of amendment to increase oxygen in the short term to attempt to satisfy the demand of the methanotroph population. The approach was unsuccessful. A third injection event used a high loading/high volume approach in an attempt to overload the pore space in the treatment area to satisfy the oxygen demand and create an excess of oxygen that would allow other microbial populations to rebound in number and become active. Results showed limited success with minor changes in field parameters/geochemistry, with decreases in COCs. Unfortunately, an aerobic environment could not be sustained. Fuel oxygenate degrading bacteria did increase for a short time in conjunction with significant decreases in methanogen populations and modulation of the methanotroph densities, but conditions have gradually returned to those pre-injection. The overall conclusion is that an aerobic environment cannot be sustained and an alternative closure strategy is being pursued.

Back to Contents

Long-Term Evaluation of Micro-Scale ZVI and Organic Carbon Reactivity in a Permeable Reactive Barrier Application

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Background/Objectives. Long-term effectiveness of *in situ* remediation applications is often based on the longevity of the amendments employed. In particular, in Permeable Reactive Barrier (PRB) applications and in cases with a continuing source, the longevity of the amendments employed will dictate the frequency of reapplication required. PRBs composed of granular Zero-Valent Iron (ZVI), have lasted for over 10 years in the subsurface. Over the last decade, injectable amendments with more fine-grained ZVI has gained popularity as installation via direct push injection in many cases is more practical, cost-efficient and less invasive. For example, EHC® is an integrated combination of controlled-release plant-derived organic carbon plus micro-scale ZVI particles, specifically formulated for application via direct injection. The first full-scale application of EHC into a flow-through reactive zone was installed in April 2005 for interception of a 2,700 ft long carbon tetrachloride (CT) groundwater plume. The target goal for the PRB set forth in the Voluntary Clean-up Plan developed for the site is to maintain a removal efficiency of at least 95% reduction in CT compared to baseline concentrations at compliance points located 70 and 140 ft downgradient from the PRB.

Approach/Activities. A total of 48,000 lbs of EHC was injected into an area measuring approximately 270 ft long x 15 ft wide x 9 ft thick on average. The reactive zone was installed along the side of a road and extended across the plume to limit further plume migration. The EHC slurry was injected into a line of injection points using direct push technology targeting an application rate of 1% EHC by soil mass. At the initiation of the field implementation, after one injection point had been completed, verification borings were collected around the injection point to confirm a radius of influence of at least 5 ft. Based on this a spacing of 10 ft was employed between injection points.

Results/Lessons Learned. CT removal rates peaked 16 months after installation at >99 percent removal. Two years after installation these rates decreased slightly to approximately 95 percent removal, and have stabilized there and remained at that level for eight years now continuously supporting treatment of inflowing groundwater. A significant increase in Dissolved Organic Carbon (DOC) was measured 70 ft downgradient from the PRB during the first 1 to 1.5 years. Since then DOC levels returned closer to background levels, suggesting that the more readily degradable carbon component (cellulose) had been consumed. However, despite declining levels of organic carbon in groundwater, reducing conditions have been maintained by low levels of DOC and from the hydrogen produced from ZVI corrosion. Since the installation of the PRB it has served to significantly reduce the size and concentration of the downgradient plume. Using an estimated linear groundwater flow velocity of 1.8 ft/day and a porosity of 30%, the PRB has treated an estimated total of 4,000,000 ft^3 of groundwater during its life-time. The reactive zone constitutes a green solution (no energy requirements) and maintenance costs are limited to groundwater monitoring over the life of the PRB.

Diffuse Downgradient Plume Management: Biobarrier Operation and Plume Delineation with HPT-GWS

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Background/Objectives. The Bountiful/Woods Cross Operable Unit 1 Site (the Site) in Utah is located in southern Davis County Utah, roughly 10 miles north of Salt Lake City and consists of a trichloroethene (TCE) plume emanating from a residual source area where contamination originated from leaks, spills, or discharges to the ground. The downgradient plume continues for approximately ½ mile to the west of the source area and encounters flowing artesian conditions toward the western edge of the plume. The treatment zone comprises heterogeneous deposits of dense, well-graded sand and gravel, alternating with layers of sandy, silty clay. A series of biobarriers have been installed to treat the diffuse downgradient plume. To better define the extent of the plume to maximum contaminant levels (MCLs), a High Resolution Site Characterization (HRSC) technique, Hydraulic Profiling Tool – Groundwater Sampler (HPT-GWS), was used to collect hydraulic and contaminant data. Membrane interface probe has also been used at the site to delineate high concentration contaminants, but HPT-GWS was selected to achieve the objective of delineating the plume to MCLs.

Approach/Activities. Biobarriers were installed using a TRIAD approach within the core of the diffuse downgradient plume in 2011. The core of the plume was defined by concentrations of contaminants exceeding 200 parts per billion (ppb); monitored natural attenuation was selected for areas outside of the core. Injections of emulsified oil were completed in 2011 and 2013 to establish adequate reducing conditions to promote reductive dechlorination; bioaugmentation with an active dechlorinating culture was also completed. Performance of the biobarriers is monitored semiannually using a series of monitoring wells. To better define the extent of the diffuse plume that exceeded MCLs, HPT-GWS was completed using a TRIAD approach. HPT-GWS provided both hydraulic characteristics of the aquifer, as well as the ability to collect groundwater samples from the primary transmissive zones that are the most likely conduits for contaminants. Use of HPT-GWS allowed for rapid delineation of the plume exceeding MCLs, guided the installation of monitoring wells in appropriate depths and locations, and minimized waste and issues associated with artesian conditions.

Results/Lessons Learned. The presentation will include a description of biobarrier installation techniques, maintenance, and performance, which has included complete reduction to ethene downgradient of the barriers. A discussion of the use of HPT-GWS to rapidly delineate the overall plume extent, including contaminants present at low concentrations, and advise future remedial action, will also be presented. The techniques in combination provide promise for delineation of plumes and to guide targeted treatment with regard to depth and aerial extent.

Design and Installation of a Permeable Reactive Barrier for In Situ Anaerobic Bioremediation of TCE in Groundwater

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Background/Objectives. Permeable Reactive Barriers (PRBs) represent a potential alternative to traditional engineered systems for the remediation of shallow groundwater contaminated with chlorinated aliphatic hydrocarbons and other contaminants. In conjunction with the U.S. Department of Agriculture (USDA), Agricultural Research Service (ARS), BMT recently completed the design and installation of a 1,000-foot PRB at the Beaverdam Road Landfill (BDRLF) site (BARC 27) at the Beltsville Agricultural Research Center (BARC), a National Priority List site located in Beltsville, Maryland, as the selected remedy for a dilute plume of trichloroethene (TCE) in shallow groundwater migrating from a former municipal waste landfill. TCE was identified in groundwater at maximum concentrations greater than 500 parts per billion (ppb) migrating from the landfill toward the downgradient wetlands and perennial stream. The objective of the PRB is to create conditions conducive to biodegradation of TCE and its degradation products via microbially-mediated reductive dechlorination and reduce concentrations in groundwater to below regulatory Maximum Contaminant Levels over time.

Approach/Activities. ARS and BMT collaborated on PRB design including an evaluation of groundwater physical and geochemical characteristics, soil lithology, groundwater flow rates, contaminant degradation rate(s), and predicted contaminant residence time within the biowall. A bench-scale study determined that the optimal PRB composition for the BDRLF site should be 30% compost, 30% mulch, and 40% sand by volume.

The two-foot wide PRB was installed in 2013 using single-pass trenching technology to a total depth of approximately 20 feet below ground surface, set 1 foot into the underlying clay aquitard ensuring that groundwater could not bypass the PRB. Ten (10) monitoring wells were installed along the wall centerline. An additional six (6) monitoring wells were also installed in a transect oriented perpendicular to the PRB along the axis of highest contaminant concentrations. Ongoing performance monitoring includes measurements of selected physical, chemical, and geochemical parameters on a biweekly and quarterly basis using field instrumentation and fixed laboratory analysis.

Results/Lessons Learned. An overview of the design and installation process, including lessons learned, will be presented. Performance results from the first four quarters have identified geochemical conditions consistent with anaerobic microbial metabolism. In September 2014, TCE concentrations of 530 and 0.37 ppb were detected upgradient and downgradient of PRB, respectively. TCE degradation products including cis-1,2-dichloroethene and vinyl chloride were detected at concentrations greater than their respective historic site maxima in downgradient groundwater, indicating that reductive dechlorination is occurring within the PRB.

Biobarrier for HCH Removal from Mine Water of a Former Uranium Surface Mine

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Background/Objectives. Lindane (γ-hexachlorohexane, HCH) was widely used throughout much of Europe in the second half of the 20th century as an effective and inexpensive insecticide. Its production resulted in large amounts of waste chemicals, namely an estimated 9 tons of inactive HCH isomers (α-, β-, δ- and ε-HCH) for every ton of lindane produced. Historically, these isomers were very often disposed of in uncontrolled dump sites. This was the case at a former surface uranium mine in Czech Republic with more than 5,000 tons of HCH waste. The dump heap area impacted a spring at 3-5 l/s and became a chronic source of surface water contamination with concentrations of HCH, chlorobenzenes (CB), Fe and Mn measured at 90 - 160 µg/l, 300 µg/l, 15 mg/l and 15 mg/l respectively. These values are well in excess of permissible Czech limits of 0.01 µg/l (lindane), 0.02 µg/l (total HCHs) and 0.01 – 1 µg/l for various chlorobenzenes. A feasibility study with an interdisciplinary focus was conducted to evaluate viable remedial alternatives and reduce/treat the discharging mine water. Passive natural treatment systems were constructed to test different treatment technologies without use of electricity and chemical reagents. The promising results of these studies will be used for construction of full scale biobarrier treatment system.

Approach/Activities. Degradation of HCH was firstly tested by column tests in a laboratory followed by field pilot tests. Two columns were operated, column 1 with combined media for sorption and biodegradation (40%wt. gravel, 20%wt. sand, 20%wt. peat, 20% wt. substrate (1:1 grout to dry maize mulch), column 2 for biodegradation (40 %wt. gravel, 30%wt. sand, 30%wt. substrate as above). Column testing was conducted over a period of 126 days with different flow rates (3, 6, 12 and 3 pore volumes per day). Four field pilot test systems were installed and operated during the one year test period: *A) Aerobic wetland system* using aerobic degradation, photodegradation and phytoremediation processes. Natural wetland is formed by 0.5m soil layer, which is planted with wetlands plants, *B) Anaerobic wetland system* consists of two stages of treatment. The first step is anaerobic bioreduction (filled by cereal scraps, wood chips) followed by natural wetland system, *C) Granulated iron barrier system* is formed by three iron filled filters followed by a sedimentation reservoir where dissolved iron is oxidized by atmospheric oxygen, *D) biologically enhanced sorption system* is formed by iron sedimentation reservoir followed by biologically enhanced sorption filters (peat and wood chips). Operational flow rates of 0.0016 – 0.2 l/s were achieved and the residence time of water in the system ranged from 1.0 to 20 days. Efficiency was evaluated on basis of averaged results. Basic parameters including pH, ORP, HCHs and CB, heavy metals, basic anions and cathions were monitored at the outlet of test systems.

Results/Lessons Learned. Column test results were confirmed by field pilot tests results. Column 1 removed 62 % of HCH concentrations and 90% of CBs, column 2 74% of HCHs and 91% of CBs at flow rates of three pore volumes per day. With higher flow rates, the treatment efficiency decreased to 34% for HCHs and 48% for CBs in column 1 and 31% for HCHs and 39% CBs in column 2 for the flow of twelve pore volumes per day. The aerobic system removed 83 – 99% of HCH and 53 – 96% of CB while the anaerobic system removed 77 – 97% of HCH and 81 – 96% of CB. The iron filter removed 56 – 83% of HCH and 37 – 63% of CB. The

Back to Contents

Microdiffusion of Pure Oxygen in Groundwater Contaminated by Biodegradable Organic Compounds and Metals

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Background/Objectives. This project was carried out for a pharmaceutical sector client, owning an operating site subject to remediation procedures for groundwater contamination due to Aromatic (BTEX) and Aliphatic hydrocarbons. As usual, in order to apply emergency measures on site, Public Authorities requested the implementation of a Pump & Treat system, but the public treatment plant to which the pre-treated water should have been conveyed didn't have enough treatment capacity.

Approach/Activities. To overcome this issue, AECOM proposed the application of Microdiffusion of pure oxygen to implement a "biodegradation" barrier by means of the Ground BIO2® system (SIAD S.p.A.). By using pure oxygen instead of air it is possible to dissolve in groundwater a concentration of oxygen that is more than four times greater than with traditional systems (AS, BS, ORC®, etc.).

First, a batch pilot test was performed with remarkable results (complete degradation of contaminants without stripping effect). After that, a field-scale pilot test of microdiffusion of pure oxygen was performed in an on-site well with some lateral and downgradient monitoring wells. This pilot test was aimed at defining the site-specific radius of influence through the use of noble gases (reached after three month from the test start) and was subsequently confirmed by the growing of generic and specific strains of degrading bacteria (from $10^{+1/+3}$ UFC/mL to $10^{+4/+6}$ UFC/mL) and by the contaminants removal rate, which, after 8 months, resulted to be higher than 95 - 99% in both lateral and downgradient monitoring wells. Moreover, while the reducing conditions created by contamination entail the dissolution of some metal (Fe, Mn and As), during the pilot test the re-precipitation of the three metals was observed thanks to the restoring of natural oxidizing conditions.

In addition, during the pilot test an excessively high oxygen consumption was observed in a localized area of the site and subsequent GC/MS fingerprint analysis highlighted the presence of some new contaminants such as Tetrahydrofuran, Dichloromethane, Acetone, etc. Consequently, a second batch test was performed, which confirmed the removal of these contaminants too, due to aerobic metabolism or co-metabolism in presence of aromatics compounds.

Results/Lessons Learned. The use of pure oxygen barriers instead of traditional P&T systems implied a great economic saving for the client. The advantages and sustainability of this technology were appreciated by Public Authorities, who finally requested the implementation of a remediation project based on pure oxygen microdiffusion. Full project design was completed in June 2014 with four curtains of oxygen microdiffusion, for a total of 44 points and a length of 160 m. The system start-up is scheduled for the end of September 2014. In conclusion, it has to be highlighted that microdiffusion of pure oxygen presents benefits also for the environment, in terms of no waste production, no contaminants transfer from one media to another, restoring of previous natural conditions, shorter remedial time than standard methods, etc. On the whole, considering its overall benefits, gas microdiffusion has the potential for further uses for remediation or engineering purposes.

The Application of ISCR Chemistries for Enhanced Dehalogenation of Contaminated Groundwater Using Permeable Reactive Barriers

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Background/Objectives. An enhanced bioremediation technique involving permeable reactive barriers (PRBs) through the injection of zero valent iron (ZVI), hydrogen donors, and microbial nutrients was implemented at a contaminated site located in the Southern United States. The contaminants of concern (COC) comprise a variety of brominated and chlorinated organic compounds including 1,2-dibromo-3-chloropropane (DBCP), 1,2-dibromoethane (EDB), 1,2-dichloroethane (EDC), 1-bromo-2-chloroethane (BCE), tetrachloroethene (PCE), trichloroethene (TCE), and 1,2-dichloroethene (1,2-DCE). The uppermost water-bearing sediment at the site is dominated by quaternary deposits consisting of silty sand, silty clay, and sandy clay. This water bearing zone sits on top of a mountain formation that prevents the downward migration of surface water and shallow groundwater into the regional aquifer. The shallow groundwater is present at approximately 5 to 12 feet below ground surface (bgs).The objective of this project is to restrict plume migration by enhancing groundwater biogeochemical conditions (e.g. pH, ORP) such that beneficial biota proliferate in the shallow groundwater, which will provide accelerated kinetics for biotic and abiotic reductive dehalogenation reactions.

Approach/Activities. A network of three PRBs was constructed in order to adjust the groundwater biogeochemistry within the PRBs, such that naturally occurring dehalogenation processes (e.g. abiotic and biotic) would be enhanced. Multiple sized ZVI particles, a combination of fast and slow release hydrogen donors, and microbial nutrients were injected at depths ranging from 5 to 15 ft. bgs. The injections were designed to emplace the remediation materials in direct contact with the dissolved phase plume. Evaluation of the PRB network performance is accomplished through a detailed groundwater monitoring program involving monitoring wells and piezometers.

Results/Lessons Learned. One year post implementation, groundwater results indicate significant decreases in the total concentrations of site COCs and improved biogeochemical parameters downgradient of the PRBs. Impacted monitoring wells and piezometers show average decreases in EDB and PCE groundwater concentrations of approximately 70 percent each; DBCP and BCE groundwater concentrations have decreased by more than 60 percent each; and EDC groundwater concentration has decreased by an average of 30 percent. However, groundwater monitoring results show average increases in TCE and 1,2-DCE of 77 percent and 95 percent, respectively. The increase in TCE and 1,2-DCE groundwater concentrations was expected because they are daughter products of PCE reductive dechlorination and should eventually be reduced to ethene. Also, improved biogeochemical conditions such as pH, ORP, dissolved iron, and sulfate concentrations have been observed across the entire area of concern. This presentation will include monitoring data through the 1st quarter of 2015.

Testing of a Permeable Reactive Barrier and Engineered Wetland for Metals Removal in a Remote Location

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Background/Objectives. Permeable reactive barriers (PRB) and engineered wetlands are passive treatments that intercept and treat contaminated groundwater or surface water prior to discharge. Both technologies can use physical, chemical and biological mechanisms to remove pollutants from water. Passive treatments such as PRB and engineered wetlands, one designed and implemented, required little further input of energy or labor. Beyond routine inspections and maintenance, these systems can be left alone and can provide long term, low cost treatment for water. They are also suitable for implementation in remote locations since they do not require an energy source or human operator.

The solubility of metals in water varies with pH. Copper and nickel are relatively insoluble at a higher pH levels. Limestone increases the pH of water, lowering the solubility of metals and causing metals to precipitate from the water. Limestone dissolves slowly; therefore, it can neutralize low pH/increase pH over extended periods of time.

Low pH and dissolved nickel and copper are present in surface water at a site in northern Ontario (Site). Passive treatment is preferred for this water due to its remote location. Remedial options identified the construction of PRB, limestone-lined channels, and a limestone-lined wetland.

Approach/Activities. A laboratory treatability study was performed to establish design parameters and guidance for the use of limestone. Elements of the study included screening different types of limestone that were available locally to the Site in order to determine the one with the greatest capacity to increase the pH of water and lower metals concentrations. Minimum hydraulic retention times of the water with the limestone and the longevity of the limestone were then tested. Finally the amount of clogging of the limestone that had occurred during the study was calculated.

Results/Lessons Learned. The results of the study showed that limestone from different sources had different removal efficiencies for metals. A limestone that was effective but still available locally to the Site was selected for further testing. The study showed that this limestone could remove metals to the required metals levels. The longevity of the limestone was improved by the presence of organic material, suggesting that the engineered wetland would have greater longevity than the PRB.

These parameters were used to create a design for full scale treatment for the removal of copper and nickel from the water. Details of the laboratory study and the full scale design will be presented.

Applications of Combined Biotic and Abiotic Processes to Establish a TCE Permeable Reactive Barrier

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Background/Objectives. Soil and groundwater at an industrial facility in Denver, Colorado had been affected by discharges of trichloroethene (TCE). The affected unconfined aquifer consists of high hydraulic conductivity unconsolidated alluvial sediments overlying fractured bedrock. Groundwater in the affected aquifer is moderately aerobic. TCE was detected in the groundwater at concentrations up to 500 µg/L and minimal degradation products were present. To prevent the TCE from migrating off-site a permeable reactive barrier (PRB) was installed on the distal end of the plum. A novel substrate which enhances both biotic and abiotic processes was selected as the substrate to establish the PRBs.

Approach/Activities. EHC®-Liquid was selected as the substrate to establish the PRB. This substrate consists of a mixture of organic substrate (emulsified lecithin substrate; ELS™), and a water-soluble organic iron. This substrate was selected because of the enhanced distribution characteristics of the incorporated lecithin, the inclusion of essential nitrate and phosphate, in the molecular structure of the lecithin, the enhanced biological processes resulting from the increased electron shuttle processes and abiotic degradation pathways resulting from the include soluble iron. The substrate was buffered using potassium bicarbonate. A dechlorinating microbial culture (SDC-9™; CBI Federal Services LLC) was injected with the substrate.
The substrate was distributed in the aquifer using direct push technology. Injection locations were spaced 20 feet on center perpendicular to the direction of groundwater flow across the plume. Baseline and performance monitoring was conducted in a monitoring well downgradient from the PRB.

Following substrate injection TCE, concentrations decreased rapidly in the down gradient performance monitoring well. Daughter products including cis 1, 2-DCE and VC were observed but at concentrations substantially less than the stoichiometric TCE concentration indicating an abiotic component to the degradation pathway. The initial barrier was demonstrated to prevent the off-site migration of the chlorinated ethene as anticipated.

The PRB was effectively established by distribution of substrate by both direct push technology. Based on the successful results of the original barrier, a second was installed up gradient of a groundwater extraction system that had been used to limit off-site migration. The substrate (EHC-Liquid) was distributed using small diameter (1-inch) injection wells installed in two off-set rows perpendicular to the direction of groundwater flow. Following injection, degradation of the CEs was observed and the extraction system was dismantled resulting in substantial saving. A third PRB was subsequently installed in a similar directly down gradient of the source area.

Results/Lessons Learned. All PRBs have been demonstrated to effectively prevent migration of the CEs from the source area to the property boundary. In each of these barriers, the combination of lecithin and organic iron resulted in both biotic and abiotic degradation of the TCE. Degradation of the TCE continued in the PRB for a minimum of 3 years.

Maximizing Performance and Minimizing Cost of EVO PRBs

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Thousands of emulsified vegetable oil (EVO) permeable reactive barriers (PRBs) have been installed over the past decade to treat a variety of groundwater contaminants including chlorinated solvents, chromium, uranium, nitrate, perchlorate, explosives, and acid mine drainage. These barriers can provide very high levels of treatment. However, there are significant costs associated with barrier installation and periodic rejuvenation. In this presentation, we will review the different factors controlling both PRB performance and cost, and present a methodology to maximize performance and minimize cost.

The primary factors controlling PRB treatment efficiency are: (a) effective distribution of EVO away from the injection wells; and (b) sufficient contact time for contaminant biodegradation. When EVO is injected, the oil droplets are transported away from the injection well by dilution and/or chase water. As they migrate through the aquifer pores, they will collide with sediment surfaces and stick. In the subsurface, the oil droplets gradually hydrolyze releasing glycerol and long-chain fatty acids (LCFAs). The high solubility glycerol will be rapidly consumed or transported downgradient by groundwater flow. LCFAs in the aqueous phase can be fermented releasing H_2, acetate, and a new fatty acid with two fewer carbon atoms. However in the subsurface, much of the LCFA rapidly precipitates or sorbs to sediment surfaces, greatly reducing substrate bioavailability and extending the useful life of the injected substrate. Acetate released from LCFA fermentation degrades relatively slowly, so significant concentrations of acetate (TOC) are often measured in monitoring wells. In contrast, H_2 reacts very rapidly and so is only present close to where the LCFAs are sorbed. Since H_2 is required for reduction of DCE to ethene, complete dechlorination requires that the contaminant come into close contact with residual LCFAs, not just acetate. If EVO is not effectively distributed away from the injection wells, there will be gaps in the PRB with little LCFA, and treatment efficiency will be reduced.

The primary cost drivers for PRB installation and maintenance are well installation, substrate purchase, labor for injection, and reinjection frequency. The amount of EVO required is controlled by: (a) oil retention capacity of the aquifer; and (b) amount of electron donor required to reduce the target contaminant and background electron acceptors. At many sites, the EVO required to match the oil retention capacity of the aquifer is much greater than the electron donor demand, and costs can be reduced by using an EVO with very low oil retention. However in some coarse-grained, high GW velocity aquifers, the high flux of background electron acceptors (O_2, NO_3, SO_4) through the PRB can rapidly deplete the available substrate, requiring frequent reinjection to maintain performance. At these sites, use of a self-emulsifying oil with large droplets and high oil retention can reduce reinjection frequency, reducing overall life-cycle costs.

Our methodology for maximizing PRB performance and minimizing cost considers the following factors in identifying the most cost-effect design: (a) site hydrogeology and groundwater velocity; (b) concentration of target contaminants and background electron acceptors; (c) aquifer minerology, particle size distribution and surface charge; and (d) oil droplet size distribution and surface charge.

Use of Constructed Wetlands to Remediate LNAPL-Contaminated Groundwater on Former Industrial Property

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Background/Objectives. An industrial property formerly owned by General Motors in Ypsilanti, MI was used for airplane and vehicle production for 68 years. Now, as a part of the General Motors bankruptcy settlement, RACER Trust has assumed responsibility for the revitalization and sale of the property. More than 40 acres on the site have groundwater contamination consisting of light non-aqueous phase liquids (LNAPL), phosphorus, and possibly trace heavy metals and volatile organic compounds (VOCs).

Approach/Activities. Our goal was to assess the feasibility of a wetland treatment system as a long term solution to this contamination. This approach involved extensive literature research and bench scale testing for proof of concept, as well as in situ pilot testing designed to simulate multiple treatment train. Phytoremediation through wetland vegetation and sorption of contaminants to native or introduced media were the primary treatment mechanisms.

Results/Lessons Learned. Based on the success of wetlands in other contaminated sites, and on a pilot study run during the summer of 2014, we have determined that a wetland and leach field system can reduce contamination below levels required by an expected NPDES permit, and will have a lower overall cost than sending the water to the local wastewater treatment plant. Cost analysis considered installation, operation, and maintenance costs of the wetland/leach field treatment system, as well as the opportunity cost of using the land the system would occupy.

Back to Contents

Full-Scale Electrokinetics-Enhanced Bioremediation (EK-BIO) of PCE DNAPL Source Area in Clay Till

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Background/Objectives. The success of in-situ remediation technologies requires effective and uniform delivery of remediation reagents through the target treatment area. Traditional amendment delivery techniques based on hydraulic advection mechanisms are often faced with limitations in areas with low permeability materials and/or highly heterogeneous geology. Transport of ionic substances, such as lactate, in an electric field is relatively independent of hydraulic properties and fluid flow. Therefore, electrokinetics-enhanced amendment delivery represents an innovative solution allowing effective in-situ remediation in areas where permeability is limited and heterogeneous.

In 2011, a field pilot test was carried out at the Skuldelev site, Denmark to assess the ability of the novel EK-BIO technology to treat PCE DNAPL source material in clay till with interbedded deposits of sand. The EK-BIO pilot test demonstrated the transport and distribution of amendments (lactate and microbial culture KB-1™) through clay soils in the target area. Results from groundwater and clay soil sampling showed significant reductive dechlorination of PCE to cisDCE, VC, and ethene coupled with significant levels of dechlorinating microorganisms (*Dhc* with vcrA), indicating that PCE dechlorination in clay soil was achieved by EK-BIO with KB-1™ bioaugmentation. Based on the successful pilot test, a full-scale remediation was implemented.

Approach/Activities. The full-scale EK-BIO implementation targeting a PCE source area at the Skuldelev site was initiated in December 2012. The treatment zone, addressed by a network of 15 electrode wells, covers an area of 100 m^2 to a maximum depth of 10 m bgl. The overall area is divided into two sub-areas, which are treated in alternating stages, each for a period of three months. The polarity of the electrodes is changed to alter the current directions and electric field orientations in alternating stages in order to optimize the EK transport efficiency and to achieve treatment of the entire target zone for remediation. Performance monitoring comprises monthly water sampling for TOC and field measurements, as well as quarterly water sampling for complete characterization of contaminant composition and degradation processes. In addition, soil sampling was also performed at the end of select stages of operation to assess treatment in clay materials.

Results/Lessons Learned. Result from the first two years of EK-BIO operation will be presented. At present, five stages (approximately 20 months) of operation and monitoring have been completed with very encouraging and expected results. Both electron donor and *Dhc* have been distributed throughout the treatment area and complete reductive dechlorination of PCE to ethene has been well established where the degree of dechlorination continues to increase. Orders of magnitude increases of *Dhc* have been observed between clay soil samples collected before remediation and following one year of implementation. Soil sampling data support the groundwater monitoring data and confirm that EK-BIO implementation has achieved active reductive dechlorination treatment within low-permeability clay materials. Successful implementation of this EK-BIO project will broaden the applicability of various in-situ remediation technologies.

Conditional Closure of Tetrachloroethene Site using Large-Diameter Treatment Column (LDTC) and Anaerobic Reductive Dechlorination

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Background/Objectives. At a former dry cleaner site in Aurora, Colorado, delivery of potassium and sodium permanganate via a dense network of discrete injections was not completely effective in oxidizing tetrachloroethene (PCE) and other chlorinated solvents to levels acceptable to the Colorado Department of Public Health and Environment (CDPHE). The concept of a large-diameter treatment column (LDTC) was developed and installed in July, 2011. This project tested both a new amendment delivery system (the LDTC) and a liquid reagent for anaerobic remediation of chlorinated hydrocarbons and redox-reactive metals, composed of a buffered micro-emulsion of slow-release, food-grade carbon (lecithin), an organo-ferrous iron compound, and a redox buffer. After initial pilot testing success, the LDTC was used to deliver bioaugmentation in the form of *dehaloccoides mycarti* (Dhc) which included the coronoid B1. Results of the original pilot-scale test will be presented including successful reductive dechlorination of PCE and stepwise dechlorination compounds over the past 3 years. In January 2014, CDPHE developed Low Risk Closure Policy for sites that can be closed with an areal environmental covenant given declining contaminant trends after active remediation ceases. This project successfully demonstrates the effective treatment of PCE to risked-based closure levels. CDPHE granted closure after presentation and defense of multiple lines of evidence in September 2014.

Approach/Activities. The LDTC is a large (36-inch)-diameter borehole advanced 30 ft into the suspected source area of chlorinated solvent impact. The LDTC was designed as a high-volume, high-surface area delivery and bio-reactor system to effectively treat contaminants within the LDTC as well as distribute amendments to the subsurface in low-permeability soils. The LDTC was sequentially backfilled with the engineered remediation products as described; in this case zero-valent iron in the backfill and the carbon-iron-redox buffered liquid amendment as noted. As pilot testing was evaluated, including the present microbial population, the LDTC was also used to bioaugment the impacted hydrogeologic system with *dehaloccoides* mycarti which contained the coronoid B1. Molecular biological tools (MBT) were used to assess how the treatments and bioaugmentation affected the microbial ecology by evaluating the microbial populations pre- and post- installation of the LDTC and addition of various amendments. This data was used to support multiple lines of evidence in achieving site closure under the new CDPHE Low Threat Closure Policy.

Results/Lessons Learned. Chlorinated ethene concentrations and other standard physical and chemical parameters were analyzed over 3 years during biostimulation and bioaugmentation. The molecular diagnostics described at pre-treatment along with contaminant profiles over time were characteristic of a non-degrading system and continued through the course of biostimulation and bioaugmentation. Post-LDTC installation data indicates that chlorinated solvent concentrations have significantly decreased in the pilot study area to levels that warranted application for conditional closure under the new regulatory guidance. Discussion will be presented on multiple lines of evidence supporting the final regulatory decision.

Targeted Delivery of Functional Nanoparticles for Soil Remediation

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Background/Objectives. Perhaps the biggest challenge facing remediation scientists and engineers is to overcome delivery limitations. The delivery of reagents into a target treatment zone is critical for success particularly when controlled reactivity is of concern. This delivery challenge is enhanced in the vadose zone where hydraulic control is minimal and the gas phase dominates the pore space. Targeted delivery of engineered nanoparticles is an emerging area of interest. The special characteristics of nanoparticles (e.g., size, large surface area, and functional capabilities) may provide a host of yet undiscovered advantages compared with conventional delivery systems. Developments in nanotechnology over the last decade have allowed engineers to make any shape, size or particle that they desire, but more importantly hollow nanoparticles can be synthesized to contain reagents that can support bioremediation. The objective of our work is to build on emerging nanotechnology developments and apply them to the targeted delivery of reagents to treat heavy hydrocarbon impacted vadose zone soils.

Approach/Activities. Our approach to use functional nanoparticles for soil treatment involves three key facets: 1) delivery of the functional nanoparticles into the heavy hydrocarbon impacted soils, 2) engineering the surface of the nanoparticles to bind at the hydrocarbon interface, and once attached 3) releasing or activating the sequestered treatment reagent or functionality. We are using a series of bench-scale experiments to establish proof-of-concept. Column experiments are being used initially to establish a degree of basic understanding and optimization, and then larger sand-box experiments will be employed to generate realistic metrics for up-scaling to field conditions.

Results/Lessons Learned. Delivery of nanoparticles into the contaminated subsurface is a critical step to enable a variety of treatment methodologies; however, nanoparticle transport through porous media has been shown to be an extraordinarily challenging proposition, due to the high surface energy and agglomeration potential of typical nanomaterials such as nano zero-valent iron (nZVI). In this work, nanoparticles have been designed for enhanced transport, and tested in a variety of model porous media. For example, surfactant-stabilized iron oxide nanocrystals were synthesized and demonstrated to be resistant to aggregation in suspension. A series of column transport experiments demonstrated that ~80% of these nanoparticles could be transported through both 15 cm and 40 cm of sand under water saturated conditions, where nZVI exhibited zero transport. These stabilized nanoparticles were also demonstrated to flow through silty sand columns (70% sand, 30% silica flour) with ~50% elution. These results represent a positive step towards delivery of nanoparticles to target subsurface contamination. This project is in the early stages, however; by the time of the presentation we expect to have made sufficient progress on the three key facets described above so that we can provide an initial picture of the potential of functional nanoparticles to be used for the treatment of hydrocarbon impacted soils.

Overcoming Artesian Conditions: Approaches in Coupling Extraction with Injection to Achieve Perchlorate Treatment

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Background/Objectives. Historical manufacturing of explosive ordnance and small volume specialty chemicals resulted in perchlorate concentrations in excess of 1,000 micrograms per liter in groundwater. The geologic setting consists of dipping beds with unconsolidated alluvial deposits extending from ground surface to approximately 90 to 130 feet below ground surface (bgs) and underlying sandstone/claystone bedrock. The unconsolidated alluvial deposits generally coarsen downward, with greater permeability and perchlorate transport in the deeper portion above bedrock.

Approach/Activities. A full-scale interim remedial action targeting in-situ anaerobic biological reduction of the perchlorate was implemented in two phases. A total of 27 injection wells were installed 30 feet apart, as shallow/deep clusters, screened from approximately 60 to 130 feet bgs to target elevated perchlorate concentrations. Upon installation and aggressive development of the injection wells, free flowing groundwater discharge to ground surface was observed at each well head under ambient artesian conditions, creating injection challenges.

An adaptive injection approach was adopted to incorporate both extraction and injection as a means of water management to achieve adequate injection capacity and treatment objectives. The first phase of injection occurred in September/October 2013 and included a large-volume injection of emulsified vegetable oil (EVO) into 18 of the 27 wells. The second phase occurred in September 2014 and targeted the additional nine injection wells to create a focused EVO treatment barrier. Concurrently, an ex-situ biological treatment approach was employed to treat perchlorate-impacted groundwater.

Results/Lessons Learned. The treatment approach employed included multiple injection and extraction configurations which were adapted during implementation to optimize subsurface EVO delivery. EVO delivery was performed under injection-only conditions, coupled injection with extraction from a single point, hydraulically-connected recirculation cells, and an open recirculation system. Each of these configurations had benefits and challenges associated with their implementation in order to ultimately establish EVO distribution across the injection transect. As expected, groundwater extraction enhanced injection capacity; however, given the artesian conditions, the benefit of extraction was not as great as anticipated. Critical design parameters included the proximity of an extraction well to an injection well, the extraction flow rate, and the consistency of extraction during coupled injection. These topics will be discussed relevant to the evolution of the EVO delivery approach under artesian hydrogeological conditions and will be highlighted more broadly for consideration in engineered injection/extraction delivery applications.

Field-Scale Demonstration of Direct-Push /Jet Injection for Amendment Delivery

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Background/Objectives. The problem of contacting contaminants lodged in low permeability soil with treatment reagents presents one of the greatest obstacles to in situ remediation. Not only are convective travel times in low permeability soil prolonged so that diffusive processes become important, but sparse heterogeneities such as sand lenses serve as preferential flow paths that are difficult to target. Hydraulic and pneumatic fracturing processes can dramatically improve injection well performance. However, induced fractures in glacial till too often form asymmetrically and propagate upward or downward away from the intended target. Consequently, fracturing projects seem to be failures because of the excessive daylighting or venting of treatment material or because excessive treatment material is required to compensate to the large portion that fails to reach the targeted interval of soil.

Approach/Activities. Fractures can be focused better into the intended target plane if the nucleation form can be made to be overwhelmingly large. A suitable nucleation shape can be created around a well by eroding soil with a water jet or a collection of jets. During the past four years, a series of increasingly intensive pilot projects and demonstrations that refined direct push tooling that incorporates six 70 MPa water jets with slurry delivery capability. The water jets eroded a web of cavities spanning more than a meter from which hydraulic fractures could be nucleated and propagated with slurry, such as zero valent iron (ZVI) suspended in cross-linked guar solution. The results of earlier pilot tests have been reported at previous conferences.

A field-scale demonstration of this approach was conducted at a site about 50 km north of Copenhagen, Denmark. The underlying glacial soils had been contaminated with chlorinated solvents as the result of manufacturing activities. An extensive site characterization program sharpened the definition of the target treatment area to some 750 square meters at depths between 4.5 and 12 meters as well as established baseline contaminant concentrations at the site. Injections were conducted at as many as seven elevations with vertical spacing of 1 or ½ meter at nineteen injection locations. At three locations, the injection slurry was augmented with different colors of sand or rhodamine dye. These fractures were readily apparent in soil cores collected upon completion of injection activities. More than fifty locations were cored.

Results/Lessons Learned. The Direct Push / Jet Injection technique created hydraulic fractures that extended farther along their intended target plane than previous fracturing efforts in Denmark. Cores collected 2 m, 3 m, and 4 m from the nearest injection location routinely revealed identifiable fractures. In some cases, magnetic susceptibility established the presence of iron, which was included in the fracturing slurry, when visual examination overlooked the fracture.

The scale of the project proved that the direct push tooling and other components of the equipment package can be made sufficiently robust for routine deployment.

Back to Contents

Bioaugmentation Using Recirculating Systems in Horizontal Wells: Strategies and Successes

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Background/Objectives. As bioremediation of soil and groundwater has gained popularity, novel approaches to the application of this technology have demonstrated significant benefits through more active treatment regimens, better distribution of substrates across contaminated zones, more reliable treatment, and reduced time to site closure.

Recirculating bioremediation systems establish a local groundwater circulation cell into which appropriate biological nutrients or other amendments are continuously injected at low application rates. By constructing these systems in combination with directionally drilled wells, circulation cells may extend across plumes or contaminated areas of substantial size, or may compartmentalize a large contaminated area into more manageable units. The simultaneous withdrawal of groundwater from one well or set of wells, combined with inoculation and reinjection of the water into corresponding injection wells provides control and management of the groundwater system, while avoiding the generation of treated or effluent water that must be disposed independently of the treatment program.

Recirculating systems also provide better control, in many cases, than single or multiple point injection programs, which rely on natural groundwater flow to mix and distribute the injected substrate through the contaminated zone. In many cases, multiple injections must be made to treat groundwater emanating from a source area, with corresponding “pulses” of more and less contaminated water moving downgradient. Recirculating systems maintain a continuous level of treatment, but one which may be adjusted to deal with seasonal variations in the water table, precipitation, or other factors.

Green and Sustainable Remediation practices strive to minimize the impact of treatment methods on the local environment. The use of recirculating systems conforms to these goals, by essentially eliminating excessive groundwater extraction for treatment, containing contaminant plumes, and utilizing low volume pumps with low energy consumption to effectively treat large volumes of groundwater. Compared with comparable single-injection treatment methods using direct push technologies at widespread points across a site, the recirculating approach using horizontal wells minimizes the impact of treatment on the site or adjoining properties. Once the system is installed there are no additional construction activities required, and directional drilling not only limits impacts on site activities, but increases the potential footprint of recirculating systems.

Approach/Activities. A typical approach to a recirculating system based on horizontal wells is discussed. In addition to the general model, several projects are described where the combination of horizontal wells and recirculating systems have accelerated site cleanup.
Results/Lessons Learned. Recirculating systems have been demonstrated to be effective at groundwater cleanup, often accelerating the time to site closure. The energy demands of these low-flow systems are considerably less than those of groundwater extraction and treatment systems, with less off-site impact and a smaller environmental footprint, since there is no ex situ treatment involved. Further, the ability to adjust the system while operating provides a more reliable and continuous treatment model than single or multiple injections done in a batch process. Treatment by recirculating systems has resulted in several site closures, completed within accelerated timelines.

Coupling GCWs and Biological RD for Effective DNAPL Source Removal: From the Lab Investigation to the Pilot Scale

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Background/Objectives. The remediation of aged source zone affected by residual chlorinated solvents DNAPL represent one of the main challenge in aquifer contamination. When biological reductive dechlorination is considered as a feasible remediation approach, effective delivery and distribution of electron donors other than bioavailability of contaminants in heterogeneous aquifers are some of the primary limitations in most hydrogeological settings. Traditional injection approaches are often limited by preferential migration of injected fluids through better permeable zones, while delivery through less permeable and contaminated layers is usually limited.

Approach/Activities. By this regards, Groundwater Circulation Wells (GCWs) could improve the distribution of soluble electron donors by creating a three-dimensional groundwater controlled circulation pattern, especially efficient in anisotropic settings where significant differences exist between horizontal and vertical hydraulic conductivity.

In this work we report on the remediation activity carried out at an operative industrial site in North Italy, heavily contaminated by different chlorinated aliphatic hydrocarbons, including 1,1-DCA, TCE, 1,2-DCE and VC at concentration up to 100 mg/L. The site is characterized by the presence of a persistent source zone in a hydrogeological complex saturated zone characterized by fine to middle sands with intercalation of less permeable sandy silts to clayey silts layers.

Results/Lessons Learned. Microbiological characterization by FISH and qPCR techniques along with results from extensive microcosm investigation with different electron donors have clearly indicated the possibility to enhance the active biological reductive dechlorination (RD) until the complete dechlorination of the occurring CAH to ethene. Among the different tested electron donors, poly-hydroxy-butyrrate (PHB), a biodegradable polymer easily fermented to volatile fatty acids and molecular hydrogen, have been experimentally verified as effective in stimulating biological RD at the investigated site. Moreover, coupling biological RD with ZVI have been considered and tested as the option to efficiently remove the spectrum of CAH present at the site.

Based on the laboratory investigation and site characterization, a 30 meter deep GCW, with three screen sections, was designed and installed at the site for a pilot testing. Groundwater is pumped, at a rate up to 2.5 m^3/h, towards two screen sections of the GCW and is reinjected into the aquifer by another screen section after passing through an above ground installed PHB (releasing electron donor) and ZVI reactor. The pumping rate can be adjusted to the progress of microbiological remediation and also the spreading of biostimulants in the subsurface can be varied. For sampling purposes and to monitor the remediation progress two Multilevel Sampling System (MLWS) and a multi cluster well are installed in the sphere of influence of the GCW.

Key performance issues from hydraulic, technical and operational standpoints will be discussed and evaluated during the presentation.

Emulsified Vegetable Oil Delivery Methods at an Active Manufacturing Facility

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Background/Objectives. Chlorinated solvents were released into a perched water formation at a confidential active manufacturing facility. Prior to remediation, the impacted groundwater was approximately 2 acres in areal extent and was present under portions of the main manufacturing building and active loading docks. Since the manufacturing activities operated during three shifts, 7 days a week during most of the year, amendment delivery for an enhanced insitu bioremediation remedy was challenging. To meet this challenge, Tetra Tech employed two delivery methods: 1) injection through permanent wells using centrifugal and water powered proportional dosing pumps (dosatron), and 2) injection using a Badger system.

Approach/Activities. Tetra Tech injected approximately 5,000 gallons of emulsified vegetable oil (EVO) in a 3 to 5-percent solution through 162 permanent injection wells. Centrifugal pumps were used to transfer water from a temporary storage tank, through a dosatron (for the incorporation of EVO), to a manifold, and then into several permanent injection wells. This phase of the injection program was implemented intermittently over a 2 month period, during times that were the least disruptive to facility operations. Subsequent to the first phase of injections, the impacted area was further delineated beyond the injected area. The area was approximately 0.3 acres in size and was located directly in front of the primary loading docks for the facility. Tetra Tech was given a three day window to complete a second phase of injections. Tetra Tech and their subcontractor injected 1,500 gallons of EVO in a 33-percent solution through 7 temporary injection points, using a Badger system in less than 8 hours. According to http://www.badgerinjectionsolutions.com/about/about.htm, the Badger system "*provides a targeted lateral hydraulic motive force (with the injectate) that creates positive and negative hydraulic polarity differentials in the subsurface pore spaces which provides about 80% more non-constricted contact in the subsfurface."*

Results/Lessons Learned. This study will compare and contrast the following results of the two delivery methods: energy consumption, water consumption, labor hours, implementability, radius of influence, groundwater performance monitoring data, and overall effectiveness in achieving remedial goals.

An Innovative Bioremediation Technology for Treating Chlorinated VOCs in Low-Permeability Saturated Soils

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Background/Objectives. Bioremediation in low permeability soil presents unique remedial challenges such as back diffusion, substrate transport, and contaminant rebound. Often contaminated sites characterized with low permeability soils are approached with long-term, expensive methods or left untreated. EOS Remediation, LLC (EOS Remediation) along with Chemical Grout Co. Ltd (CGC) have engineered an in situ technology for effectively addressing sites impacted by chlorinated solvents (cVOC) under low permeability conditions. This technology, BioJet™, is based on hydrogen diffusion which determines the spacing of horizontal slices cut into the low permeability soil while delivering a proprietary slow release electron donor for enhanced reductive dechlorination. The electron donor was specially developed to withstand the high pressure associated with the BioJet™ technology. A former dry cleaning site located in Tokyo, Japan was selected for demonstrating this new technology.

Approach/Activities. The former dry cleaning facility was impacted by perchloroethylene (PCE) and trichloroethylene (TCE), as well as the associated degradation daughter products. The objectives of the BioJet™ field demonstration were to: 1) increase immediate contact between contaminants, EOS® engineered electron donor, and indigenous microbes to accelerate biodegradation in low permeability soil matrices, and 2) decrease the distance that hydrogen gas generated by fermentation must diffuse through the saturated soil, thereby stimulating reductive dechlorination, decreasing the remedial time frame and cleanup costs.

In October 2011, two highly contaminated test locations at a Tokyo dry cleaning facility were chosen for injection using the BioJet™ technology. The Japan EPA cleanup goals are targeted toward soil leachate concentrations and groundwater concentrations. Starting soil leachate concentrations of PCE and TCE ranged from 24 mg/L and 2.7 mg/L, respectively.

Approximately 264 gallons of dilute electron donor was introduced in each test location via BioJet™. The effective treatment zone was 6.5 feet in diameter and 10 feet in vertical thickness. Trends in groundwater and soil leachate contaminant concentrations were monitored for over two years.

Results/Lessons Learned. The results gathered demonstrate that the BioJet™ technology effectively delivered an engineered electron donor into low permeability zones resulting in enhanced reductive dechlorination of target cVOCs. Two years after injection, cVOC concentrations were reduced as much as 99% and 95% in some groundwater and soil leachate samples, respectively. Chlorine number calculations on the molar concentrations of cVOCs in groundwater reflected the degradation of TCE (Cl# =3.2) to less chlorinated daughter products (Cl# =1.9), which supported biodegradation as the mechanism for removal. However, bioremediation of soil leachate is a relatively slow process and additional time will be required to meet several of Japan's soil cleanup standards. This presentation will describe additional background information and results of this innovated technology demonstration for a common, worldwide problem.

Factors Affecting Preparation and Injection of Shear-Thinning Fluids for Delivery of Bioremediation Amendments

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Background/Objectives. Enhanced anaerobic biodegradation (EAB), with amendment delivery using shear-thinning fluids, was selected to treat a residual chlorinated solvent source area and dissolved phase plume at the Well 12A Superfund Site in Tacoma, Washington. In order to provide better vertical distribution of amendment across variable-permeability lithologies, shear-thinning fluids were utilized for amendment delivery. Shear-thinning fluids, such as xanthan gum, tend to increase amendment flow through low permeability zones relative to high permeability zones because the viscosity of the fluid is lower in the fine-grained low permeability zones, thereby allowing for amendment to remain in close proximity, and potentially penetrate, the silt unit. To date, a total of approximately 850,000 gallons of shear-thinning fluid amendments with commercial emulsified oils and waste vegetable oils have been injected at the site. Based on the experiences of these injection activities, several factors related to the rheological properties of the fluid and properties of the aquifer must be considered in order to optimize amendment injection and distribution.

Approach/Activities. Various amendment mixtures were tested in the laboratory prior to field-scale implementation to evaluate effect on fluid viscosity. Variables include xanthan gum concentration, emulsified oil type and concentration, and concentrations of additives such as tracers and buffers. Additionally, hydraulic properties of the injection wells, particularly specific capacity, were used to evaluate the ability of a well to accept amendments at varying viscosities and determine optimal xanthan gum concentrations and target fluid viscosity prior to injection. Injection testing of several amendment mixtures was used to correlate laboratory-measured viscosity and rheological properties to achievable injection flow rates and pressures.

Results/Lessons Learned. The primary factors affecting the ability to prepare and deliver EAB amendments using shear-thinning fluids are the fluid viscosity and the specific capacity of the injection well. Ionic strength of the amendment solution at the time of xanthan gum hydration is extremely important, as lower ionic strength during xanthan hydration resulting in fluids with higher viscosity. Following complete xanthan hydration, the fluid viscosity and rheology is not significantly affected by adding tracers, buffers, or additional EAB amendments. Injection wells with higher specific capacities generally accept higher-viscosity shear-thinning fluid, which helps prevent significant loss of amendment to preferential pathways resulting in a more uniform vertical amendment distribution. Determination of rheological properties of proposed site-specific amendment mixtures, combined with an adaptive field strategy to adjust amendment viscosity during injection in response to observed injection rates and pressures, are valuable in order to efficiently complete injection of large volumes of shear-thinning fluids.

EISB Treatment of Chlorinated VOCs by Biobarrier and Source Approach

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Background/Objectives. Enhanced in situ bioremediation (EISB) using emulsified vegetable oil (EVO) was selected to treat chlorinated VOCs (primarily trichloroethene [TCE], >10 mg/L) in groundwater in a glacial till aquifer beneath an urban setting in the northeastern U.S. to remove the source and provide for monitored natural attenuation (MNA). The 900 ft long plume originates in an on-site source area in the upper portion of the aquifer and follows a downward gradient to the lower portion of the aquifer off-site. A lense of more uniform clean sand occurs in the till at depth and represents a preferential flow pathway. The 100 ft thick impacted glacial till aquifer resides over less impacted Triassic basin bedrock aquifer. Two microcosms and a pilot test demonstrated that addition of electron donor and bioaugmentation can achieve complete reductive dechlorination of TCE in Site groundwater. EVO was selected given its longevity to provide a more passive approach in this difficult urban setting. Injection through permanent monitoring wells (installed by rotosonic drilling) was selected given the difficult drilling environment (tight till with gravel and cobbles). Treatment is focused in the upper aquifer in the source area (where residual DNAPL is present) and in the lower aquifer at off-site "biobarriers" to intercept the dissolved VOC plume.

Approach/Activities. Injection wells were installed in the source area and along the 400 ft barrier during the first quarter 2014 for a total of 33 injection wells. 14 Injection wells are spaced roughly 10 ft in the source area and 20 ft in the barrier. While only 5 ft radius of influence (ROI) was assumed for the injections in the barrier, advection/dispersion is expected to provide overlap of the resultant hydrogen plumes originating from the injected electron donor based on 2-D finite difference fate and transport modeling. Also, greater ROI will likely be achieved within the sand lense portion of the biobarrier. Baseline groundwater sampling was conducted in May 2014 and the data were used to evaluate the amount of donor to inject and whether it would be necessary to buffer the aquifer (to adjust pH). Two approaches, A) stoichiometric demand and B) injection porosity, were considered for calculating the amount of donor to inject. These approaches yielded significantly different results, 6,700 lbs (A) and 34,840 lbs (B). O'Brien & Gere decided to attempt to inject the larger amount with the lesser amount as a contingency. The actual final amount will be a function of how the aquifer actually performs in receiving the donor solution and consideration of practical time to complete the event. As site conditions (e.g. pH, alkalinity, buffering capacity) were considered marginal and how the groundwater pH would actually respond to the donor was not known, it was decided to evaluate the aquifer response and the need to buffer after donor injection and before culture injection. Injection of Newman Zone™ was conducted September/October 2014.

Results/Lessons Learned. Presentation will include: an evaluation of installation and performance data to assess EISB effectiveness; a reflection on key implementation decisions (e.g. well spacing, amount of donor, buffering); and, dynamic assessment of the path forward during the early phases of EISB (including the amount of culture to inject and when).

Horizontal Remediation Injection Wells (HRIW): Solution to Slow Uptake via Vertical Injection Wells

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Background/Objectives. The use of horizontal injection wells (HRIWs) can markedly improve the rate of uptake of bioaugmentation and biostimulation fluids into lower permeability formations.

Approach/Activities. A case study comparing the two methodologies (a vertical injection well line versus one HRIW) will demonstrate the increased application rates to the subsurface provided by the HRIW for a project conducting large scale in situ bioaugmentation treatment for perchlorate contamination in a lower permeability aquifer. The project used a HRIW for treatment of a plume segment underneath a building that could not be accessed for vertical well installations; but, also where the economics were favorable for HRIW installation and system operability for a plume segment that was accessible for vertical wells.

Results/Lessons Learned. Site remediation goals require certain design and operational necessities including efficiency of well placement, targeted delivery of fluids into the contaminant plume(s) as well as increasing the rate for delivery of treatment fluids into impacted zones. These operational necessities have been shown to be enhanced by the use of horizontal remediation injection wells in-lieu of vertical injection wells. Increased sophistication of well screen design and the accuracy of installation to zones of contamination, as well as the major increase of the injection well screen area that is applied to the zones requiring treatment can provide enhanced treatment product delivery and henceforth shorter timeframes to reach remediation goals.

Shallow Soil Mixing of Lime Catalyzed Persulfate for Treatment of Organochlorine Pesticides in the Saturated Zone

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Background/Objectives. A small industrial site in central New Jersey experienced a release of 17 different organochlorine pesticides and xylenes to shallow soils in the late 1960’s. Investigations in the late 1980’s and early 1990’s identified a small pesticide source area in saturated soils with up to one percent of total organochlorine pesticides that was contributing to a larger shallow groundwater plume. Several remediation strategies were attempted, including; dig and haul, pump and treat, air-sparge soil-vapor extraction and electro-chemical geooxidation with limited success. The state regulatory agency requested a more aggressive remedial strategy to mitigate additional migration of the pesticides to groundwater. The selection of in situ chemical oxidation (ISCO) using a base-catalyzed persulfate (BCP) was based on the positive results of treatability studies conducted from November 2007 to March 2008. ISCO, using BCP, was determined to be the most effective technology, of those technologies evaluated in the study, based on achieving a 90% reduction of total pesticides and an 89% reduction of total xylenes in the saturated soils in the 20 days allotted for the study.

Approach/Activities. In situ shallow soil mixing (via large-bore auger with an injection head) was selected as the method for implementing the ISCO treatment due to the heterogeneity of the soils and the shallow location of the impact of less than twenty feet below ground surface. The shallow soil mixing approach also assures more efficient distribution of the BCP and better contact of the BCP with the contaminated soils. The BCP mixture includes hydrated lime (calcium hydroxide) as the base catalyst. The combination of lime and sodium persulfate has the added benefit of reacting to form gypsum, which reduces the permeability of the soil while also stabilizing the soil for future use. The reduced soil permeability and stabilization will result in reduced flux of any residual untreated pesticides from the saturated soils and further reduce their migration potential to ground water. Preparation of the Site for shallow soil mixing included removal of an old treatment shed, twelve subsurface metal pilings and removal of the top five feet of soil. ISCO via shallow soil mixing was conducted immediately following the site preparation work on July 11, 2011 and was completed on July 20, 2011. A total of approximately 2,700 cubic yards of soil was mixed with 140,000 pounds of persulfate activated with just over 200,000 pounds of hydrated lime.

Results/Lessons Learned. Post treatment performance sampling of soils in the treated area after 3 months showed 68% reduction of pesticides and 86% reduction of xylenes. Post treatment soil sampling also indicated formation of gypsum that is a byproduct of persulfate-lime reaction that will provide both stabilization and a potential source of sulfate for long-term sulfate reduction processes. Significant reduction in both xylenes and pesticides have also been observed in groundwater based on quarterly sampling of wells in the source area with xylenes reduced from a separate phase to approximately 1,000 µg/L and dissolved phase pesticides reduced by 65%. Problems encountered included subsurface structures that had to be removed prior to shallow soil mixing.

Back to Contents

Accelerated Biodegradation Facilitated by an In Situ Colloidal Sorption Technology

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Background/Objectives. Enhanced biodegradation and monitored natural attenuation (MNA) are effective, widely-used tools for elimination of organic contaminants in groundwater. The timeframe for treatment by these methods is on the order of months to years, during which time the contaminants are biodegraded to non-toxic end products. To significantly improve bioremediation performance, a new *in situ* colloidal sorbent technology has been developed that accelerates biodegradation and drastically shortens the timeframe for reaching groundwater treatment goals.

Approach/Activities. This work demonstrates the efficacy of a colloidal *in situ* remediation agent that consists of highly sorptive activated carbon particles (1-2 microns in size) stabilized to transport widely through an aquifer upon injection. The stabilized colloids then deposit in the subsurface, forming a layer on soil particles that traps contaminants until they are biodegraded. Some advantages of this approach include: rapid decreases in groundwater concentrations, immobilization of contaminants, and the protection of property boundaries or receptors. The protective effects of the colloidal agent are hypothesized to last many years after its application.

Microcosm studies containing soil, water, and contaminant were performed to evaluate the biodegradation of both benzene and PCE in the presence of the colloidal sorption agents. Contaminant concentrations in water were monitored weekly over the course of the studies by static headspace using GC-FID or GC-ECD methods.

Results/Lessons Learned. In both studies, the colloidal agent facilitated >90% destruction of contaminant within 28 days compared with controls. To further the understanding of the process, full-bottle extraction methods were developed to measure contaminant mass across all phases in the bottles (soil, water, and colloidal sorbent). The extraction data confirmed that colloidal agents rapidly reduced groundwater contaminant concentrations via sorption (70-90% in the first 24 hours), and subsequently accelerated biodegradation of the contaminants. All conditions were run in triplicate, and results analyzed for statistical significance.

The performance of the colloidal biomatrix material will be reviewed in detailed comparison between sterile and live control samples, as well as those treated with traditional enhanced bioremediation methods. Benefits of the colloidal technology will be discussed, including advantages for treatment of sites exhibiting matrix back-diffusion of contaminants. A brief summary of performance in multiple field applications will also be presented.

Performance of Full-Scale Bioremediation Remedy in Complex Geology Using Shear-Thinning Fluids

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Background/Objectives. Enhanced anaerobic biodegradation (EAB) was selected to treat a residual chlorinated solvent source area and dissolved phase plume at the Well 12A Superfund Site in Tacoma, Washington. A thin silt unit, containing extremely high concentrations of trichloroethene (TCE), cis-1,2-dichloroethene (cis-DCE), and 1,1,2,2-tetrachloroethane (PCA), has been mapped over a large area of the site, and this unit acts as a continuing source of contamination to high-permeability layers above and below. Therefore, EAB treatment is targeted in the interval immediately adjacent above and below, as well as within, the silt unit. In order to provide more uniform amendment distribution across variable hydraulic conductivities, including delivery of amendment directly into the silt, shear-thinning fluids containing emulsified vegetable oil amendments were injected into wells screened across the silt unit. Shear-thinning fluids act as a less viscous fluid when flowing through low-permeability lithologies, resulting in a more uniform vertical distribution of amendment across varying lithologic units. Delivery of EAB amendment directly to the low-permeability silt unit will allow for more efficient degradation of sorbed contaminants and reduce mass flux from this source.

Approach/Activities. During pilot study and full-scale application of EAB at the site, a total of approximately 850,000 gallons of amendments were injected into a total of 43 injection wells. The shear-thinning fluid viscosity was varied at each injection well based on the specific capacity of the particular injection well, and concentrations of emulsified oil were varied between 3% and 5% depending on the contaminant concentrations present in soil and groundwater at each well location. The target radius of influence at each injection well ranged from 15 to 25 feet. A dynamic strategy was implemented in the field to determine the appropriate viscosity of the shear-thinning fluid amendment, and the viscosity of amendment injected at a particular well was increased or decreased in response to observed injection rates and pressures.

Results/Lessons Learned. Soil borings completed following test injection activities verified the presence of amendment in all lithologic units intersected by the injection well, validating the assumption of more uniform distribution of amendment. Carbon from amendment injections was observed at monitoring wells outside of the design radius of influence within three months of injection. Areas where amendment was delivered quickly established reducing conditions, and conversion of TCE and 1,1,2,2-PCA to cis-1,2-DCE, trans-1,2-DCE, and vinyl chloride was observed within three months. The higher viscosity of the shear-thinning amendment prevented migration of the injected fluid into high-permeability pathways, and allowed reducing conditions to be quickly established and reductive dechlorination to commence within the lithologic units where most mass flux occurs. Subsequent monitoring will evaluate the longevity and effectiveness of the shear-thinning fluid amendment at reducing the mass flux from the silt unit.

In Situ Bioremediation Using the BioNets™ System to Passively Degrade Contaminants in Soil and Groundwater

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Background/Objectives. Over the next several decades, federal, state, and local governments and private industry will commit billions of dollars annually to clean up sites contaminated by hazardous waste and petroleum products from a variety of industrial sources. This ongoing commitment will result in a continuing demand for hazardous waste site remediation services and technologies. More of these sites can be remediated by a less expensive, less intrusive and more natural approach that EPA has successfully demonstrated with Foremost Environmental Solutions (FES) on a variety of contaminants in numerous soil types. One of EPA's intents is to make this efficient and effective remediation system available to the general public, via sublicenses from FES, EPA'S Cooperative Research and Development partner. FES has the World-wide Exclusive License to EPA's installation method and SOS patent (US Patent #7,252,986).

Approach/Activities. The approach that will be discussed implements EPA's patented systems called BioNets™ or BioLuxing™ which is an enhanced system for in-situ bioremediation of contaminated soil and groundwater, wherein, Isolite® Ceramic Granular pellets (porous inorganic support spheres made from diatomaceous earth), are treated by the inoculation of selected nonpathogenic microbes for converting or destroying the contaminants. The contaminants may be hydrocarbons, chlorinated solvents, sulfides, frac flow back water, produced water, cyanides, arsenic, nitrates, heavy metals and other chemicals. The internal, open-ended, and ideal pore size distribution of the Isolite® treatment slurry provides an excellent microbial carrier, a long-term proppant, a safe home for the microbes and a preferential pathway for the contaminants to contact the selected microbes. The slurry also includes water, nutrients and EPA's patented solid oxygen source (SOS), slow-releasing encapsulated pellets that work synergistically with the porous Isolite, to help sustain the life of the augmented colonies of microbes, evenly distributed in the Isolite/SOS slurry throughout the treatment zone.

The EPA recognized that aerobic in situ bioremediation was very dependent on providing an adequate supply of oxygen for most microorganisms and did something about it. The EPA developed a long-term pellet as a solid oxygen source (SOS). The EPA cooperatively tested and contended that the EPA's SOS pellets were very effective and easy to install, using their patented BioNets™ that came out of the full-field, actual demonstration with Foremost Environmental Solutions. The EPA researchers determined that the slow-releasing SOS pellets provided adequate amounts of oxygen throughout the entire treatment zones for 22 months, eliminating continuous ongoing and expensive injections.

Results/Lessons Learned. The BioNet™ slurry/injection system is a very efficient and enhanced system. A number of various industrial sites will be examined that were successfully remediated with aerobic, in situ bioremediation; and also how a large industrial site in South Carolina that was contaminated by chlorinated solvents. This site was very significant and one of the first and largest industrial sites cleaned by enhanced in situ bioremediation. EPA and Foremost Solutions had cooperatively developed this enhanced system since April 1995.

Application of Biodegradable Oils (VOS™) for Treatment of cVOCs in the Vadose Zone

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Background/Objectives. There are few active remediation alternatives currently available to treat residual chlorinated solvents (CVOCs) within the vadose zone. Conventional treatment methods such as soil vapor extraction, soil washing, and excavation and off-site treatment/disposal can be costly, energy-intensive, and impractical for sites with extensive vadose zone contamination. Likewise, in situ biological treatments with liquid electron donor substrates, despite well-documented success for CVOC destruction in groundwater, are generally ineffective in the vadose zone because injected substrates either migrate downward out of the treatment area or do not provide the necessary saturations required for long-term contaminant biodegradation.

Approach/Activities. Scientists at the Savannah River National Laboratory (SRNL) have developed an effective in situ biological treatment technology to address CVOC contamination in the vadose zone. VOS™ (US Patent Nos. 7,896,577 and 8,211,687) is a thixotropic (shear thinning) formulation of oil, water, nutrients, buffers and a *Dehalococcoides* strain that is easily injected into the vadose zone and retains a high saturation to maintain reducing conditions. Ultimately, the VOS™ technology prevents continued downward migration of contaminant mass from low permeable source zones via contact and partitioning while promoting suitable conditions for long-term contaminant biodegradation of CVOCs in situ. An ongoing field pilot study was initiated at the Department of Energy's Savannah River Site (SRS) to evaluate the effectiveness and longevity of VOS™ to mitigate CVOC contamination in low permeability zones along an abandoned process sewer line. Entrapped CVOCs in these low permeability zones represent a slow but continuous source of contamination primarily by gas diffusion. Approximately, a total of 230 gals of VOS™ was injected into three injection wells in February 2010.

Results/Lessons Learned. Performance monitoring of VOS™ was accomplished primarily through monitoring of soil gas in the vicinity of the injection points. After VOS™ injection, a rapid and significant decrease in Tetrachloroethene (PCE) and trichloroethene (TCE) gas concentrations was realized by partitioning into VOS™. Within several weeks, daughter products were measured showing reductive dechlorination of PCE and TCE is possible, along with a complete reduction to ethene. Carbon dioxide and methane increased and oxygen decreased within the treatment area, suggesting that injection of VOS™ into an aerobic vadose zone can rapidly establish anaerobic conditions. The longevity of VOS™ in situ, however, was much shorter than expected as indicated by a gradual and partial rebound in soil gas PCE, TCE, and oxygen concentrations. Recent soil and soil gas data collected in 2014 indicate source degradation did occur and is ongoing although at a slow rate after four plus years. The original formulation of VOS™ was improved to include greater carbon content and an oxygen scavenger to increase longevity.

Antimethanogenic ISCR Reagent for Safer, More Efficient Remedial Actions

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Background/Objectives. Over the past 25 years, many formulations of organic substrates, with or without zero-valent metals, have been added to impacted aquifers with the intent of liberating hydrogen to enhance reductive dechlorination reactions or help induce in situ chemical reduction (ISCR) conditions. A very common problem is that indigenous methanogens also propagate following the addition of the organic hydrogen donors, competitively consuming available hydrogen to generate large amounts of methane gas. There are at least three important consequences of this response: i) practitioners must apply additional hydrogen donors to account for methanogenesis, potentially increasing total amendment costs by more than 30%; ii) rapid growth of methanogens consumes alkalinity while generating acids thereby accelerating aquifer acidification. Acidification slows beneficial microbial activity and may liberate heavy metals to cause secondary contaminant issues; and iii) excessive methanogenesis can cause groundwater to exceed current and pending regulation limits and pose serious health and safety risks by accumulating in utilities and structures.

Approach/Activities. We describe herein a genuinely new ISCR reagent that uniquely combines multiple sources of vitamin/nutrient rich, engineered-release, hydrophilic carbon sources + ZVI + other reagents along with a proprietary mixture of Monacolin K and other natural statins. This combination, packaged as Provect-IR™, has shown to provide steady bioavailability of hydrogen donor to beneficial microbes as well as inhibit enzyme systems that are responsible for the production of methane. Methanogen suppression using Monacolin K has been widely used in the cattle industry for decades to manage rumen microbiology: this technology is now being applied to the environmental industry as a remedial supplement, a landfill/sewer gas management tool, *et cetera*. Provect-CH4™, a stand-alone mixture of Monacolin K and other natural statins, can be used to augment other ERD amendments such as molasses, sugars, (emulsified) oils, lecithins *et cetera* to make them safer and to improve their overall efficacy by an estimated 30%, or more.

Results/Lessons Learned. Data from laboratory and field studies will be presented to demonstrate effective antimethanogenic activity during the course of hydrogen donor fermentation. For example, when Provect-CH4 is applied at *ca*. 40 mg/L, the supplement reduced the concentation of methane in biogas from 65% to 0% within 5 days time while maintaining reducing conditions (<-300 mV) and without changing pH. In general, applying 50 mg/L of Provect-CH4 costs between $0.10 to $0.15 per ft^3 of groundwater treated, which is a fraction of the typical organic amendment costs. The effects of statins on *Dehalococcoides* spp. (as determined via qPCR analysis for structural genes) or overall heterotrophic bacterial production (as determined via ^{3}H-leucine incorporation method) or organic contaminant mineralization to $^{14}CO_2$ (as measured in laboratory radioassays using field groundwater samples) were also measured. Performance data (e.g., contaminant removal, methane data and measurement tools), cost information and technology application scenarios will be presented, including application at a large, operating industrial site where excessive methane generation has been problematic.

Back to Contents

Antimethanogenic, Liquid ERD Amendment for Safer Remedial Actions

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Background/Objectives. There are recognized benefits to methanogens and of limited methanogenesis. For example, i) methanogens are known to play important roles in synergistic microbial ecology, ii) their metabolic activity can help maintain anoxic conditions in treatment zones (through seasonal changes), and iii) the activity of methane mono-oxygenases and other enzymes can stimulate co-metabolic activity of TCE/DCE/VC in redox-recovery zones. Hence, limited production of methane is part of a healthy ERD/ISCR application. However, excessive methane production represents a costly waste of amendment (generating just 20 mg/L of methane constitutes greater than 33% of the total amendment consumption based on moles of H2; Mueller *et al.,* 2014). Moreover, excessive and extended production of methane can result in elevated in groundwater concentrations (as high as 1,000 ppm have been reported) which can lead to accumulation in soil gas subsequently impacting indoor air, accumulating in basements, under slabs/foundations and/or migrate along utility corridors. Accordingly, State specific regulations for methane in groundwater have been promulgated. As a result, many remedial practitioners proactively design costly contingencies for conventional ERD implementation in the event that methane exceeds a threshold level ranging from 1 to 10 ppm groundwater.

Approach/Activities. To yield a liquid ERD amendment that enhances reductive dechlorination reactions while minimizing the production of methane we supplemented a proven ERD substrate (ABC™) with Provect-CH4™, a source of Monacolin K and other natural statins to inhibit the growth and proliferation of Archaea *i.e*., methanogens (Scalzi *et al*, 2013, 2014). The resulting product, ABC-CH4™, contains 60% water soluble carbon consisting of: glycerin as fast-release H donors, soluble lactic acid as mid-release H donors, ethyl lactate as a green solvent/H donor, dissolved fatty acids as long-term release H donors, plus dipotassium phosphate for micronutrients and pH buffering, and/or potash or bicarbonate for pH control. This is the only liquid ERD reagent designed to actively control the production of methane.

Results/Lessons Learned. In August 2014, ABC-CH4 was added proximal to an existing monitoring well (MW-207s) to treat groundwater at an active shopping mall in Georgia, USA that was impacted by PCE and its catabolites (TCE, DCE and VC) from a former dry cleaning operation. At the same time, the same amount of a standard ERD amendment (no methane inhibitors) was added proximal to another existing monitoring well (MW-4) that was located ca. 200 feet cross gradient. Prior to amendment application, baseline groundwater analysis were conducted for dissolved methane and COIs. Six weeks post application, groundwater samples were collected for similar analysis. At that same time, analysis of the head space gases in MW-4 and MW-207s was conducted using both a Thermo/Foxboro TVA-1000B PID/FID Analyzer (PID sensitive to 2,000 ppm CH4; FID sensitive to 50,000 ppm CH4) and a LandTec GEM5000 Landfill Gas (LFG) Meter (infrared detector calibrated to 15% methane). Well head space gases were analyzed from top of the well heads immediately upon opening the well caps with readings recorded every minute for 5 minutes. Data showed that MW-4 (water depth 11.9 ft bgs; pressure 0.11 in) treated with an ERD substrate only had over 30% CH4 in the headspace gas as measured by the GEM5000 LFG meter (note – TVA detectors exceeded their level of sensitivity and shut down). By comparison, the well headspace gas in MW-207s (water depth 18 ft bgs; pressure 0.24 in) had only 0.5% CH4.

Antimethanogenic Supplement for ERD Amendments

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Background/Objectives. Enhanced reductive dehalogenation (ERD) has demonstrated success in the *in situ* remediation of numerous sites impacted by various constituents, most commonly chlorinated ethenes. One seemingly universal phenomenon has been the biological production of methane, especially during the early phases of the process. There are recognized benefits to methanogens and of limited methanogenesis; however, excessive methane production represents a costly waste of amendment (generating just 20 mg/L of methane constitutes greater than 33% of the total amendment consumption based on moles of H2; Mueller *et al.,* 2014). Moreover, excessive and extended production of methane can result in elevated groundwater concentrations (as high as 1,000 ppm have been reported) which can lead to accumulation in soil gas subsequently impacting indoor air, accumulating in basements, under slabs/foundations and/or migrate along utility corridors. Accordingly, State-specific regulations for methane in groundwater have been promulgated, and remedial practitioners proactively design costly contingencies for conventional ERD implementation in the event that methane exceeds a threshold level ranging from 1 to 10 ppm groundwater.

Approach/Activities. Active measures to control the production of methane can offer multiple advantages in terms of cost, treatment efficiency, treatment time and safety. Such measures have included the use of slowly released carbon sources, excess nitrate/sulfate, ethylsulfonates, ethylformate, low level toxins, et cetera but these are not specific to methanogens and the efforts have met with limited success. Recently, the use of statins as effective inhibitors of protein and enzyme systems specific to Archaea (*i.e.,* methanogens) was described for environmental applications (Scalzi ***et al***, 2013, 2014). Provect-CH4™ provides a unique source of Monacolin K and other natural statins that interfere with the biosynthesis of psuedomurein (found only in Archaea) which prevents cell wall biosynthesis. Hence, growth and proliferation of methanogens is limited: this inhibitory affect is not observed in other microbes (bacterial cell walls are composed of peptidoglycan or murein). When added to liquid ERD amendments such as (emulsified) oils, lecithin, sugars, lactates or any other H2 donor, the production of methane is thereby minimized. This enhances reductive dechlorination reactions by allowing slower-growing *Dehalococcoides* spp. to better compete. Moreover, minimizing the production of methane improves cost effectiveness, treatment efficiency, treatment time, and overall safety.

Results/Lessons Learned. In August 2014, Provect-CH4 was used to supplement EOS™ emulsified oil injections in an effort to control methane production and enhance DCA removal at a site managed by EPA Region 8 in Montana. This site had a history of petroleum hydrocarbon releases. USTs were excavated and an air sparge/soil vapor extraction system was installed and successfully operated. However, residual concentrations of DCA remained in the groundwater. Lactate was injected to enhance anaerobic dechlorination but DCA levels remained elevated at approximately 150 ppb. Analytical data indicated that methylated organic compounds such as trimethylbenzene were being produced. To address these issues, a combination of Provect-CH4 and EOS reagents were used for the final injection event. Analytical results will be presented to document the effectiveness of this approach. Data will also be presented from controlled laboratory studies designed to assess the effectiveness of statins in decreasing methane production while increasing the removal of CVOCs without reducing *Dehalococcoides* activity.

Enhancing the Efficiency of Electron Donor Utilization in Bioremediation of Chlorinated Solvents

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Background/Objectives. Groundwater remediation of chemical contaminants by reductive dechlorination has been achieved since at least the early 1990's by the addition of a carbon substrate. As this method gains popularity, substrate selection requires cheaper and accessible products, particularly for projects with larger plumes where substrate volumes contribute largely to total project costs. Although significant research efforts have rendered in the industry favoring the use of low cost carbon substrates with minimized groundwater flow impacts-such as emulsified vegetable oils as carbon and energy source-less attention has been given in meeting minimum specific nutrients demand by microorganisms undergoing engineered degradation.

To reduce costs, many in the industry have moved toward cheaper, less refined substrates, which alone may show poor kinetics and low efficiency.

Approach/Activities. Other industries have learned to create the necessary conditions to stimulate and benefit from sulfate and methane respiring microorganism in industrial digesters for wastewater, medical and ruminant applications. Knowledge transfer to the groundwater remediation community can help overcome the challenge of meeting adequate and sufficient nutrient concentrations to support biomass growth and metabolism. As a basic example, the relative ratios of nutrients favorable for natural degradation are in the order of 100 Carbon / 10 Nitrogen / 1 Phosphorous / 1 Potassium / 1 Sulfur has been confirmed in similar industries, making it a standard practice to measure and compare the C:N ratios that microbes rely on to break down organic contaminants.

Along these lines, remediation techniques have continued to develop as shown in a second example concerning amendment addition. Despite limited evidence that supports the claim that yeast extract enhances the efficiency of electron donor utilization in bioremediation, practitioners have added it to promote the activity of contaminant degrading bacteria in bioremediation of halogenated hydrocarbon-impacted groundwater. On the other hand, the ruminant industry has taught us that metabolites produced during the anaerobic fermentation of an unmodified strain of botanical classification Saccharomyces cerevisiae, is a better choice than yeast extract. Its role in increasing the rates of bioremediation are obtained by increasing the efficiency of electron donor utilization and providing a source of sugars, proteins, vitamins and amino acids contained in yeast cells and extracellular metabolites. In addition, metabolites produced from Saccharomyces cerevisiae aid in maintaining circumneutral pH.

Results/Lessons Learned. This presentation will help understand how a borrowed technology offers the potential to complement existing bioremediation techniques. Particularly, the manufacturing know-how of a product rich in proper metabolites offers an In Situ amendment that will work with microorganisms to more efficiently take advantage of existing or injected substrates (electron donors) and accelerate contaminant degradation rates.

Sulfidated Zero-Valent Iron for Remediation of Chlorinated Contaminants

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Background/Objectives. Zero-valent iron (ZVI) is one of the most prevalently used engineered materials for groundwater and soil remediation. Incorporation of a small amount of catalytic metals, most commonly Pd and Ni, on the ZVI surface gives rise to iron-based bimetallic nanoparticles (BMPs) with significantly enhanced particle reactivity for treating chlorinated contaminants. However, the primary concern regarding field application of BMPs is the particles stability in the real groundwater environment containing common background constituents (e.g., Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-, phosphate, and humic acid). Previous studies and recent results by the authors indicate that both Pd-Fe and Ni-Fe BMPs were prone to rapid deactivation when the particles were exposed to common groundwater solutes. In addition, potential concerns over leaching of Ni or Pd into the environment and the high cost of Pd also limit the widespread application of BMPs.

Approach/Activities. Surface sulfidated zero-valent iron (SS-ZVI), formed by a modified particle synthesis procedure (for nanoscale ZVI) or through a facile pretreatment of commercial iron powder using abundant reduced sulfur compounds, emerges as a promising approach to increasing the iron reactivity. This study is to identify optimal surface treatment parameters and to examine the reactivity of SS-ZVI for reductive dehalogenation of trichloroethene as well as the aqueous stability of SS-ZVI in simulated groundwater environment over extended immersion periods (up to 6 months) in laboratory batch reactors. In addition to aqueous experiments, surface and solid phase analyses were employed to elucidate the structure of SS-SZVI and its effect on TCE degradation rates and reaction pathways.

Results/Lessons Learned. The preliminary results indicate that SS-ZVI, including sulfidated nanoscale ZVI and bulk iron power, have significantly increased reactivity treating chlorinated contaminants compared to un-amended ZVI. Although TCE dechlorination rates by SS-ZVI are lower than those of the freshly made Pd-Fe and Ni-Fe BMPs, reaction rates are comparable after aging particles in groundwater matrices due to SS-ZVI having remarkably higher tolerance of background organic matter and anions. The reactivity of SS-ZVI is sensitive to the type of sulfur precursor, sulfur loading, and the conditions used during sulfidation treatments. On-going product distribution analyses, electro-chemical characterization, and surface analysis (*e.g.*, with X-ray photoelectron spectroscopy) will unravel the role of sulfur in enhancing the reactivity of ZVI particles. These results will be used to assess the potential of adopting SS-ZVI as a more effective and environmentally benign alternative to the conventional forms of ZVI materials for groundwater remediation.

Improving Performance and Reducing Costs with Combined EVO and ZVI

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Background/Objectives. Laboratory studies suggest that nano-scale ZVI (nZVI) and micro-scale ZVI (mZVI) can be very effective for in situ treatment of chlorinated solvents (CVOC) and other oxidized contaminants. However, there are significant challenges in cost-effectively applying this technology in the field. Material costs for both nZVI and mZVI are significantly higher than other electron donors, so practioners often try to use the minimum amount of material required. This can be problematic since much of the ZVI is often consumed in side reactions with background electron acceptors (O_2, NO_3, SO_4). If too little ZVI is injected, contaminant concentrations drop immediately after injection, then rebound after a few months when the ZVI has been depleted.

Effectively distributing nZVI and mZVI is also a major challenge. Multiple field studies and supporting laboratory experiments have shown that transporting these materials more than a few feet away from the injection point can be very difficult. In many cases, thin layers of ZVI are transported away from the injection well through high permeability zones or fractures, leaving much of the formation untreated. This can dramatically reduce treatment performance since CVOC reduction by ZVI is a surface mediated process where the contaminant **must** come into direct contact with the ZVI surfaces to be degraded. If there are zones with little or no ZVI, the CVOCs can pass through the injection area without being treated.

Approach/Activities. EOS Remediation has been working to develop a cost-effective, reliable and effective technology for in situ treatment of contaminated aquifers with ZVI. We do this by coating mZVI with oil droplets (EOS ZVI). The oil droplets have a negative surface charge which prevents agglomeration of the ZVI particles and also reduces attachment to sediment surfaces. The small particle size of the product (D_{50} =0.9 µm, D_{90} = 1.5 µm) allows effective transport through most aquifers. Once emplaced, the oil droplets provide a low cost electron donor to consume completing electron acceptors, extending the ZVI life.

Column tests were run to measure the transport of mZVI, EOS Pro, and EOS ZVI in fine sand with varying amounts of clay. Experimental results were then fit to a colloidal transport model to estimate empty bed sticking efficiency and maximum retention. Once developed, these transport parameters were used to develop optimized designs for different aquifer conditions (e.g. silt/clay content, groundwater velocity, O_2, NO_3, SO_4 and CVOC concentration) using the ESTCP EVO design tool.

Results/Lessons Learned. mZVI can be used to stimulate in situ degradation of a wide variety of contaminants. However, uniformly distributing these materials in the subsurface can be challenging. To maximize treatment and control costs, the injection design should be tailored to match the transport characteristics of the ZVI and site conditions.

Back to Contents

A Sustainable Bioremediation Approach for Chloroethane Contaminated Groundwater Treatment

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Background. An anaerobic bioreactor (ABR), configured to treat applied groundwater in a peat/sand bed, provides a sustainable approach for treating chlorinated ethenes and ethanes as opposed to traditional physical/chemical approaches. While chlorinated ethenes can be readily dechlorinated to ethene, reductive dechlorination processes for chlorinated ethanes, such as 1,1,1-TCA or 1,1-DCA, often do not progress beyond monochloroethane (chloroethane) under anaerobic conditions. The objective of this study is to mitigate aqueous concentrations of chlorinated ethanes via a combination of anaerobic and aerobic processes in series. Reductive dechlorination in ABRs is designated as the primary method of 1,1,1-TCA and 1,1-DCA degradation while O_2 dosing by means of permeable tubing is utilized to decrease the resulting chloroethane concentrations.

Approach. Using an engineered peat/sand mix-media, a two-stage pilot-scale ABR system was operated in series inside a greenhouse to evaluate degradation of chloroethane produced from reductive dechlorination of 1,1,1-TCA and 1,1-DCA. The 1^{st} stage of the reactor sequence was used to dechlorinate 1,1,1-TCA to chloroethane, which served as the influent feed for two, 2^{nd} stage beds that were operated in parallel. Aerated conditions for chloroethane dissipation were achieved by using 24 feet of porous Silastic tubing distributed in a 1 inch sand layer along the 2.16 feet flowpath of the 2^{nd} stage beds. Pressurized breathing air (45 psi) was applied to the tubing resulting in an O_2 loading of 16.5 mg/day. Chlorinated ethanes were analyzed in influent and treated water using gas chromatography with a flame ionization detector. A microcosm study using the 2^{nd} stage influent to observe chloroethane changes under aerobic, anaerobic, and kill controlled conditions was also conducted using a core of the aerated zone as microcosm media. Microcosm samples were analyzed weekly using a flame ionization detector and aerobic bottles were amended with oxygen immediately following each sample episode. Additionally, discrete site-specific calculations, using published data from various sources and justified assumptions, concerning CO_2 emissions and energy associated with a Superfund Site's operation were performed to compare ABR vs. physical chemical treatment approaches of groundwater impacted by chlorinated solvents.

Results. Loading of 1^{st} stage reactors was 0.358 $g/m^2/day$ of 1,1,1-TCA. In the 1^{st} stage ABR beds, approximately 880 µg/L (13.6 µmol/L) of chloroethane and 260 µg/L (2.62 µmol/L) of 1,1-DCA were produced from complete dechlorination of approximately 4,310 µg/L (32.3 µmol/L) 1,1,1-TCA. No apparent dechlorination of chloroethane was observed in the 1^{st} bed sequence. The bottom 50% of the 2^{nd} stage ABR beds were anaerobic; oxygen was introduced using tubing just above the anaerobic zone. Additional dechlorination (>90%) of 1,1-DCA was observed in the anaerobic portion of the 2^{nd} bed system without decreases in chloroethane concentration. Decreases in chloroethane concentration, following exposure to the aeration zone of the 2^{nd} stage beds, of 41±1.3% were observed in the effluent of the reactors. Calculated oxygen uptake rates under optimal mixing conditions using a core sample of the aeration zone showed a demand of 2.48±0.05 mg D.O./g_{sed}/day. Additionally, dissolved oxygen tests of ports within the aeration zone of 2^{nd} stage reactors showed values < 1 mg/L in porewater. The microcosm study using cores from the top half (after aeration) of one of the 2^{nd} stage columns yielded significant losses (86.09±0.08% of initial chloroethane concentration; $p=0.003$) under Oxygen Amended treatment. No significant changes in chloroethane concentrations were observed in Kill Control ($p=0.184$) or Anaerobic ($p=0.053$) bottles. The sustainability calculations showed that a decreased dependency on Sodium Hydroxide (19 to 3.8 tons per year) and Sulfuric Acid (5,400 to 0 pounds per year), from implementation of an ABR system at the Site, resulted in an implied net decrease of approximately 60 tons of CO_2 per year and 29 MegaWatt-hours of electricity per year associated with production of these chemicals. The sludge production at the Site, after ABR implementation, decreased by roughly 91%. The implied carbon dioxide emissions and energy associated with refinery of the petroleum necessary to transport sludge, before and after ABR implementation, were calculated to be reduced by 6.27 tons CO_2 and 127 GigaJoules of electricity per year, respectively.

Long-Term Remediation of Water Polluted With Perchloroethylene

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Background/Objectives: The objectives of this work were *(i)* to evaluate the effect of coupling a zero-valent side filter to anaerobic fluidized bed bioreactors (AFBBs) on remediation of water polluted with high concentrations of PCE, *(ii)* to assess the degradation of the nonionic surfactant Tween 80, a mixture of fatty acids by the consortium of the bioreactors, *(iii)* to determine the PCE remediation potential of bimetallic nanoparticles (NP) ZVI/Pd with different ratios of Pd to reduce costs, and directed to their possible use in the side filters, and *(iv)* to study the dehalogenating consortia harbored in the AFBBs using molecular and physicochemical techniques.

Approach/Activities: Four fluidized bed bioreactors, two of which had a filter with iron filings (ZVI, these bioreactors were identified as HFBB) were implemented. All bioreactors were seeded with a methanogenic consortium and fed with increasing concentrations of PCE (80, 165, 278, 393 mg/L) dissolved in methanol and Tween 80 to give a constant concentration of 1 g/L COD in the feed.

Results/Lessons Learned: *(i)* The HFBB removed a higher amount of PCE and presented lower concentrations of metabolites than the plain methanogenic, filter-lees bioreactors (MFBB) in all four periods of operation. In general, mass of metabolites in the effluents, gas trap (volatilized PCE and metabolites) and sorbed onto bed bioparticles represented less than 5% of the input PCE mass. Average PCE removal efficiencies significantly decreased in the Periods with highest PCE concentrations, for both types of bioreactors. Bioreactors with coupled ZVI filters were more efficient regarding PCE and metaoblites removals than MFBBs.
*(ii)*The Tween 80 batch biodegradation tests using inocula from the AFBBs, showed that denitrifying bioreactors had the highest surfactant removal. Indeed, at the end of the batch operation, the remaining concentration was 87 mg COD-SumFA/L, i.e. 70% removal, concluding that Tween 80 could be used as the solec carbon source by the consortia. No toxic effects of Tween 80 were observed. It was concluded that the Tween 80 present in the feed to the AFBBs could contribute to methanol as degradable sources of carbon during the reactor operation.
(iii) Concerning the *NP* experiments the highest PCE removal was attained in the treatment with NP made of 70% of Fe and 30% of Pd (FP2) with a PCE removal of 85% whereas treatment FP1 (50% of Fe and 50% of Pd) and FP3 (90% of Fe and 10% of Pd) removals were 83 and 76% respectively, after 16 h of contact. Since the FP3 treatment has a significant economic saving of 40% compared to treatment FP1 due to lower Pd content, a trade-off is required regarding the criteria time and removal efficiency.

(iv) After the selective pressure of operating the AFBBRs at PCE high concentrations a consortium rich in dehalogenating bacteria (dehalogenating consortium LB5) was developed. We found genera such as *Dehalobacter spp., Desulfurospirillum spp., Desulfitobacterium spp., Dehalococcoides spp.* and *Methanosarcina spp.* The specific gene rate (r_g) in both FBBs improved over periods, mostly in the HFBBR. This suggests that the combined effects of ZVI-filters and the development of a significant dehalogenating capability in bioreactor consortia boosted performance of the HBBRs.

Degradation of PCBs in a Compost System with a Thermophilic Aerobe

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Background/Objectives. Polychlorinated biphenyls (PCBs) are complex mixtures of homologs noted for their toxicity and persistence. This research was designed to assess the efficacy of a novel bioremediation approach to the degradation of PCBs. The protocol is unique in that it uses a specialized strain of the thermophillic bacterium *Geobacillus midousuji,* in a single-step aerobic process in contrast to an anaerobic-aerobic treatment train. Degradation rates were obtained for total and subsets of PCB homologs on soil from an industrial site in the Northeast dominated by the hexachlorinated Arochlor 1254. This study using a solid –phase compost system builds on favorable results generated from previous slurry-phase bioreactor studies in preparation for the development of full-scale composting treatment application.

Approach/Activities. Laboratory scale pilot tests were done on 1.5 kg soil batches using a solid-phase incubation in 20 liter composting reactors. These incubations were maintained at greater than 50°C with sufficient humidification, aeration and a defined nutrient supplement using the thermophilic aerobe originally isolated from a compost pile in Japan. Parallel incubations that served as the controls were done the same way but without the bacterium. A time series was analyzed for PCB homologs using the gas chromatography, mass spectrometry EPA method 680 to assess the rates of degradation.

Results/Lessons Learned. Results of the solid-phase experiments present an average degradation rate (k) of .15/day for total homologs (half-life of 4.6 days). This corresponded to an average k value for of .19/day (half-life of 4.5 days) in previous experiments using a 1 liter slurry-phase bioreactor. Based on these ongoing studies, we will be scaling up and reporting on an outdoor composting system and expect to obtain similar results to the slurry-phase and solid-phase applications. Also, data on individual Arochlor levels, as a subset of the total Arochlor reduction data, are now being analyzed by EPA 8082 at this writing and will be reported on. Degradation was consistent with a first-order reduction characteristic of enzymatic reactions. PCB homolog analyses suggest rapid degradation of tetra-, penta-, and hexa-chlorinated PCBs, and, while further short-term studies are required, it appears that the highly chlorinated PCBs are degraded such that lower chlorinated forms do not accumulate. Thus, our results have proven this to be a scalable process that can ultimately be implemented in the field as a simple low-cost composting process in order to remediate PCB contaminated soils and sediments.

Co-Composting of Soil Impacted by Hydrocarbons

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Golder Associated Ltd was retained to assess the best remedial approach and methodology to be used at a former Petroleum site (the “Site”). The soil is impacted by Bis(2-chloroethy) Ether (BCEE), BTEX, petroleum hydrocarbons and PAHs. The site conceptual model has been used as the starting point to evaluate the potential remedial alternatives for the Site. The model has revealed that the contamination is mainly located in shallow and non-saturated soils consisting of fine silty backfill material overlying the bedrock on most of the Site. The contamination is also sparsely distributed on the Site, potentially caused by various individual spills and/or backfilling activities. Based on the Site conceptual model, in situ technologies have been mostly discarded due to the fact that contamination in soils is mainly located in shallow and unsaturated soils for most of the contaminated areas. Considering those site constraints, the excavation and combining of those affected soils into biopiles for aerobic biodegradation have been selected as the remedial alternatives for petroleum hydrocarbons affected soils only. The objective of the remediation was to meet the Québec industrial limit criteria.

In order to asses the feasibility of the bio treatment, laboratory testing and pilot testing were performed in 2010-2012. The laboratory tests was intended to lower the incertitude associated to the facts that there is little information available on the biodegradation of BCEE and PAHs high molecular weight (4-6 rings) are known to be recalcitrant contaminants for biodegradation . A biotreatability treatability study was designed to define the effectiveness and the optimal conditions for the biodegradation of contaminants of concerns (COCs). The treatments used in this test were two different nutrients and a surfactant, used alone or in combination. The efficacy of the treatments was measured using both chemical and biological indicators. The biological indicators used were bacterial enumeration of total heterotrophic bacteria (THB) and hydrocarbon degrading bacteria (HDB). A total of four biopiles were set up at test initiation. The aeration rates were checked and recorded throughout the testing. The bioreactors were sampled on days 0, 30, 60, 120 and 180 for the COCs, HDB and THB. Following the laboratory study, biopile and co-composting pilot tests were performed in 2011-2012. Co-composting is a process in which impacted soil are mixed with organics amendments such as chicken manure to promote contaminant degradation by microorganisms at elevated temperatures (40-65 oC) under aerobic conditions. Co-composting promotes thermophilic and mesophilic growth, increase nutrients and contaminant bioavailability. The pile tested volumes ranged between 0.2 to 210 m3 of impacted soil treated in HDPE reactors or small scale biopiles. Several mixes (horse, laying hens, roasters manure and wood shaving) and organic loading (25-75%) were tested. The extraction system consisted of regenerative blowers; knock-out drums, activated carbon filters and a leachate recirculation system. The biopiles was equipped with soil gas implants in order to monitor closely the soil gas concentration within the pile. Based on the laboratory and pilot tests, the full-scale design of the co-composting system was performed in 2012. 54 piles of 700 m3 volume were constructed. The piles were connected to 6 extraction systems consisting of 36 regenerative blowers. Air treatment was performed using activated carbon filters and biofilters. The treatment of 120 000 m3 of impacted soil begun in 2013 and it is planned to be completed in 7-years.

Pseudo first-order degradation rate constant were estimated and the nutrients, as well as the air requirement and composting amendments mixture determined in laboratory and during the pilot tests were used to design the full scale treatment system. The full-scale results revealed that the biodegradation of the COCs is performed in less than the predicted 24 months timeframe. The mass effect of the piles is beneficial to composting has the heat period is significantly longer in comparison with lab and pilot scale tests. The co-composting is also efficient to break the cohesion of the clay material which resulted in high removal efficiency and fast degradation kinetic for TPH and PAH. The co-composting piles generate significant VOCs emissions (up to 1000 ppm) and the minimal target temperature of 55 0C within the pile has been achieved and maintained for at least 1-month. The biggest challenges of co-composting are the management of the water generated and the control of nutrient level within the piles.

Back to Contents

Sustainable Wastewater Treatment at the Boston Mills Historic District Cuyahoga Valley National Park, Brecksville, OH

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Background/Objectives. The Boston Mills Historic District in Cuyahoga Valley National Park (CVNP) is listed in the National Register of Historic Places as a significant intact example of a 19th-century "canal village" for its concentration of intact 19th century architecture. On the banks of the Cuyahoga River, it is adjacent to the historic Ohio & Erie Canal Towpath Trail and Valley Railway. CVNP owns 11 structures within the Boston Mills Historic District; only four had properly functioning wastewater treatment systems. Several alternatives were evaluated to address wastewater needs of the buildings in the Boston Mills District while preserving the cultural and natural resources of the park.

Approach/Activities. An Environmental Assessment was completed (2009), resulting in a constructed treatment wetland being selected as the environmentally preferred alternative based on the following: ensuring that the CVNP owned buildings in and around the Boston Mills Historic District continue to have functional sanitary services through a system that is capable of achieving treatment goals that are protective of human health and the environment; preservation of the cultural and historic integrity of the CVNP owned structures located within and around the Boston Mills Historic District, preservation and protection of the archeological resources within and around the Boston Mills Historic District and ensuring continued improvement of water quality within the Cuyahoga River Watershed.

The constructed treatment wetland has a design flow of 10,000 gpd and consists of:

- Septic tanks
- Flow equalization
- Subsurface flow wetland initially planted with Blue Flag Iris, Green Bulrush, River Bulrush, Duck Potato, and Prairie Cordgrass
- Three tiered free water surface wetlands (evapotranspiration/infiltration)
- Recirculation

Results/Lessons Learned. Using phytoremediation to achieve water quality standards, constructed wetlands provide a cost-effective alternative to traditional wastewater treatment while providing consistent and predictable performance. Advantages include lower capital costs, less long term maintenance, no generation of hazardous by-products requiring further treatment, high public acceptance, and less energy requirements. The treatment wetland system was brought on-line in 2011. Monitoring results confirm that the system has met treatment goals and permit limits. The wetland system has proven to be a sustainable alternative that is complimentary to the mission of the CVNP to protect and preserve the Cuyahoga Valley and its resources.

Comparisons of Biotic, Abiotic, In Situ, and Ex Situ Methods for Remediation of Mining-Influenced Water

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Background/Objectives. CDM Smith is continuing treatability studies for remediation of mining-influenced water (MIW), with the goal of designing passive or semi-passive treatment methods for use either in situ within mine systems, or ex situ in biochemical reactors (BCRs). Treatment of MIW often relies on active methods, such as addition of hydrated lime, to raise pH and precipitate metals. Active treatment requires considerable maintenance and power, but passive and semi-passive treatment methods are challenging due to space requirements, varying flow rates, and seasonality of discharges. In situ treatment of MIW provides an opportunity to overcome issues associated with space, flow, and seasonal discharge, but requires detailed knowledge of the underground system. MIW must be evaluated on a case-by-case basis to determine the most appropriate method of treatment.

In the Coeur d'Alene Basin, Idaho, MIW types include near-neutral, low-sulfate MIW with elevated cadmium, lead, and zinc, as well as acidic water with elevated sulfate and metals. Treatability testing was completed using ex situ and in situ approaches. Biotic (sulfate-reduction based) and abiotic (geochemical manipulation) treatment methods were tested for their ability to reduce metal loading to local streams.

Approach/Activities. CDM Smith completed geochemical modeling and batch testing to determine appropriate abiotic treatment methods. Then, column testing was completed to simulate in situ and ex situ abiotic and biotic treatment methods. Columns were constructed using BCR-type materials (wood chips, sawdust, compost) for ex situ treatment. Abiotic and in situ columns were constructed with gravel and sand; the abiotic column was first acidified through addition of carbon dioxide, and then neutralized using limestone; in situ columns were designed to allow addition of liquid or slurried substrates (ethanol, methanol, and ChitoRem®). Pretreatment of the low-sulfate water through addition of gypsum or magnesium sulfate was required to increase the sulfate concentration. pH, redox, conductivity, dissolved oxygen, alkalinity, sulfate, and sulfide were measured, and periodic sampling for metal removal, sulfate reduction, and sulfide production was completed to monitor column effectiveness.

Results/Lessons Learned. The presentation will include a discussion of testing design and setup, column operation, and results of the study and potential next steps. Results to be presented include comparisons of metal removal and water chemistry of the treated effluent for biotic and abiotic approaches, pretreatment methods and implementation, dosing rates, amendment longevity, and application methods for abiotic, biotic, in situ, and ex situ treatment.

Wastewater Treatment Coupled with Chromium Metal Recovery and Energy Production using Microbial Fuel Cell

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Background and Objective. Chromium (Cr) containing materials have been widely used in a variety of industrial applications such as electroplating, leather tanning, metallurgy, catalyst for corrosion inhibitors and wood preservatives for several years now. Cr exists in the aqueous phase either as hexavalent chromium [Cr (VI)] or trivalent chromium [Cr (III)], of which Cr (VI) is more hazardous. Due to its high toxicity and tendency to accumulate in living organisms, the removal of heavy metals from wastewaters critical. Several treatment techniques such as chemical precipitation, coagulation–flocculation, ion exchange, membrane filtration, biosorption and biological treatment methods have been applied to treat wastewater containing heavy metals. Although these treatment techniques are effective, they have some inherent disadvantages that include high energy requirements, excessive consumption of chemicals, and generation of a large quantity of secondary pollutants and toxic waste sludge. As an alternative, if wastewater treatment technology is coupled with recovery of metals, which can then be reused in industrial processes, industries will readily adopt this technology. It is the objective of this study to present one such novel approach. Treatment of Cr (VI) contaminated wastewater was investigated using microbial fuel cells technology.

Approach. Here, Cr (VI) containing wastewater has been electrochemically or bio-electrochemically reduced to a non-toxic form in the presence of an organic electron donor in a dual chambered microbial fuel cell. Synthetic wastewater containing Cr (VI) was prepared and used as catholyte, while artificial wastewater inoculated with anaerobic sludge was used as anolyte. The experiment was carried out in laboratory scale.

Results. Cr (VI) at 100 mg/l was completely removed within a time period of 48 hours (initial pH 2) and 49% of total chromium was reduced in 96 hours. The maximum power density achieved was 141 mW/cm^2 (0.532 mA/cm^2). The experiments conducted so far verify the possibility of simultaneous electricity production and cathodic Cr (VI) reduction.

Back to Contents

Assessment & Biological Treatment of DNAPL Sources in Fractured Bedrock

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Background/Objectives. DNAPL sources in fractured bedrock are one of the greatest challenges facing the Department of Defense at many of their chlorinated solvent sites. Identifying the location of the DNAPL sources is one of the key challenges at these sites, as many of the tools and approaches used for identifying DNAPL sources in overburden materials are not appropriate or have not been demonstrated in fractured bedrock. Assessment of DNAPL mass, flux, and architecture also is needed to properly design remedial approaches and determine overall remedial success. Published efforts for bioaugmentation of DNAPL sources in fractured bedrock that incorporate evaluation of DNAPL mass removal and architecture are not readily available. Thus, such efforts are needed to fully evaluate the efficacy of bioaugmentation for treating DNAPL sources in fractured bedrock.

Approach/Activities. PCE DNAPL sources in fractured bedrock at Edwards AFB were evaluated using a combination of discrete interval groundwater sampling, passive flux meters, and partitioning tracer tests (single well push-pull tests and interwell tracer tests in discretely packered borehole intervals). Additional borehole geophysical and pump testing were used to assess the fracture flow field relative to the DNAPL sources. Using a groundwater recirculation system, bioaugmentation (consisting of addition of lactate, nutrients, and a commercially available culture containing *Dehalococcoides* sp.) was applied to target the fracture zones where DNAPL sources were identified. Straddle packers are being used in both injection and monitoring wells to isolate fracture zones where DNAPL is present. DNAPL mass removal and dechlorination are currently being monitored in these discrete intervals, and a second partitioning tracer test is planned after completion of treatment to assess DNAPL mass removal.

Results/Lessons Learned. Results to-date show that DNAPL sources are present within the fractured bedrock, as both single well push-pull and multiwell partitioning tracer testing indicated that DNAPL sources were present. Preliminary tracer testing further suggests that significant mass transfer limitations exist between the DNAPL sources and groundwater flow paths. Initial estimates of DNAPL mass suggest that the DNAPL occupies a very small fraction of the fracture volume (<5%).

Preliminary results (obtained within 1 month of bioaugmentation, which was performed at the end of August, 2014) indicate that electron donor is being effectively delivered to the DNAPL sources. In addition, increases in *Dehalococcoides* sp. have been observed at nearby downgradient monitoring points. DNAPL dissolution and dechlorination rates will be carefully monitored over the next several months to assess the overall effectiveness of bioaugmentation in this challenging system.

A Dual Biorecirculation System to Facilitate VOC Mass Reduction and Hydraulic Control in Fractured Bedrock

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Background/Objectives. Groundwater underlying and downgradient of a former industrial complex contains volatile organic compounds (VOCs), especially chlorinated solvents, in dissolved and non-aqueous phases. The VOCs are present predominantly in fractured bedrock in the source area and overlying alluvial deposits downgradient. The fractured bedrock geology has complicated historical source area remediation efforts, while the downgradient alluvial deposits have facilitated contaminant mass transport. Past remedial activities have included several emulsified oil injections to develop an offsite biobarrier and control downgradient flux, as well as manual removal of non-aqueous phase liquids (NAPL) in source area wells. CDM Smith designed a dual biorecirculation system to both provide hydraulic control and to speed site remediation in source areas with higher concentrations via reductive dechlorination.

Approach/Activities. CDM Smith designed, constructed, and now operates two stages (two loops) of an automated system that includes pulsed groundwater extraction, amendment with electron donor, and reinjection into injection wells. Both biorecirculation loops include injection and extraction wells that were installed with enhanced hydraulic permeability via hydraulic fracturing to maximize the efficacy of the wells. The hydraulic fracturing was performed following downhole geophysics and high-resolution NAPL vertical profiling with FLUTe liners. The wells installed in the upgradient source area loop were installed with zero valent iron that was emplaced into the fractures to accelerate remediation further. The reach of the hydraulic fractures was characterized via tilt-meter data collected during installation, and pressure transducers were installed into monitoring wells during startup activities to gain a better understanding of hydraulic connectivity within the upgradient source area recirculation loop.

Results/Lessons Learned. The operation of both recirculation loops began in September 2014. Operational data and best practices for installation and operation of a biorecirculation system in fractured bedrock will be presented, as well as the discussion of the multi-loop strategy to simultaneously eliminate offsite migration of VOCs while reducing contaminant concentrations in the source area.

Innovative Top-Down Pilot Test for Bioremediation of TCE in Fractured Carbonate Bedrock

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Background/Objectives. Trichloroethene (TCE) is present in fractured bedrock under an industrial site in upstate New York. The bedrock consists of multiple layers of carbonate rock overlying a deeper gypsum-rich unit (called the "D3" unit). The D3 unit is more highly conductive to groundwater than the overlying units and occurs more than 38 meters (m) below grade. A dual-phase groundwater extraction system was installed at the site and has removed over 48,000 kilograms (kg) of TCE, cis-1,2-dichloroethene (cDCE), and vinyl chloride (VC) from the shallow bedrock source areas since 2001. Natural attenuation via biological reductive dechlorination is active and is also destroying contaminant mass. There is interest in using enhanced in-situ biodegradation (EISB) to augment the ongoing natural attenuation and potentially replace the groundwater treatment system in the shallow bedrock. In addition, EISB in the shallow bedrock source areas may be beneficial at simultaneously remediating the deeper bedrock units down to the D3, due to large downward hydraulic gradients.

Approach/Activities. The approach tested involved drilling six injection wells in a known TCE source area. The injection wells are screened in the upper intermediate bedrock (called the "I1" unit), located 12 to 14 m below grade in the pilot test area. 18,410 kg of potassium lactate and 653 kilograms of emulsified vegetable oil (EVO) were initially injected into these wells in July and September 2013, respectively, with a second injection of 18,410 kg of potassium lactate occurring in June 2014. The potassium lactate and EVO were injected to treat TCE in the I1 unit, which is present at concentrations in excess of 100 milligrams per liter (mg/L). The potassium lactate was injected as a full strength (60%) solution having a low viscosity and a density of 1.33 grams per liter (g/mL). Thus it is denser than water and was anticipated to migrate downward through vertical fractures in the bedrock due to density driven flow and the large downward hydraulic gradients, likely following similar pathways as the original TCE. Monitoring wells are located both in the I1 unit around the injection zone, and in the D3 unit approximately 250 m downgradient at the property boundary.

Results/Lessons Learned. Monitoring during the injection phase showed good distribution of the potassium lactate and EVO away from the injection wells in the I1 unit. Substantial additional reductive dechlorination of TCE to daughter products has been observed over 18 months of performance monitoring. For example, the average concentrations of cDCE and VC increased by 93% and 85%, respectively, while concentrations of ethene and chloride in the I1 unit increased by an average of 100% and 140%. The results of compound-specific isotope analysis (CSIA) also show a positive shift in the average delta ^{13}C values for TCE, cDCE and VC in the I1 monitoring wells over the 18 month performance monitoring period.

In the D3 unit, increasing levels of volatile fatty acids (VFAs) and total organic carbon (TOC) were observed in the monitoring wells along the downgradient property boundary approximately six months after the first injection event. The levels have continued to increase over time, demonstrating that injection of electron donors in the shallow bedrock is capable of impacting conditions within the deep bedrock at this site.

Bioaugmentation of DNAPL in Fractured Bedrock and Low Permeability Soil

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Background/Objectives. Tetrachloroethene (PCE) dense non-aqueous phase liquid (DNAPL) was detected in the overburden and fractured bedrock at a site located in northern New Jersey. Previous remediation includes injecting of Hydrogen Release Compound (HRC) and Slow Release Substrate (SRS) during two pilot studies. After the injection of organic substrates, PCE concentration in groundwater decreased at the pilot study area temporarily, and the concentrations of the daughter products, cis-1,2-dichloroethene (DCE) and vinyl chloride (CV) had stalled. During the most recent sampling event, the concentration of PCE at 110 milligrams per liter (mg/L) indicated the presence of DNAPL. To reduce the source mass and contaminant mass flux, a bioaugmentation culture using SDC-9 and emulsified vegetable oil (EVO) was proposed at the entire source area and downgradient areas

Approach/Activities. The field implementation will be conducted between October and November 2014, and the baseline sampling was completed in September 2014. The most elevated PCE concentration was detected in the overburden/weathered bedrock, which consist of glacial till with low permeability. DPT and existing wells will be used to injection EVO and SDC-9 into the overburden and existing wells, respectively. To maximize the injection volume into the overburden, real-time data recording will be performed to allow timely responses and injection adjustments. In addition, the site is an active facility, and extensive coordination will be required for the field implementation.

Results/Lessons Learned. The preliminary results of the bioaugmentation implementation will be available before May 2015. The results will provide the effectiveness of bioaugmentation on the DNAPL and reduction of the mass flux. With the presence of DNAPL, reductive dechlorination of cis-1,2-DCE may be slowed. However, when substrate is well distributed in the subsurface, the stall at cis-1,2-DCE could be overcame. The results will confirm whether the real-time data can enhance the injection efficiency and create better substrate and SDC-9 distribution.

Back to Contents

Edible Oil Injection Event Monitored Using Conductivity Transducers at a Fractured Bedrock Site

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Background/Objectives. A persistent chlorinated solvent plume was the target of voluntary bioremediation efforts at a fractured bedrock site in southeast Pennsylvania. The history of the plume and the hydrogeologic circumstances associated with designing an in situ bioremediation remedy in this fractured bedrock aquifer are examined.

The site is located in the Triassic Age Newark Basin and is underlain by the Brunswick Shale of the Newark Supergroup and surrounded by intrusive diabase dikes and sills. These rocks have low primary porosity and transmit groundwater via fractures and along weathered bedding planes. Flow along these secondary features results in groundwater movement being controlled by local and regional topography, formation bedding, and regional groundwater use. Shallow groundwater is affected by chlorinated solvents to a much higher degree than deeper groundwater at the site. This indicates that a high degree of attenuation occurs, as shallow groundwater seeps into the deeper bedrock aquifer. Additionally, the data suggest that shallow groundwater is in direct and continuous communication with the underlying bedrock aquifer; as a result, the aquifer was treated as a single unit, and the in situ groundwater remedy was designed with that conceptual flow system in mind.

Approach/Activities. A remediation event involving injecting a patented soybean oil substrate was undertaken in June 2014. Approximately 2,500 gallons of diluted substrate solution was injected into the bedrock aquifer through two injection wells located approximately 20 feet apart. To evaluate the aquifer response to the injection, transducers measuring water level, temperature, and conductivity were deployed in downgradient monitoring wells before, during, and after the injection event. To evaluate the reaction of the aquifer to the amendment, bimonthly samples were collected in downgradient monitoring wells.

Results/Lessons Learned. This paper will provide an assessment of project design, substrate injection, and evaluate issues associated with practical aspects of undertaking injection programs in a fractured bedrock aquifer.

Overcoming Inhibition to Enhance Bioremediation in the Source Zone of a Fractured Bedrock Aquifer Impacted by Mixtures of Chlorinated Compounds

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Background/Objectives. Despite mixtures of chlorinated compounds and potential inhibition issues, propylene glycol injection successfully stimulated reductive dechlorination of 1,1,2-TCA, 1,2-DCA, TCE, DCE, and vinyl chloride in a fractured basalt aquifer. Across most of the treatment zone, decreases in parent compound concentrations were accompanied by isotopic enrichment, formation of daughter products, and increases in populations of organohalide respiring bacteria. The lone exception was a distinct area near a former brine outfall where high concentrations of chloroform (>2 mg/L) appeared to limit growth of *Dehalococcoides* strains capable of vinyl chloride reduction. The current study focuses on efforts to overcome chloroform inhibition in this area and promote long-term biodegradation of vinyl chloride.

Approach/Activities. For biostimulation in the inhibited area, groundwater is extracted from a downgradient pumping well and reinjected just upgradient of the inhibited area. Intermittently, the recirculated water is amended to 25% (w/v) propylene glycol and buffered with potassium bicarbonate. To date, a total of 9000 m^3 of downgradient groundwater has been extracted and reinjected. For the first bioaugmentation event, 300 m^3 of onsite groundwater, pumped from a well that had high *Dehalococcoides* concentrations, was recirculated to the injection wells. In addition, approximately 100 kg of chloroform-, dichloromethane-, chloroethene-, and chloroethane-degrading bioaugmentation cultures (from University of New South Wales) were mixed with anaerobic site groundwater and injected upgradient of the inhibited area. QuantArray analysis is routinely performed to evaluate microbial community dynamics and the potential for reductive dechlorination of chlorinated ethenes, TCA, DCA, and chloroform. Compound Specific Isotope Analysis (CSIA) is conducted with selected groundwater samples from wells within the treatment zone and across the site.

Results/Lessons Learned. After targeted recirculation, biostimulation and/or bioaugmentation efforts in the inhibited area, *Dehalococcoides* populations increased substantially and were greater than 10^4 cells/mL in nearly all of the monitoring wells located in the formerly inhibited area. Moreover, vinyl chloride reductase gene copies increased by an average of three orders of magnitude and were greater than the operating target of 10^3 gene copies/mL in nearly all of the wells influenced by the system. After biostimulation, chloroform reductase genes and dichloromethane fermenting strains, which had not been detected prior to recirculation, were present. Moreover, the positive impact of system operations extended downgradient effectively promoting growth of halorespiring bacterial populations in off-site locations. Although dilution contributed to observed decreases in parent compound concentrations including chloroform, system startup was accompanied by substantial growth of halorespiring bacteria, increases in the concentrations of daughter products, and CSIA results indicating enhanced biodegradation. Overall, the microbial, chemical, and geochemical data indicated that recirculation, biostimulation, and bioaugmentation had alleviated chloroform inhibition permitting growth of halorespiring bacteria, substantially stimulating biodegradation of the chlorinated hydrocarbons.

Rapid Assessment of Remedial Effectiveness and Rebound in Fractured Bedrock

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Background/Objectives. Although many technologies have been shown to be effective for reducing dissolved chlorinated solvent concentrations in bedrock during active treatment, contaminant rebound following active treatment has resulted (in many instances) in non-attainment of remedial objectives. Often the failure of selected remedial approaches and the extent of rebound caused by the various mass transfer and flow mechanisms indigenous to fractured bedrock aquifers are not recognized or confirmed until after significant resources have been allocated to the project. Thus, it becomes imperative to determine methods to rapidly assess potential remedial performance of a selected technology at fractured bedrock sites so that determination can be made at early stages as to whether or not the technology will be effective for attainment of remedial goals. The overall objective of this demonstration project is to develop and evaluate the use of a novel "Push-Push" remedial assessment technique, coupled with compound specific isotope analysis (CSIA), for use as a rapid and cost-effective means to assess the limits of bioremediation and other in situ remediation strategies on long-term groundwater quality. A standardized protocol for application of this Push-Push assessment technique also will be developed. This demonstration is being performed at two different sites: the former Naval Air Warfare Center (NAWC) in Trenton, New Jersey and the former Naval Construction Battalion Center (NCBC) Davisville (Site 07 - Calf Pasture Point) in North Kingston, Rhode Island.

Approach/Activities. The Push-Push methodology is an adapted technique that is a hybrid of conventional push-pull tests coupled with our flushing and high-resolution sampling technique. The overall approach is to rapidly remove TCE in conductive fractures in or near the source area, then measure the rate and extent of contaminant rebound after oxidant removal. In the first step of the test, chemical oxidant that is injected into the injection well will react rapidly to oxidize PCE and TCE that is contacted, and will serve as a means to rapidly remove dissolved contaminants in conductive fractures. This is the first "push" of the test. Non-contaminated water will then be injected into the injection well (second "push"). The initial pulse of injected groundwater will be used to flush any remaining permanganate from the conductive fractures, thus terminating the PCE and TCE oxidation reaction. TCE concentrations will be monitored in the MLS well to assess the extent of rebound during a continued slow injection of clean water into the injection well. Testing will continue until steady state or asymptotic levels are attained.

Results/Lessons Learned. Detailed bedrock characterization activities, including drilling and rock coring, laboratory treatability testing to determine the natural oxidant demand of the rock, borehole geophysical logging, and borehole discrete interval testing and sampling were completed at the NAWC site during early- to mid-2014; with target interval selection and packer installations in both the injection and multi-level sampling well occurring in June 2014. A borehole dilution tracer test is currently being performed to verify the groundwater velocity and estimate the effective (fracture) porosity. This borehole dilution testing also will provide an estimate of the ambient groundwater flow rate through the borehole, which will be used to determine the injection flowrate during the Push-Push test. The results of the bedrock characterization and tracer testing, along with the field testing methods, findings and lessons learned from the initial "Push-Push" testing to be completed at NAWC over the next several months, will be presented.

Optimization and Lessons Learned: Biorecirculation to Enhance Degradation of Trichloroethene/1,1,1 -Trichloroethane in Fractured Rock

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Background/Objectives. The long-term operation of a full-scale in situ bioremediation project for a Pennsylvania Superfund site will be described in terms of its engineering, hydrogeological and microbiological components. Monitoring data for chlorinated compounds, mineral nutrients, and electron donors for four years of operations will be presented. The microbiological effects of long-term continuous recirculation of nutrient-amended groundwater will be discussed using both pre- and post- well redevelopment monitoring data.

Full-scale operation of the automated biological treatment system for a carbonate rock aquifer at the Site began in 2010. The major compounds in site groundwater are the chlorinated volatile organic compounds (VOCs) trichloroethene (TCE), cis-1,2-dichloroethene (cDCE) and 1,1,1-trichloroethane (TCA) . The system consists of a central anaerobic amendment mixing tank connecting 7 injection and 5 extraction wells, sodium lactate as the electron donor, and mineral nutrients to supply ammonia and phosphate that are metered into the tank. The amended groundwater is reinjected within the source area to promote the in situ treatment of VOCs and to enhance natural attenuation downgradient.

Approach/Activities. A sustained decline in groundwater elevations and total flow throughout the system was experienced from May 2012 to March 2013. When groundwater elevations rebounded in the spring of 2013 and flow through the system was not restored, an optical televiewer inspection was conducted and revealed the likely presence of biological fouling on the extraction well screens. A microcosm study was conducted in December 2013 to May 2014 to confirm the health of the site-specific *Dehalococcoides ethenogenes (Dhc)* strain in the system extraction wells.

Well redevelopment activities were initiated in July 2014 using both physical treatment methods and sulfamic acid to restore production from the system extraction wells. The groundwater flow rates and field parameters including pH, oxidation-reduction potential, and dissolved oxygen concentrations, were monitored carefully following well redevelopment to ensure optimal conditions for anaerobic reductive dechlorination were restored in the aquifer. Following well redevelopment activities, a trace mineral distribution study was conducted, as prompted by the results of the December 2013 – May 2014 microcosm study. Adjustments in system operations were made, as necessary, to optimize the distribution of electron donor and mineral nutrients and enhance the rate of dechlorination. The AISB treatment system is operating continuously and monitored at monthly intervals.

Results/Lessons Learned. This presentation will discuss the results of the microcosm study as they apply to changes in microbial conditions in the aquifer over time, and address measures implemented to ensure sufficient trace mineral concentrations were achieved in the field. The approach and field techniques employed during well redevelopment will be presented, as well as adjustments in operations that were made to continue VOC reduction, maintain pH and appropriate redox levels, and mineral nutrient and electron donor levels.

No Further Action: A Case Study on High Resolution Site Characterization and Bioremediation in a Fractured Bedrock Setting

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Background/Objectives. Past operations at a truck stop operated in Richmond, KY resulted in multiple gasoline releases to the subsurface. Over a period of 20 years, site investigation activities have revealed a 320 feet long dissolved BTEX plume within the fractured bedrock beneath the site. The subsurface lithology at the site consists of a thin, approximately one to three feet thick clay overburden, underlain by Upper Ordovician Calloway Creek Limestone, Garrard Siltstone, and Clays Ferry Formation. Monitoring wells at the site were installed with screened intervals varying from 10 feet to 40 feet in length, and screened across multiple formations. Groundwater samples collected from nested wells indicate the presence of dissolved benzene in both the shallow and deep wells at various locations throughout the plume.

Approach/Activities. A bedrock remedial design characterization (RDC) utilizing multiple geophysical investigative techniques and high resolution field data collection were conducted to determine the transport mechanism of the dissolved BTEX plume and determine the effectiveness of the chosen in-situ technology. The RDC and pilot test included four key components: 1) a 2-dimensional electrical resistivity imaging survey (2-D ERI) to identify new borehole locations within the plume, 2) borehole geophysical logging to delineate the vertical extent, orientation, and aperture size of the bedding planes and fractures, 3) discrete groundwater sampling from identified fractures/bedding planes using a custom designed straddle packer assembly with an eighteen inch sample interval, and 4) high resolution water level monitoring of the surrounding well network during air rotary drilling and pilot injection test using pressure transducers to define the horizontal connectivity between existing monitoring wells and the vertical connection between formations.

Based on the data collected from the RDC and pilot test, a clear picture of the subsurface lithology and structural features was obtained. Multiple weathered zones were identified from the 2-D ERI where the additional boreholes were installed, and the borehole geophysical logging identified the horizontal bedding planes that were targeted in the discrete groundwater sampling and pilot injection test. The data collected from the discrete groundwater sampling, provided information to assist in injection location and remediation product loading. The product selected for the pilot test was Remediation Products Inc.'s BOS 200® based on the proven success displayed controlling the back diffusion of petroleum contaminants in fine-grained soils. The BOS 200® was injected via high pressure/high flow injections using Well Improvement Company's specialized pump and straddle packer system. Data collected from the pressure transducers during the pilot injection test demonstrated the radius of influence of the 150-gallon injections, ranged from 45-70 feet at the deeper injection intervals (deeper than 13 feet), and 20-30 feet in the shallower intervals (less than 10 feet).

Results/Lessons Learned. Post pilot test groundwater sampling results show the targeted monitoring well with historical benzene concentrations greater than 6 mg/L, below laboratory detection limits of 0.001 mg/L for seven consecutive quarters. Using the data collected from the pilot test, a full-scale injection was implemented in April 2014. The full scale BOS 200® injection was successfully placed in the identified zones of contamination throughout the plume, intersecting all impacted monitoring wells, with three consecutive quarterly sampling results exhibiting results below the target remediation goals. Based on the post-injections groundwater results from the pilot test and full-scale injection, a No Further Action letter was issued in February 2015.

Optimal Treatment Zone Moves during Enhanced Reductive Dechlorination in Fractured Bedrock

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Background/Objectives. An enhanced bioremediation pilot test was implemented at an industrial facility in Charlotte, North Carolina, USA to study the efficacy of enhancing in situ reductive dechlorination of tetrachloroethene (PCE) in shallow weathered bedrock where some intrinsic degradation to cis-1,2-dichloroethene (cis-1,2-DCE) was observed without further degradation to vinyl chloride or non-toxic ethene. Little or no detectable *Dehalococcoides* spp. was found within the study area.

Approach/Activities. 1,500 gallons of aqueous injectate was gravity fed into a well. Performance was monitored for two years in companion monitoring well AC-13D located ten feet downgradient from the injection point. The injectate was manufactured by mixing 2,700 pounds of a commercially available blend of anaerobically fermentable carbon substrates into 1,200 gallons of native anaerobic groundwater that contained *Dehalococcoides* spp. at a density of approximately 1,400 cells/mL and whose ratio of genes coding for vinyl chloride reductase enzymes to *Dehalococcoides* spp. approached unity.

Results/Lessons Learned. Direct connectivity between the injection well screen and performance monitoring well AC-13D was evidenced during the gravity-fed injection process. Groundwater in monitoring well AC-13D responded in the first six months by quickly degrading nearly all of the PCE to cis-1,2-DCE, but without further observed degradation. Other initial changes in analyte behavior included abundant increase in total organic carbon (TOC), mild oxidizing conditions, significant decrease in pH, no apparent growth of *Dehalococcoides* spp., and abundant growth of *Dehalobacter* spp.

Post-injection monitoring continued with the intent to assess the prospect that the biostimulation was effective somewhere beyond monitoring well AC-13D. Patience was rewarded when, after two years, cis-1,2-DCE was almost completely degraded to non-toxic ethene. The effective latent dechlorination in monitoring well AC-13D was accompanied by more modest TOC, mild to moderate reducing conditions, upward rebound of pH to near circumneutral levels, abundant growth of *Dehalococcoides* spp. (6.8E05 cells/mL), ratio of *Dehalococcoides* to total bacteria of 0.12, and ratio of genes coding for vinyl chloride reductase enzymes to *Dehalococcoides* spp. of 0.8.

The following lessons were learned:

- The heart of the active injection zone may inhibit effective dechlorination to completion.
- Poor dechlorination within the injection zone does not preclude effective treatment at some more-optimum distal fringe of the treatment zone.
- Initial observations suggested apparent failure of treatment; however, patient monitoring supported the conclusion that the effective treatment zone (or more-optimal fringe) first moved outward from the injection zone and then receded back toward the injection point over a period of about two years.

Achieving MCLs in Fractured Bedrock: 1,2-Dichloroethane Source Treatment and Reduced Bedrock Flux

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Background/Objectives. A highly-impacted 1,2-dichloroethane (DCA) source area in fine-grained soil at an active chemical manufacturing facility is being remediated, and significant improvements are being observed in the underlying bedrock groundwater. DCA has been detected at up to 5 grams per liter (over half its aqueous solubility) within the overburden source area. Overburden groundwater discharges downward into the shallow fractured bedrock, and bedrock groundwater migrates toward an adjacent river and tributary. In spite of strong downward hydraulic gradients, bedding plane fractures in the bedrock are nearly horizontal, promoting a strong horizontal component of flow; multiple groundwater discharge seeps have been located and sampled on steep cliffs above the adjacent waterways. The one seep that was formerly impacted by 1,2-DCA is located along the tributary, approximately 900 feet from the overburden source area.

Approach/Activities. Prior to remediation, the bedrock was characterized using: fracture lineament analysis; coring, including select locations along lineaments; hydraulic testing; optical televiewer measurements of fracture spacing and orientation; and hydraulic head evaluation. Due to the strong vertical hydraulic gradient, head data from wells at different depths were interpolated vertically into reference planes at select elevations to allow contouring of heads in map view. A conceptual site model of bedrock groundwater hydraulics was developed before remediation started, linking the affected seep to the source area via a 1,050-foot-long conceptual pathway following intersecting lineaments. The bedrock CSM informed the pre-remediation assessment of DCA attenuation along the pathway between the overburden source area overburden and the formerly affected seep. Increases in DCA daughter products (ethene, ethane, chloride) and geochemical indicators (dissolved iron, sulfide, methane) demonstrated robust, natural biological attenuation. Following successful bench-scale demonstration, a focused enhanced reductive dechlorination (ERD) program was implemented in the overburden source area using emulsified vegetable oil (EVO).

Results/Lessons Learned. Following five years of operation, significant improvements in water quality have been observed. Sustained reductions in DCA concentrations have been observed at the edge of the source area, including reductions from approximately 1 g/L to below the MCL (5 µg/L) for three years (99.98% reduction). All except one of the bedrock wells has reached the MCL (58 – 99% reduction relative to baseline). The sole impacted seep location, which represents the primary exposure pathway, has also been below the MCL for three years. While DCA mass remains within the overburden source area, these results demonstrate that reducing DCA mass flux to the underlying fractured rock system has significantly improved downgradient bedrock groundwater quality. The success of this remedy started with a clear conceptual site model incorporating groundwater hydraulics, solute transport and degradation processes. These results suggest that in some settings, bedrock matrix diffusion does not prevent bedrock groundwater treatment, attainment of MCLs and elimination of prior risk pathways.

Enhanced In Situ Bioremediation of Commingled 1,1,1-TCA and Chlorinated Ethenes in Overburden and Fractured Bedrock During Site Redevelopment

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Background/Objectives. An in situ groundwater remediation program was implemented at an active industrial site undergoing redevelopment in the northeast United States to address the chlorinated volatile organic compounds (CVOCs) in groundwater, primarily 1,1,1-trichloroethane (1,1,1,-TCA) (up to 784 ug/L), tetrachloroethene (PCE) (up to 4 ug/L), trichloroethene (TCE) (up to 25 ug/L), and carbon tetrachloride (CT) (up to 10 ug/L). Overburden and weathered bedrock are both impacted and hydraulically connected. The target overburden treatment area is approximately 20,000 square feet, with a target treatment thickness of 8 – 10 feet. Overburden consists of red-brown sand, silt, gravel, and cobbles resting on intensely weathered fractured red-brown shale, mudstone, siltstone, and sandstone of the Passaic Formation. The target bedrock treatment area is approximately 40,000 square feet with a target treatment thickness of 25 feet, from 10 to 35 feet below ground surface. The primary remediation objective is aggressive reduction of CVOC concentrations in the multiple overburden and bedrock strata that constitute the residual source area.

Approach/Activities. The groundwater cleanup approach employed a combination of fast and slow release carbon sources to enhance bioremediation via enhanced reductive dechlorination (ERD) in combination with bioaugmentation. Carbon substrate solutions were added to the subsurface through a network of injections wells. Initial average well spacing of 25 feet in overburden and 90 feet in bedrock was designed based on injection/extraction tracer testing. Sequenced injections of lactate and emulsified vegetable oil (EVO) were accomplished through a network of 32 overburden and 9 bedrock wells. Lactate and EVO diluted in anaerobic water were injected at as a 2% (v/v) solution in overburden and 5% (v/v) solution in bedrock, followed by anaerobic chase water, a bioaugmentation culture, and a final dose of anaerobic chase water. The distribution of amendments in the bedrock was optimized through simultaneous extraction of groundwater from wells around the point of injection. In addition to optimized distribution within the target treatment zone, combined extraction/injection pumping allowed for reuse of extracted groundwater in the injection process. Both the overburden and bedrock treatment zones extended a substantial distance beneath a newly constructed corporate office building, requiring the incorporation of remote injection and monitoring points within the building foundation to adequately distribute amendments in a manner that will expedite remediation.

Results/Lessons Learned. The in situ groundwater injection activities occurred in August and September 2014. The total injection volume was about 80,000 gallons. Visual observations of EVO in the extraction and monitoring wells confirmed an optimal distribution of amendments in the treatment zone. An evaluation of the first 6 months of performance monitoring data (CVOCs, water quality, geochemistry, and microbial parameters) will be presented. The performance of direct push injection versus injection wells will be discussed.

Experimental Design for Assessment of Electrokinetically Enhanced Delivery of Lactate and Bacteria in 1,2-cis-dichloroethylene Contaminated Limestone

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Background/Objectives. Leakage of chlorinated solvents into limestone aquifers from contamination in overlying deposits and long-lasting back diffusion from the limestone matrix pose an increasing threat to drinking water supplies, e.g. in Denmark. Often dechlorination of PCE and TCE contamination in limestone accumulates cis-DCE due to inadequacy of advection-based remediation technologies to deliver bioremediation additives. Therefore, there is a need for a remediation scheme capable of establishing contact between the contaminant, bacteria capable of degrading cis-DCE, and donor within the low permeable limestone matrix. EK offers some unique transport processes, which potentially overcome the diffusion limitations of ERD. A novel technology combines ERD and EK for enhanced delivery. The combined technology (EK-BIO) has shown promising results in the low permeable media clay. However, until now no studies have been performed with limestone.

Approach/Activities. A bench scale study of transport during EK-BIO in limestone was performed. Focus was on the transport abilities of EK for enhanced delivery of the donor lactate and a bacteria culture containing the dehalorespiring bacteria *Dehalococcoides (Dhc)* in limestone cores contaminated with cis-DCE. For the experiment, methods were developed for sampling of intact bryozoan limestone cores, saturation and contamination of the limestone cores using vacuum properties, and for monitoring throughout the limestone cores. In addition, an experimental set-up was designed to comply with the challenges of EK-BIO in limestone, e.g. the strict anaerobic bacteria, volatile contaminants and extreme pH developments prompted by electrode processes. The latter can be severe for the degrading bacteria if not managed.

Results/Lessons Learned. An experimental set-up was successfully designed. However, issues with the recirculation pumping for neutralization of pH were experienced. Therefore, suggestions for improvements of the experimental design were made. The performed preliminary test and assessment of EK-BIO in limestone revealed a critical pH development in the electrode compartments. Nevertheless, the buffering capacity of the limestone maintained a pH range within the limestone appropriate for the *Dhc*. Observations on transport processes included faster diffusion in the control reactor without EK, than predicted. However, the delivery of the donor lactate was uneven, whereas migration of bacteria was not observed. For the reactor exposed to EK, lactate was delivered more evenly by electromigration causing an increase in electric conductivity. Furthermore, fermentation of lactate with an increase in pH indicated migration of bacteria by electrophoresis. Whereas, an initial test on EOF in limestone as well as the assessment of EK-BIO indicated that the properties of limestone hindered the establishment of EOF as opposing to clay.

During the experimental work on EK-BIO in limestone, EK was demonstrated to be promising in establishing enhanced contact between the donor lactate, bacteria and the chlorinated compound cis-DCE within the limestone matrix. Therefore, degradation is expected to occur. Thus, back diffusion limitations in the limestone matrix potentially are overcome, which is essential for the overall time perspective of a remediation.

A Case Study on Remediation of Chlorinated Ethenes via ISCR at a Redevelopment Site

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Background/Objectives. A former dry cleaner facility and surrounding properties in River Edge, NJ were being redeveloped into a retail mall. The dry cleaning operations ended in late 1990s. Discharge of PCE wastes directly onto the ground surface resulted in two source areas at the site. Since the removal of source material in early 2000s, concentrations of PCE, TCE and c-DCE have decrease but still remain significantly above the NJDEP Ground Water Quality Standards (GWQS).

The sub-surface geology is complex and consists of unconsolidated silt and sand with clay as the overburden unit ranging in thickness from 5 to 25 ft. Weathered and fractured rock is encountered underneath the overburden. Groundwater is typically encountered at 15 ft bgs. Following a comprehensive subsurface investigation to map the site-specific geologic features, hydrogeology, geochemistry and contaminant distribution using state of the art investigation tools, a Conceptual Site Model (CSM) was developed that helped understand the contaminant fate and transport. Concentration of PCE in source area monitoring wells ranged from 5,000 to 25,000 ug/L.

Approach/Activities. Remediation strategy was largely driven by the redevelopment aspects of the site in terms of timing and that there would be no future access at the site for continued treatment. The CSM indicated that the geochemical conditions in the targeted treatment zone supported an in situ chemical reduction (ISCR) approach. ISCR would also provide both short and long-term treatment which was a key consideration. Remediation goals were to achieve a significant reduction in mass of total CVOCs within two years.

As defined herein, ISCR describes the synergistic effect of combining ZVI (or other reduced metals) with an organic carbon substrate to significantly lower the redox state of an aquifer. EHC® is an ISCR amendment consisting of ZVI and organic carbon for treatment of chlorinated solvents. A total of seventeen injection points were installed in the two source areas based on an estimated radius of influence of 25 ft. EHC was injected via pneumatic fracturing by creating 175 fractures through these injection points. Approximately 1,500 lb of EHC was injected in each fracture. The injections were completed in March 2012.

Results/Lessons Learned. Hydraulic fracturing was very effective in achieving a ROI greater than 50 feet. Rapid reduction of PCE accompanied by temporal fluctuations of degradation products TCE, DCE and VC was observed. Complete reduction of PCE to below 1 ug/L was noted at several key well locations. Development of the Site is underway as post-injection monitoring continues to support MNA as the final remedy for groundwater.

Direct Introduction of Abiotic and Reductive Dechlorination Remediation Reagents Utilizing Soil Mixing in a Challenging Lithology

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Background/Objectives. At a site in metro Denver, Colorado with a historical dry cleaning operation, groundwater is impacted with contaminants of concern (COCs) including tetrachloroethene (PCE) and trichloroethene (TCE). Cis-1,2-dichloroethene (cis-DCE) has been measured at low concentrations throughout the site. Lithology at the site is known to include minimal unconsolidated overburden overlying consolidated fractured bedrock. The site remains developed with multiple buildings. Impacted groundwater flows primarily in bedrock fractures and to lesser degree within thin interbed or stringers of silt and clay. Source areas were difficult to determine and delineate due to fractured bedrock conditions, but are suspected to originate inside the building with potential migration pathways including downward fractures and as exfiltrate from sanitation sewer pipes. Groundwater monitoring has been ongoing as early as 2006. Remediation activities at the site have included installation of permanent injection wells manifolded to a potassium permanganate mix tank and dosed regularly from 2007 until 2011. Initial remediation effort consisted of gravity feed delivery of potassium permanganate solution into fifteen injection wells placed in proximity to suspected source areas. Minimal changes in concentrations were noted over the course of injection, generally attributed to a lack of understanding of the hydraulic characteristics and flow at the site resulting in inefficient or no reagent distribution. The site is currently overseen by the State Voluntary Clean-up Program and importance has been placed on addressing on-site impacts as concentrations in property-boundary wells have exhibited an increasing trend.

Approach/Activities. In-situ mixing was utilized at the site to directly introduce zero-valent iron (ZVI) and ELS into two subgrade mixing areas suspected to be source areas, and Daramend into a third downgradient mixing area. Approximately 5,000 pounds ZVI and 80 gallons ELS were mixed with an axial mixer at depths up to 19 feet below ground surface (bgs). At these depths, the native fractured siltstone and claystone bedrock was observed. The mixer was able to break apart the bedrock while the ZVI and ELS mixture was added across the slightly-saturated zone from 10 to 19 feet bgs. In the downgradient in-situ mixing area, roughly oriented as a permeable reactive barrier, approximately 1,000 pounds Daramend was mixed, from approximately 14 to 19 feet bgs to provide additional anaerobic bioremediation.

Results/Lessons Learned. In-situ mixing has been effective to introduce abiotic and biotic reagents into a difficult lithology where fracture flow is the dominant transport mechanism at a site at which traditional injection techniques have previously failed. Through one sampling event post mixing, concentrations of PCE in three in-excavation wells which were reinstalled have decreased by 99.5% and 84.7%, respectively. Cis-DCE concentrations have increased in other areas, suggesting both abiotic and reductive dechlorination remediation is occurring. Prior to the May 2015 Battelle event, two to three additional sampling events will have occurred providing additional data with respect to potential matrix back diffusion, evaluation of further downgradient wells, and continued geochemical indicators of remediation. To date, outside-of-excavation wells have shown minimal if no concentrations changes, but slow groundwater movement at the site predicted this result. In summary, at sites where traditional techniques including direct injection are not feasible, in-situ soil mixing creating direct contact between reagents and COCs while providing long-reactive chemistries may be effective.

Back to Contents

Environmental Sequence Stratigraphy Applied to Complex Geologic Settings: Glacial Deposits

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Overview. Bioremediation requires that contaminant migration pathways are well defined, which is problematic in complex geologic settings such as glacial deposits. Glacial deposits are commonly lumped as a heterogeneous morass of sediment when using industry standard data sets, but can be parsed into meaningful, high resolution genetic packages of sediments that better define contaminant migration pathways. Environmental Sequence Stratigraphy is a methodology that provides an effective means of identifying depositional environments amidst boring-to-boring variation to define the subsurface heterogeneity. A stratigraphic "sequence" is a repeatable vertical profile of lithologic change evident in boring logs and geophysical data which, when recognized, can be used to group and map subsurface sediments. Identification and correlation of environment-specific packages of sediments increases the resolution at which site heterogeneity can be characterized with important implications for optimization of remediation and/or site management strategies. Several project case studies from the Midwestern USA and Canada are presented to demonstrate the success of this methodology.

Background/Objectives. Glacial sediments dominate the surficial geology of the Midwestern USA and most of Canada. In these areas groundwater and contaminants migrate through or are stored within these sediments. Project technical staff and managers must realize the value of understanding glacial stratigraphy at the highest resolution possible for cost-effective and successful site remediation. Unfortunately most available map resources for Quaternary Geology are of a small scale (i.e. 1:500,000), never meant to be used for detailed site investigation. In contrast, typical remediation sites are mapped at detailed scales of 1:1,200 to 1:24,000. At such scales the glacial site sediments are typically interpreted as either indecipherably heterogeneous or unrealistically homogeneous. It is the objective of this presentation to provide case studies that demonstrate successful bridging of this gap between observations and available resources with implications for remediation.

Approach/Activities. Three site examples are provided from Michigan and Ontario. Environmental Sequence Stratigraphy methods were applied to existing lithology data that included cone penetrometer logs and traditional borehole logs. The Michigan sites are characterized by proglacial lake basin, shoreline, and outwash as well as modern fluvial incision into extensive underlying outwash and morainal tills. The Ontario site is characterized by drumlin landforms surrounded by proglacial lacustrine deposits. An iterative approach is used to create a best fit between geologic observations, groundwater elevations, and analytical results. An example of a revised site stratigraphy and its implications for increased efficacy of a common augmented bioremediation strategy, emulsified vegetable oil injection, is presented.

Results/Lessons Learned. Modern analogs, facies models, and outcrop examples demonstrate the scales of lithologic variability to be expected in glacial sequences in general. The site-specific sequence-based correlations created the stratigraphic framework of a more effective Conceptual Site Model which aided in understanding existing groundwater and analytical data, and helped create a predictive framework to guide future data collection and remedy design.

Sulfate-Reduction to Remediate a Site with Complex Geology

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Background/Objectives. A site located in northern New Jersey has very complex geology and impacted by organic contaminants including benzene and chlorinated solvents. Various remedial technologies were evaluated for this site, but sulfate-reduction was selected for the benzene impacted zone. The effectiveness of sulfate reduction has been tested via an on-going column and microcosm study. Following the bench-scale will be tested via a pilot test before the full-scale implementation.

The site is located on a geological fold, and shows extremely complex geological conditions, evidenced by interlocked clay, silt, and sands. The site shows such heterogonous conditions that no distinctive aquifer can be identified. A layer of dense-dry silt on the top of bedrock is the only geological feature can be classified throughout the site. The previous remediation entails an extensive sitewide excavating the vadose soil. The objective of the bench-scale study is to identify the effectiveness of sulfate reduction at this site and the remedial objective is to reduce the contaminate mass within the source area and prevent off-site migration.

Approach/Activities. Many sites impacted by hydrocarbons have anaerobic and reductive conditions. The common remediation technology for benzene entails introducing oxygen into the subsurface to generate aerobic degradations. However, keeping the aquifer aerobic can be problematic for this site because of the high heterogenic subsurface. A predesign investigation showed that sulfate reduction has been occurring at the site, but benzene concentrations did not decrease because of the lack of sulfate in the impacted areas.

A column test using site groundwater and soil was setup in August 2013 in the Langan Treatability Facility at New Jersey Institute of Technology (NJIT). Two sets of columns were setup to represent two areas, which are adjacent to each other and show significantly different soil characterization. Each set has three columns (or treatments) including control, sulfate, and sulfate/iron. The sulfate/iron column is investigating the role of iron and nutrient on promoting sulfate reduction. In parallel, since May 2014, microcosms were set up to replicate the column study condition, to identify the feasibility of sulfate reduction. Benzene, sulfate, sulfide, and iron were monitored periodically, and the soil samples from the column will be test for microbial and mineral composition using electric scan microscopic in October 2014.

Results/Lessons Learned. The preliminary results from the both bench-scale studies indicated that sulfate reduction required a fermentable carbon source to support microbial growth and iron to precipitate sulfide. However, the degradation kinetics has been much slower than expected. Investigation on microbial population and potential inhibitory factors has been performed, in order to enhance the degradation kinetics. The bench-scale studies will be concluded in early 2015. If favorable results can be obtained, the field pilot study will be initiated in the summer of 2015.

Back to Contents

State of the Practice in Managing and Treating Large Dilute Plumes

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Background/Objectives. Large dilute groundwater contaminant plumes represent one of the most challenging systems to restore. Often, remedies include multiple treatment technologies that require management over many decades. Recent innovations in the state of the practice and lessons learned from Sites which have been undergoing remediation for decades has resulted in a better technical and logistical understanding of these Sites, which can be leveraged to develop more cost-effective, and realistic, management plans acceptable to Site stakeholders and decision-makers.

Approach/Activities. Key advances in the state of the practice include characterization technologies that allow for elucidation and modeling of biotic and abiotic contaminant degradation mechanisms, including more obscure reactions, relevant over the timescales that the plume is undergoing restoration. In addition, a more holistic conceptualization of contaminant plumes as dynamic systems can be achieved with new, and innovative, tools and technologies that more accurately measure phenomena such as contaminant and groundwater hydraulics, chemical diffusion and aquifer geochemical conditions which often vary over space and time and dictate which attenuation mechanisms are prevalent throughout the plume. In addition, advances in contaminant fate and transport modeling allow for integration of biotic, geochemical and hydraulic field measurements for quantitative assessment of contaminant fate resulting in more accurate predictions of contaminant mass flux and concentrations over the relatively long restoration timescales.

Results/Lessons Learned. A review of characteristics that result in the development of large dilute plumes will be provided. In addition, the state of the art in developing realistic conceptual site models that account for natural attenuation processes that support better remediation decision-making focused on managing risk will be discussed, along with how to integrate tools and technologies effectively over the life cycle of the remedy.

Microbiological and Molecular Tools to Understand Bacterial Function in Aquifer Sediments in Multi-contaminant Plume at Hanford

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Background/Objectives. Past plutonium enrichment and recovery processes at the Hanford site have resulted in sediments contaminated with carbon tetrachloride, uranium, chromium, technetium-99, iodine-129, nitrate and tritium. Often these contaminants are co-mingled, exhibiting complex biogeochemistry, which complicates efforts to find remedial alternatives. Initial efforts to understand biogeochemistry in sediment and groundwater samples recovered from beneath the 200-UP-1 Operable Unit in the Central Plateau of the Hanford Site have provided valuable insight that could be used in developing bioremediation strategies for the complex contaminants found at the site.

Approach/Activities. Split-spoon core samples were taken from three depths (10, 30 and 50 ft.) below the water table for a well being drilled to extract groundwater. Physical (bulk density, particle density, and particle size) and chemical (specific conductance, alkalinity, pH, metals, anions, uranium and other radionuclides) properties were analyzed on these Ringold formation sediments. In addition, aerobic and anaerobic enrichments using a number of carbon and electron sources, as well as electron acceptors found in these environments were performed. Molecular biological tools were used to compare differences in phylogenetic and functional diversity of the community at the different depths. Metagenomes based on the 16S rRNA gene were used to compare phylogenetic diversity. Quantitative polymerase chain reaction (qPCR) using primers for aerobic heterotrophs, chemilithotrophs, nitrate reducers, iron reducers and sulfate reducers were used for analysis of functional genes present in the aquifer.

Results/Lessons Learned. The sediment microbial community from Ringold sediments from the Hanford 200W Area appeared to be dominated by α-,β and γ-*Proteobacteria*, followed by *Actinobacteria* and *Acidobacteria* species. Cultivable microorganisms in these oxic sediments were primarily represented by aerobes, fermenters and denitrifying communities; however some iron reducing bacteria were present also. Analysis of functional genes supported these results, with a predominance of genes related to nitrate reduction. These preliminary results indicate that while oxic conditions predominate in these sediments samples, that facultative anaerobes with the functional capacity to biotransform radionuclide contaminants in the aquifer exist and would likely grow if carbon was added to the aquifer.

Biosensors for Predicting and Monitoring Environmental Perturbations and Microbial Response across a Uranium-Nitrate Contaminated Watershed

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Background/Objectives. At the Department of Energy's Oak Ridge field research site, 243-acres of contaminated area is located within the along the Bear Creek valley watershed. In this study, we conducted a survey of 100 groundwater wells in order to (1) characterize key microbial populations at geochemically distinct locations and (2) identify associations between environmental gradients and microbial communities. The overall goal was to determine the predictive power of biosensors, including bacterial communities, to quantitatively characterize the environment.

Approach/Activities. To identify key microbe-environment associations, k-medians clustering algorithm was used to group 818 wells into 100 clusters based on 14 geochemically similar measurements. Within each cluster, wells for sampling were chosen randomly or by accessibility to the well. For each well, *in situ* groundwater measurements were recorded and groundwater samples were collected for both geochemical measurements and analyses of microbial communities. Microbial communities within each well were collected onto a 10.0µm pre-filter and 0.2µm-membrane filter and then extracted using a Modified Miller method. To identify potential stress indicators, filtered groundwater was collected through a 0.2 mm pore size Sterivex filter for phospholipid fatty acid analyses (PLFA). Total lipids were extracted using the modified Bligh-Dyer method and separated by polarity using silicic acid chromatography

Results/Lessons Learned. Evaluation of divergence of microbial communities across all the wells indicates the microbial communities are fairly distinct. Metadata correlations of all the wells show many of the geochemical parameters are independent of each other. To assess geochemical and microbial associations, a contamination model was developed using the machine learning algorithm, Random forest. Results demonstrate this model is able to use DNA to accurately predict geochemical features and distinguish between uncontaminated and contaminated sites. Analyses of PLFA biomarkers and levels of contamination in each well across the watershed showed more lipid diversity in highly contaminated wells as compared to profiles in non-contaminated wells. Stress indicators for Gram-negative populations, such as those associated with pollutants and nutrient limitation, are present in 32% of the wells sampled. Increase of these indicators may be attributed to increased anaerobic metabolism. Overall, results from this study demonstrate the importance of microbial community structure and PLFA biosensors in predicting environmental constraints. Such predictions may provide the ability of microbial monitoring for natural attenuation at legacy sites and be enabling for ENIGMA for more specialized questions on microbial community and network structure and function

Treatment of Contaminants in Low Permeability Zones

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Background/Objectives. Groundwaters contaminated with chlorinated solvents represent one of the largest challenges to the groundwater remediation profession. Due to their large storage potential, addressing contaminant storage and release from the low permeability (k) soils of source zones and plumes is of interest.

Approach/Activities. Six identical laboratory tanks with alternating layers of transmissive and low k TCE-impacted field soils were employed to produce a comparative analysis of treatment technologies for contaminants in low k zones.

The experiments involved flushing with a saturated aqueous solution of TCE (52 days), flushing with clean-water (28 days), treatment (27 days), and post-treatment flushing with clean-water (82 days). The six treatments were: 1) no-action control, 2) enhanced water flushing, 3) potassium permanganate flush, 4) KB-1 microbial inoculum with lactate, 5) KB-1 with lactate and xanthan gum injection, and 6) sulfate-reducing bacteria (SRB) inoculum with lactate and magnesium sulfate.

Results/Lessons Learned. Order-of-magnitude (OoM) (i.e., 3 OoM = 99.9%) reductions in effluent TCE concentrations at the end of the study, relative to the end of the TCE flushing were: no-action control (2.59), enhance flushing (2.58), permanganate (3.05), KB1-lactate (3.15), KB1-lactate-xanthan gum (3.19), and SRB-lactate-sulfate (3.75). Effluent TCE concentrations from all tanks range from 2.79 (control) to 1.63 OoM (SRB-lactate-sulfate) above the TCE MCL at the end of the 189-day study. Effluent cis-DCE and VC concentrations above MCLs were observed during and after the biological treatments were applied.

Primary findings from this work include: 1) consequential contaminant storage and release time-frames associated with low k zones, 2) enhanced flushing failed to sufficiently drive the TCE out of the low k zones to produce a long-term reduction in effluent concentrations, 3) penetration of permanganate into the low k zones was visually and analytically shown to be limited by diffusion, the oxidant demand of the low k soils, and potential clogging of pore space by manganese dioxide, and 4) all three of the biologically mediated treatments saw multiple OoM reductions in effluent TCE, followed by rebounds, which were most likely caused by exhaustion of the electron donor. Overall, constrained performance in the studies is consistent with observed treatment and rebound of chlorinated solvent concentrations at many field sites. Furthermore, results indicate that *even under ideal laboratory conditions*, common treatment technologies applied to systems with contaminants in low k zones were limited. Findings suggest that in addition to providing a long-term source for contaminants, low k zones rendered the considered remediation methods ineffective at large OoM reductions in long-term effluent CVOCs. These results suggest that care is needed in setting the strategies and expectations involved in these treatments at field sites with potentially significant low k storage.

Long-term Bioremediation and Management for a Co-mingled Chlorinated Solvent and 1,4-Dioxane Source Area and Plume

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Background/Objectives. Historic releases of 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and tetrachloroethylene (PCE) at a former industrial facility impacted underlying soil, weathered bedrock, and shallow groundwater. Investigations found that the resultant chlorinated volatile organic compounds (CVOC) groundwater plume extended more than 13,000 feet downgradient of the former facility and was up to 1,200 feet wide and 70 feet deep in certain portions of the site. The principal compound of concern was 1,1-dichloroethene (1,1-DCE), a breakdown product of TCA and, to a lesser extent, TCE. In addition, 1,4-dioxane has been found at moderate concentrations (approximately 100 mg/L) within the footprint of the former facility. A multi-component remedy and site management strategy has been implemented for over 15 years, consisting of hydraulic containment, enhanced in situ bioremediation, monitored natural attenuation, and vapor mitigation.

Approach/Activities. In the source area, hydraulic containment is being used to prevent contaminants from leaving the site. The treatment system extracts groundwater, removes the chlorinated solvents using an air stripper, reduces the 1,4-dioxane concentration with an advanced oxidation process (AOP), and re-injects the treated water. A residual DNAPL source area (total VOC concentrations as high as 25,000 to 30,000 mg/L) is located beneath a large industrial warehouse that houses an active business. For the downgradient plume, bioremediation has been implemented in three discrete areas using emulsified vegetable oil injections. The downgradient plume has also caused vapor intrusion concerns for residential areas. Geosyntec implemented a comprehensive indoor air sampling program, with several hundred homes receiving vapor mitigation systems to date. Geosyntec also implements a comprehensive monitoring program to track attenuation of contaminants throughout the remainder of the plume.

Results/Lessons Learned. The hydraulic containment system has successfully cut off flux of VOC contaminants from the source area to the downgradient plume. Proper operation of the treatment system has eliminated surface water discharges for the last 4 years, saving tens of thousands of dollars in testing, evaluation, and treatment costs. When the AOP component of the treatment system was failing, it was determined that upgrading the system rather than replacing it was feasible, and resulted in a savings of more than $150,000.
The bioremediation injections have been successfully conducted in residential neighborhoods and have resulted in concentration reductions of up to 98% for VOC contaminants. MNA monitoring has shown that VOC concentrations have declined in more than 90% of offsite wells. The indoor air sampling and vapor mitigation program was among the first to be implemented in the state of Colorado, and set precedent for the state approaches vapor intrusion sites.
The presence of 1,4-dioxane limits potentially applicable remediation technologies for the source area. While technologies exist that could treat both the CVOCs and 1, 4-dioxane, evaluation of alternatives has shown that any source remediation would cost significantly more than the present value of several decades of hydraulic containment, primarily due to the difficulty in access caused by the site building. In addition, while remediation could potentially reduce contaminant mass in the source area, it is likely that even after remediation, the hydraulic containment system would still be required. Therefore, the current strategy is to continue operation of the hydraulic containment system with offsite remediation, vapor mitigation, and monitoring.

Bioremediation of a Large
Chlorinated Solvent Plume, Dover AFB, DE

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Background/Objectives. In summer 2006, Oak Ridge National Laboratory (ORNL) and URS (now AECOM) implemented accelerated anaerobic biodegradation (AAB) to remediate several large chlorinated solvent groundwater plumes at Dover Air Force Base (DAFB) in Delaware. The largest of the plumes is called Area 6 and is approximately 1 mile in length and over 2,000 feet wide. Contaminants originate from at least five separate source areas in the industrial portion of the Base and comingle in the subsurface to form the large plume. The main contaminants are chlorinated ethenes (PCE and TCE) and to a lesser extent chlorinated ethanes (1,1,1-TCA) and their degradation products. Remediation focuses on the source areas and the downgradient plume core to reduce contaminant flux to the more distal portions of the plume.

Approach/Activities. AAB began with targeted direct-push injections in source areas that included maintenance facilities, unlined lagoons, oil water separators, and solvent spills. Contamination at these locations is confined to the upper portion of the water table aquifer typically between 5 and 20 feet below the ground surface. Dissolved-phased contaminants migrate downgradient from the source areas and downward in the aquifer with increasing distance from the sources. Once in the deeper portion of the aquifer the individual plumes comingle and become one large plume. The majority of the contamination is located between depths of 35 to 45 feet below the ground surface. AAB in this downgradient part of the plume is applied using permanent wells installed 50 feet apart along transects perpendicular to the flow of groundwater. Multiple transects were installed across the plume cores' flow paths so that contaminants pass through several reductive zones over time. A total of 103 wells were installed to form 9 transects across the plume, downgradient from source areas.

A substrate mixture of sodium lactate, emulsified vegetable oil (EVO), and nutrients is used to promote microbial activity and subsequent contaminant degradation. Mobile treatment trailers extract groundwater from alternating wells, add substrate and nutrients, and inject the mixture into the remaining wells of a transect. This method enhances the distribution of substrate in linear zones across plume cores. It also is relatively easy (and thus less costly) to maintain, produces no wastes, can be flexibly applied to avoid interfering with Base infrastructure and activities, and enables multiple reinjections of substrate.

Results/Lessons Learned. Eight years of AAB has reduced the contaminant mass within the 80-acre treatment area by over 99 percent. Prior to AAB treatment, a total of 93 pounds of dissolved solvents were present in the groundwater within this area. As of August 2014, a total of less than 1 pound of dissolved solvent mass remains. This successful application of AAB has stopped the flux of contaminants to the more distal portions of the plume. While more time is needed for effects to be seen in the distal plume, AAB injections will soon be discontinued and the remedy will transition to natural attenuation only.

Hydrogeologic Limitations to In Situ Remediation of a Dilute VOC and 1,4-Dioxane Plume in the North Carolina Piedmont

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Background/Objectives. During site investigation activities, a low concentration (total volatile organic compounds [VOCs] of 100 micrograms per liter [µg/L] or less) plume of 1,1-dichloroethene, 1,1-dichloroethane, and 1,4-dioxane approximately 1,200 ft in length was delineated across two undeveloped properties. North Carolina's default groundwater standards for highest beneficial use were required as remedial goals (RG). A focused feasibility study (FFS) was prepared to evaluate active and *in situ* remedial technologies to address (1) the low VOC concentrations observed, (2) treatment challenges of 1,4-dioxane (RG of 3 µg/L), and (3) the complex site geology of saprolite and partially weathered bedrock (PWR).

Approach/Activities. The FFS included an (1) *in situ* treatability study to evaluate anaerobic and aerobic bioremediation in the former source area to address VOCs and localized polynuclear aromatic hydrocarbons in soil and groundwater; (2) an anaerobic *in situ* bioremediation (ISB) pilot test in the former source area for VOC treatment; (3) a granulated activated carbon (GAC) treatability test for a potential application of a passive adsorptive barrier wall for treating VOCs and 1,4-dioxane along the downgradient portion of the plume; (4) a hydrogeological study of the saprolite and PWR; and (5) evaluation of monitored natural attenuation (MNA). The ISB treatability study indicated native microbial populations were sufficient for reductive dechlorination; therefore, biostimulation using emulsified vegetable oil (EVO) as an electron donor was employed in the source area during the ISB pilot test. The GAC treatability study incorporated batch adsorption isotherm tests to evaluate 1,4-dioxane sorption at varying concentrations and a column study (GAC/sand mixture) to evaluate the efficacy of the proposed adsorptive barrier wall at the observed groundwater flow velocity to achieve the 1,4-dioxane RG.

Results/Lessons Learned. Anaerobic conditions did not develop adequately in the treatment area during the ISB pilot test due to the poor distribution of electron donor resulting from preferential transport pathways in the saprolite and PWR. The GAC study results indicated no adverse competition between VOCs for sorption sites and an adsorption equilibrium that would achieve RGs; these results suggested a passive GAC barrier may be effective at removing VOCs and 1,4-dioxane from the downgradient plume over time. More critically, hydrogeological data from the plume revealed varying thicknesses and densities of saprolite/PWR that influenced saturated thicknesses, and stained fractures in the shallow bedrock that indicated fracture flow. Coupled with the evidence of preferential flow in the source area during the ISB pilot test, the constructability and the effectiveness of capture using a passive barrier wall were in doubt. With the absence of viable human and ecological receptors, a MNA approach that relies on physical attenuation mechanisms was ultimately employed as the most reasonable, cost-effective groundwater remedy to address the site's hydrogeological and chemical challenges. This approach also maximized our client's redevelopment opportunities for the downgradient parcel.

Back to Contents

Emulsified Oil Injection and Full-Scale Groundwater Remediation System Operation

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Background/Objectives. Historical fertilization mixing and application practices resulted in the migration of nitrates into the vadose zone and groundwater at this site. Subsurface lithology for both the unsaturated and saturated zone consists primarily of alluvial soils that are highly heterogeneous, ranging from poorly graded sands to clay. Groundwater lies approximately 50 feet below ground surface and has a relatively flat hydraulic gradient, and the resulting nitrate plume is approximately one square mile. The site is further complicated by the occurrence of significant heavy commercial/industrial development in the area. The objective for the site is to restore groundwater quality to state standards.

Approach/Activities. Results from tracer/emulsified oil injection pilot testing were utilized to optimize in-situ bioremediation design to support the full-scale remediation system design and installation targeting the approximately one square mile plume and an estimated 450,000 pounds of nitrates. The bioremediation system consists of a network of pumping wells that transfer contaminated groundwater from hot spots to a network of in situ treatment cells where bioremediation occurs. Each in situ treatment cell consists of one or more injection wells, each surrounded by four extraction wells. Untreated water from the hot spots is directed to the injection wells where an engineered hydraulic gradient draws the untreated water through a treatment zone consisting of pre-emplaced emulsified oil.

Results/Lessons Learned. Pilot testing results were used to optimize and provide the basis for injection of EOS for the full-scale bioremediation system. Spacing between injection and extraction wells was 40 feet.

Bioremediation Pilot Study for a Large and Dilute Chlorinated Solvent Plume

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Background/Objectives. Within Marine Corps Base Camp Pendleton, contaminated groundwater was identified as a potential threat to human health due to the potential for the groundwater to migrate to a base production well that supplies potable water. The most effective remedial approach was determined to be a pilot study to treat a portion of the chlorinated solvent (i.e., trichloroethene [TCE], cis-1,2-dichloroethylene [DCE], trans-1,2-DCE, 1,1-DCE, and vinyl chloride) groundwater plume using bioremediation technology. Ten nested performance monitoring wells and 21 injection wells were installed, focusing on the “hot-spot” areas of the dissolved-phase TCE plume. After installation, approximately 6,000 lb of emulsified vegetable oil (EVO) and 6,300 lb of buffer were delivered to the subsurface as a long-term amendment for the pilot study. This presentation outlines the pilot study and the results of the four quarterly groundwater monitoring events.

Approach/Activities. For the pilot study, a total of 10 nested performance monitoring wells were installed. Seven dual nested wells were installed with screened intervals of 7 to 25 and 30 to 50 ft below ground surface (bgs), and three triple nested wells (one with a maximum depth of 50 ft bgs and two with a maximum depth of 75 ft bgs) were installed. The performance monitoring wells are located upgradient of the EISB pilot study to serve as a background well, downgradient of the EISB pilot study to confirm the groundwater flowrate of 100 ft/yr, and cross-gradient of the EISB pilot study to monitor the radius of influence (ROI) of the injected amendment and lateral movement of contamination. In addition, a total of five injection locations, in three rows (perpendicular to groundwater flow direction) approximately 50 ft or 6 months of groundwater travel time apart, were installed. Injection locations are 30 ft apart in the cross-gradient direction to provide sufficient coverage (assuming a ROI of 15 ft). Each injection location contains three injection wells with screened intervals of 10 to 20, 25 to 35, and 40 to 50 ft bgs.

In July 2013, all groundwater monitoring wells were sampled during a baseline groundwater monitoring event which was conducted prior to injection field activities. After that, approximately 6,000 lb of EVO was delivered to the subsurface as a long-term substrate for the pilot study followed by four quarterly monitoring events.

Results/Lessons Learned. Based on analytical results from the fourth quarter groundwater monitoring event, reductive dechlorination of TCE is occurring in the subsurface at the study site. Although low-level TCE concentrations are not yet lower than the MCL, multiple lines of evidence support the conclusion that bioremediation is occurring at the site. However, minimal concentrations of VFAs and low levels of DHC cells detected at the site indicate the substrate is not sorbing onto the soil to allow DHC to proliferate, which leads to a slow rate of reductive dechlorination. The dilute nature of the contaminant plume, the low concentrations of VOCs (i.e., less than 100 μg/L), and low sorption properties of the formation will make reduction of VOCs to below their respective MCLs within a reasonable time frame (i.e., within the pilot study) a challenge. For that reason, the fourth quarter sampling results will be evaluated to determine if follow-up substrate injections or the addition of another remedial approach would benefit the pilot study.

Enhanced Anaerobic Bioremediation with Neat Vegetable Oils for Long-term Treatment of Chlorinated Solvent Sites

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Background/Objectives. Enhanced anaerobic bioremediation (EAB) using non-emulsified and emulsified vegetable oils have been implemented for in-situ remediation of volatile organic contaminants (VOCs) at thousands of commercial and military field sites globally. Burns & McDonnell, Inc. was retained to implement a remedial action plan at an active manufacturing facility in Kansas, located approximately 25 miles from Wichita. The site overlies the Equus Beds aquifer, the main drinking water source for many municipalities in central Kansas, including Wichita. The non-emulsified vegetable oil blend (CAP 18® Anaerobic Bioremediation Product) was selected as the electron donor substrate due to its compatibility with high groundwater seepage velocities, low cost, and extended longevity and reactivity in the subsurface. The groundwater plume targeted for full-scale treatment encompassed approximately 63 acres and the vertical treatment interval ranged from 15 to 40 feet below ground surface (bgs). Prior to full-scale EAB treatment, Burns & McDonnell completed a pilot test at the site to determine the effectiveness of CAP 18. Results of the pilot test indicated the groundwater in the treatment zone became more anaerobic and exhibited decreased concentrations of the primary contaminant, trichloroethene (TCE), and associated degradation products. Based on the positive results of the pilot test, full-scale EAB was selected as the remedial option for impacted groundwater at the site.

Approach/Activities. In the summer of 2007, Burns & McDonnell injected approximately 147,000 pounds of CAP 18 to create a total of six (6) vegetable oil substrate treatment curtains for passive in-situ treatment. The substrate curtains were comprised of 265 direct-push injection points. During full-scale follow-up EAB injections conducted in 2013, an additional 85,000 pounds of CAP 18 were injected to create four (4) substrate curtains in previously untreated areas, including a source area. For both full-scale injection events, each treatment curtain consisted of two rows of injection points installed on 15-foot spacing, oriented perpendicular to the prevailing groundwater flow direction. The spacing distance between points was determined by the total substrate dosage requirement, the projected injection radius of influence (ROI), and the hydrogeological conditions at the site. The substrate was injected in 2-foot vertical intervals from the water table down to the base of the contaminated aquifer zone. In total, 232,000 pounds of vegetable oil substrate have been injected for a cost of approximately $300,000.

Results/Lessons Learned. Significant remedial progress (i.e. concentration reduction) has been achieved throughout the targeted treatment area at the site. A unique aspect of this site is the lack of EAB degradation products beyond cis-1,2-dichloroethene (cis-DCE). No detectable concentrations of ethene, ethane, or vinyl chloride have been detected in any sample collected over several years of monitoring at the site. In addition, while cis-DCE concentrations increase during the EAB treatment process, cis-DCE subsequently degrades without generating detectable concentrations of vinyl chloride or ethene. This presentation will include potential explanations for complete dechlorination without the formation of degradation products. Overall, progress toward remedial objectives for the site is expected to continue without the generation of undesirable dechlorination products.

In Situ Chemical Reduction with SRS-Z at Maxwell Air Force Base, Alabama

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Background/Objectives. A novel combination of emulsified vegetable oil and zero valent iron (ZVI) was recently developed. SRS-Z is a form of NASA's emulsified zero valent iron, but contains 40% ZVI, 36% soybean oil, food grade emulsifiers, organic (sodium lactate, yeast extract, and Vitamin B12) and inorganic nutrients, and a stabilizer to keep the ZVI in suspension. The ZVI was HePure's Flow with an average particle size of 80 microns. SRS-Z is highly viscous (about 3,300 centipoises) and is considered a non-Newtonian fluid in that it thins out when subjected to high pressures such as when it is injected.

Approach/Activities. In a 12 acre plume in a silty sand formation at Maxwell AFB, Alabama, the maximum levels prior to treatment of PCE were 41 mg/L, 4,060 mg/L TCE, 40 mg/L cis-1,2-DCE, and 4.0 mg/L vinyl chloride. The SRS-Z was injected by Geoprobe direct push technology into 141 injections points spaced about 30 feet apart with lines spaced about 100 feet apart. For much of the area, dual injection of the SRS-Z with a Geoprobe grout pump and chase water with a double diaphragm pump was used.

Results/Lessons Learned. Monitoring after nine months showed 93.6% to 95.9% reductions in total PCE, TCE, DCE, and VC in wells where TOC levels were greater than 10 mg/L. Where there were elevated TOC readings, substantial increases in ethene and ethane were also observed. Increases in the hydrogen concentration from the baseline to the June 2014 sampling event were observed in all wells except two. Lactate was not detected in any of the samples collected in month 9 samples which was anticipated since lactate is often consumed quickly, often within 1 to 3 months. VFAs including acetic, butyric, formic, and proprionic acids were generated in many wells. Competing electron acceptors like dissolved oxygen, nitrate, sulfate, manganese, iron, and methane were variable. Methane increased in all wells. Increased chloride potentially from the reductive dechlorination process was observed in seven of the eleven wells. The SRS-Z injections impacted wells an estimated 13 to 15 feet from the injection locations.

Right-Sizing Your Remediation in a Performance Based Remediation World

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Background/Objectives. A 4,500 feet long trichloroethene (TCE) plume at the former Virginia Air National Guard (ANG) Base in Sandston, Virginia presented a challenge to the remediation team when the performance based remediation (PBR) project was awarded in 2010. Historical attempts to locate the source of the groundwater plume had limited to no success. Enhanced reductive dechlorination was challenging due to the groundwater pH in the low 4 – 5 range with aerobic oxidizing redox conditions. The TCE concentrations in groundwater had to be reduced from greater than 5,000 ppb to 160 ppb in a five year period of performance within a fixed budget. The project objectives are to achieve risk-based Interim Remedial Goals (IRGs) through accelerated remediation.

Approach/Activities. The two keys to properly sizing the groundwater remediation were: (1) identify and remove the source, and (2) understand the subsurface conditions so that time and money was not wasted remediating “clean” groundwater.

First, the source area was identified in a previously uncharacterized area of the site using a combination of high-resolution site characterization techniques including membrane interface probe and intensive, discrete depth groundwater sampling coupled with a an onsite laboratory with a patented analytical method that analyzed volatile organic compounds in approximately five minutes. This real-time investigation was expensive: however, it allowed the project team to identify the source and also provided a detailed understanding of the subsurface conditions: a narrow (5 – 20 feet wide) paleo-channel acting as a preferred pathway and two distinct aquifer sections, with the “lower” aquifer exhibiting a much faster groundwater flow than the “upper” section.

Once identified, the source, including saturated soils, was removed and the excavation was backfilled with a hydrogen release compound, which was chosen for its extended, controlled release of lactic acid. A groundwater recirculation system with pH buffer addition was set-up powered by a solar panel due to the lack of commercial power at the site. These actions, while costly, resulted in achievement of the first major performance milestone, 50% total contaminant reduction.

The project team then tackled the issue of “right-sizing” the groundwater remediation by conducting a dye test to evaluate the dispersion of injected substrate into the spine/core of the plume versus the periphery on either side of the spine/core. The team wanted to determine if remediation of the plume required grid-like injections or if transect injections could be utilized, which would be a more economical approach. The dye study determined that a combination of grid injections in the source area combined with transects in the downgradient portion of the plume could be effective in achieving project objectives. Another remediation design element that required “right-sizing” was the substrate to be injected. It was determined that in situ injections using zero-valent iron and sodium bicarbonate amended carbon substrate was optimal for the source area plume with the highest concentrations. However, this substrate was not cost effective for the entire plume, so emulsified vegetable oil amended with sodium bicarbonate was selected for the downgradient section of the plume with lower concentrations. Substrate concentrations were modified by depth in the downgradient section of the plume to continue “right-sizing” the remediation.

Results/Lessons Learned. Spending resources (money) up front to understand subsurface conditions allows for efficient use of remediation funds. In situ injection substrates must be carefully chosen for each portion of a contaminated groundwater plume. The designer should not be afraid to deploy different substrates in different design configurations and delivery methods throughout a contaminant plume. This allows the remedial designers to match the correct substrate mix with the contaminant levels and geochemical conditions as well as achieving optimal subsurface contact.

Implementing Sustainable Biostimulation in Bedrock to Expedite Site Closure of a Large Dissolved TCE Plume

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Background/Objectives. A full-scale bioremediation approach via stimulation of the indigenous microbes to achieve anaerobic reductive dechlorination was developed and implemented to remediate trichloroethene (TCE)-impacted ground water at an industrial facility in Northern Georgia. This low-energy sustainable strategy replaced an ineffective and energy intensive electro-chemical remedy that had been operational for over 5 years. The full-scale biostimulation design included both source area treatment to address elevated residual TCE concentrations and a permeable injection biobarrier to mitigate additional migration of dissolved phase TCE offsite.

Approach/Activities. A total of 70 injection wells were installed in December of 2008 and insoluble substrate (emulsified vegetable oil) injections were conducted in January and February of 2009. Thirty-five injection points were installed at a spacing of 15 feet in the TCE source area, which covers an approximate area of 150 by 120 feet. The injection points were installed to the top of bedrock between 20 and 50 ft below ground surface (ft bgs) in a saprolite overburden. A total of 35 injection points were also installed at a spacing of 15 feet over a linear distance of approximately 500 feet down water table gradient of the main TCE source area to generate the permeable injection biobarrier. The emulsified vegetable oil solution (NewmanZone) was injected into each point at a flow rate of approximately 2 to 4 gallons per minute (gpm) at a pressure of less than 30 pounds per square inch gauge (psig). This low flow and pressure helped to minimize potential short-circuiting to the surface that is common during substrate injection programs. The total combined injection volume for all 70 injection points was 98,000 gallons of solution comprised of 95,000 gallons of water and 3,000 gallons of the substrate. Ground water pumped from a bedrock well was used to provide the mixing and flushing water together with hydrant water, as ground water is the best source of water that is compatible with the indigenous anaerobic microorganisms.

Results/Lessons Learned. Analysis of ground water in the source area continues to show the lowest TCE concentrations since sampling began in 1993 (from an average concentration of 6 mg/L to < 5 µg/L). Innocuous reductive dechlorination end products ethene and ethane were also detected at concentrations as high as 120 ppb in three of the source area wells. This is a significant increase over the <1 ppb detected prior to implementing the full-scale biostimulation program. Monitoring wells downgradient of the injection barrier also continue to show a decreasing trend 4 years after completion of the substrate injections. Data from two of the downgradient wells also indicate the lowest TCE concentrations ever detected at those locations, including detections of ethene and ethane, an indication that the biobarrier continues to remain effective more than two years after the initial biostimulation. Trend analysis of data from the site monitoring wells indicates that natural attenuation can be proposed as the final remedy for an additional 2-year period that is anticipated to lead to site closure approximately 15 years ahead of the original closure estimates.

Establishing a Cost-Distribution Relationship: How to Optimize Injection Points versus Injection Volumes

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Background/Objectives. Gilbane Federal (Gilbane) was tasked with remediating several large groundwater TCE plumes at former missile sites by United States Army Corps of Engineers. The costs of remediation for these sites were evaluated as being in the multi-million dollar range. The remediation approach at most of these Sites was to use bioremediation technologies such as emulsified vegetable oil (EVO) injections. Usually aggressive source treatment is performed in combination with bio-barriers to treat and arrest migration in downgradient plume. The typical challenge with distributing EVO is to identify the number of injection points and corresponding injection volumes to achieve effective distribution within subsurface. If there are more injection points, the injection volumes are decreased and better resolution can be achieved however installation costs could increase dramatically. On the other hand, if injection volumes are increased, the number of injection points is reduced, minimizing installation costs, however the injection time-frames can expand and the distribution resolution may be compromised. Gilbane's objective for the remedial implementations was to find the optimum balance between injection points and volumes that would achieve distribution goals while also being cost-effective.

Approach/Activities. A deterministic model and a stochastic model were created to evaluate the optimization objective. The models were applied for two different former missile sites that had large TCE plumes. In addition the models were also retroactively used to evaluate optimization goals at two other large TCE plume sites where bioremediation technology had already been applied.

The main optimization parameters that were used include: the cost of each injection point for materials; the cost of the amendments; the cost of labor for each aspect of implementation; the time needed to install each injection point; the supply of water; the anticipated flowrates; the hydrogeological parameters; the size of the injection grid, the radius of influence (ROI) observed in pilot test; and other site constraints. The goal was to find the optimum number of injection points and the corresponding injection volumes.

The deterministic model was created using linear programming principles in MS Excel. The optimization algorithm was run using Excel's built-in "Solver" suite of commands. Upper and lower limits were defined for various site constraints such as the available volume of water, the range of ROIs, and the number of injection points. An optimization formula was set up with cost as the driving function; and Solver was run to determine the minimum cost that would result within the parameters, as established, to obtain effective distribution.

The stochastic model was created using Monte Carlo methods. Visual Risk software from Palisade was used to setup the model. In this model, the uncertainty range for each parameter was defined - for example, a porosity range from 0.15 to 0.3 was used. The software then performs the Monte Carlo simulation and thousands of simulations are run to obtain a probability distribution. The optimum solution with an acceptable factor of risk is then identified from this distribution.

Results/Lessons Learned. The factors driving the optimization equation varied from site to site. Within the two new sites, water availability was an issue at one site while the depth of the plume was a problem at the other. When water was the issue, the optimization solution recommended more injection points with tighter spacing to reduce injection volumes. When the depth of plume was the issue, the optimization solution recommended less injection points and larger injection volumes as a more cost-effective method. For the two older sites, one site was confirmed as having an optimum balance between injection points and volumes, while another site showed that fewer points could have been used to achieve a more cost-effective solution.

Back to Contents

In Situ Degradation of DNAPL/Sorbed Contamination in Soil and Fractured Bedrock using a Low Grade Thermal Enhancement

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Background/Objectives. The kinetics of desorption and degradation being dependent on temperature, thermal enhancement has been used at a variety of sites to speed up biotic and abiotic reactions and accelerate decontamination. The degradation rates of chlorinated compounds (PCE, TCE, DCE, VC, TCA, DCA and CA) and toluene were researched in the laboratory at temperatures between 10 and 40^{o}C as well as in three sites in the full scale using a combination of biotic and abiotic degradation. The objective is to develop and implement means for more rapid and cost-effective remediation leading to closure.

Approach/Activities. The three sites are those of a plant that produced chlorinated solvents, of a plant that produced vinyl chloride monomer and of a manufacturing plant that used degreasing solvents, with original quantities of VOCs of 1000, 150 and 30 metric tonnes respectively in the geological formation. The first site was contaminated mainly with PCE, TCE and 1,1,2,2 TeCA, the second one mainly with 1,1,2-TCA, 1,2-DCA and VC and the third one with mainly 1,1,1-TCA, 1,1-DCA, CA and toluene. DNAPL was recovered and a hydraulic barrier was installed at the property limit to intercept the plume and treat the extracted groundwater at each site. Nearly all of the DNAPL was extracted at the first site without thermal enhancement whereas thermal enhancement constitutes part of the remediation strategy at the two other sites. In the second site, groundwater from one end the interception trench is used as cooling water to condense and recover the chlorinated solvent and is returned hot at the other end of the trench. The heat accelerates in turn the in situ degradation in the fractured clay in the downgradient part of the site. In the third site, hot solutions of electron donors and electron acceptors were injected in the deep fractured bedrock of the source zone. In each case, degradation was accelerated and a mass balance was calculated based on the concentrations of VOCs and chlorides. With initial dissolved VOC concentrations above a million µg/L and a high mass flux of dissolved contaminants over decades, large masses of non-dissolved contaminants had to be addressed in the soil and fractured bedrock of these sites. The combination of enhanced degradation and other remediation used at each site will be presented, in particular for the site where most of the VOC elimination was achieved through in situ degradation.

Results/Lessons Learned. In the laboratory, degradation was approximately 5 times faster at 35 ^{o}C than at the normal groundwater temperature of 10^{o}C. On site, the remediation activities led to the elimination of approximately 97% and 74% of the VOCs at the first and third site. Full scale remediation is currently starting at the second site. These projects led to a better understanding of the kinetics of biotic and abiotic reactions and to a better appreciation of the measures that can be taken to speed up the elimination of these contaminants.

Understanding the Potential for Bioremediation of ^{129}I at the Hanford Site, Washington

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Background/Objectives. Microbial radioactive iodine (^{129}I) redox cycling in saturated soils is not well understood and provides a novel avenue for bioremediation studies. ^{129}I, one of the most tenacious anthropogenic radionuclides in the biosphere, is a by-product of nuclear fission, and is of environmental concern due to its long half-life (~16 million years), toxicity, and mobility in the environment. The 200 West area of the Hanford Site contains two separate plumes covering 1,500 acres where ^{129}I concentrations average 3.5 pCi/L in Hanford soils.

Approach/Activities. The aim of this study was to determine the microbial diversity present within these ^{129}I plumes, and to identify any organisms that may affect iodine speciation by means of redox reactions. Biological traps were placed in groundwater contaminated with a range of ^{129}I levels ranging from high, low, and background concentrations, each for 50 and 150 days. Molecular tools were utilized to define the structure and spatial distribution of the indigenous bacterial communities throughout. Microorganisms were isolated and characterized to determine the potential for iodine biotransformation via redox activity.

Results/Lessons Learned. The plumes were dominated by *Alpha-, Beta-,* and *Gamma-proteobacteria*. Organisms such as *Rhizobiales* (*Alphaproteobacteria*) were identified and have been previously described for their ability to reduce iodate.
Additionally, *Desulfovibrio* and *Shewanella* (*Deltaproteobacteria*) are also known to have iodate reducing capabilities and were present here. These molecular tools, along with diversity statistics, reveal that the microbial diversity increases as the exposure to ^{129}I increases.

An iodate reducing organism, designated as *Agrobacterium tumefaciens* strain AD35, was isolated from biological traps material incubated for 50 days in a high ^{129}I concentration plume. Iodate (200µm) was reduced by 36.3% in cultures transitioning from aerobic to anaerobic growth and 47.8% in anaerobic cultures in the presence of 10mM nitrate, which was reduced 81.4% and 80.9% respectively. Iodate was also shown to be reduced by 84.0% and 69.2% in transition and anaerobic growth conditions respectively when nitrate was re-spiked into the growth media. These data allow us to understand how microbial communities differ throughout the Hanford Site with varying exposure levels to radioactive ^{129}I, and provide a foundation for future bioremediation strategies integrated with knowledge of the community present.

Technical and Policy Challenges for Remediating Metals and Radionuclides in Deep Vadose Zone Environments

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Background/Objectives. Many of the subsurface remediation problems are some of the most complex encountered, including extensive and challenging groundwater contamination and large quantities of contaminants residing in deep vadose zone (DVZ) environments. The DVZ is defined as the sediments below the zone of practicable excavation and removal, but above the water table. Implicit in this definition is an assumption that contamination in DVZ environments is isolated from exposure such that direct contact is not a factor in its risk to human health and the environment. Rather, transport of contamination from the DVZ and discharge (flux) to the groundwater creates the potential for exposure and risk to receptors. Therefore, while the DVZ is not considered a resource requiring restoration, limiting flux from contaminated DVZ is key for protection of water resources.

Approach/Activities. Remediation of the DVZ is typically linked to meeting cleanup goals for groundwater. As such, the prospect for success of any DVZ remediation technology needs to be considered within the regulatory context. Herein lies the challenge; applying vadose zone remediation to reach an acceptable rate of contaminant transport while effectively dealing with considerable uncertainties associated with estimating and measuring contaminant transport at the field scale. However, this construct affords the opportunity to view remediation strategies for the vadose zone as targeted to mitigate the source of contamination and reduce transport to receptors, in contrast to meeting a specific concentration measured at some location within the vadose zone. This approach, however, requires technology development, methods, and protocols to demonstrate that groundwater will remain uncontaminated or that contamination will remain below levels of concern in the future, and achieve in situ remedial performance that is sufficient to support a remedy decision.

Results/Lessons Learned. The inherently challenging properties of deep vadose zone environments also provide opportunities for remediation including:

- Incremental enhancements may meet remediation goals, given typically slow unsaturated flow conditions
- Long times enhance opportunities for interactions with sediments and remediation amendments because of slow transport rates
- Capillary forces resist movement in some cases and hold contaminants in fine-grained units
- The driving force for water flow, recharge from surface infiltration can be controlled and reduced by surface structures (e.g., infiltration barriers)
- Gas-phase advection for distribution of remediation amendments can potentially be effective over large zones of influence
- Water added in relatively small quantities, although increasing the downward driving force, will only minimally impact the overall rate of movement.

Evolution of a Remedial Injection Program in Metamorphic Bedrock

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Background/Objectives. TCE from multiple release locations beneath and outside of a building have migrated 250+ feet deep into bedrock and offsite to multiple properties. Site characterization data indicated existing groundwater conditions were suitable for the biodegradation of Trichloroethene (TCE) to carbon dioxide. However, the metamorphic granite and diorite formation with steeply dipping fractures was anticipated to be a significant technical challenge for an in-situ groundwater remedy since the state of the science for the remedial injection of reagents at the start of this project had largely been limited to soil and sedimentary bedrock with defined bedding planes that could be improved with low pressures. A key to the remedy effectiveness was the ability to vertically and horizontally distribute the reagents in the metamorphic formation in the source areas that were largely beneath an existing building.

Approach/Activities. Conceptual injection approach was to create horizontal fractures in the shallow bedrock that would inter-connect the vertically dipping fractures to create a lattice like system that would improve the horizontal and vertical distribution of the vegetable oil emulsion within the source zone. Fracturing was chosen to improve the radius of injections to reduce the total number of injection wells. Injection wells were designed to a maximum of 100 feet bgs with the theory that the vertical fractures would facilitate transport to deeper zones and thus facilitate biodegradation. Three injection phases were performed. The pilot-test (Phase I) focused on an easily accessible area and was limited to the upper bedrock (10 to 100 feet bgs). Phase II expanded to additional source areas and added injections into the saturated, unconsolidated Saprolite. Phase III further modified the injection techniques used during Phase II but on a larger scale.

Results/Lessons Learned. Multiple changes in the mechanical process of the cutting of the initial kerf and subsequent nucleation of the fractures resulted in increased efficiency and success. The fracture creation success rate increased from 31% during Phase I to 100% during Phase II. Modifications between Phase II and Phase III created improvements in safety by reducing the use of high pressure systems while maintaining the 100% fracture creation rate. The Phase III modifications also resulted in a 40% decrease in the unit cost per fracture/injection event. The consistent ability to create fractures allowed for the controlled vertical distribution of the reagents. In addition, the conceptual plan of reagent distribution below the injection zones via the near vertical dipping fractures was proven by reagents observations at depths approximately 100 feet below the deepest injection depths. The horizontal distribution throughout all three phases was highly variable in direction and length. Phase III maximum horizontal injection distance of 118 feet was visually observed along a specific direction. The typical horizontal ROI ranged between 50 and 70 feet. The overall program made significant improvements in process, safety, effectiveness and cost that helped reduce business interruption issues of the tenant and achieve the remedial goal of enhancing the biodegradation of the source.

Field-Scale Application of Biostimulation and Bioaugmentation of Chlorinated Ethenes in Groundwater

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Background/Objectives. The purpose of this pilot-scale study was to evaluate the potential for biostimulation followed by bioaugmentation for in situ bioremediation of chlorinated solvents in groundwater at a site in Southern California. The groundwater contains elevated concentrations of the following chlorinated volatile organic compounds (cVOCs): tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), and 1,1-dichloroethene. The natural attenuation evaluation indicated that reductive dechlorination was occurring in several of the on-site monitoring wells. However, the rate of natural attenuation was not promoting complete reductive dechlorination of the cVOCs.

A bench-scale study was performed to evaluate the potential effectiveness of various biostimulation and bioaugmentation amendments on the biodegradation of cVOCs. The results of the bench-scale study indicated that the indigenous microbial population was not able to successfully degrade PCE to ethene. However, when a *Dehalococcoides* consortium was added to the microcosms, along with a carbon source, complete reductive dechlorination was observed. Based on the results of the bench-scale study, lactate was selected as the initial carbon substrate to promote highly anaerobic conditions in the aquifer. The second highest level of reductive dechlorination, occurred when EOS® and a *Dehalococcoides* consortium was added to the microcosms.

Approach/Activities. A pair of recirculation wells was installed to inject the carbon source and microbial population containing *Dehalococcoides* into the groundwater. Once the ORP was less than -150 mV, the *Dehalococcoides* consortium was injected into groundwater and recirculated using the paired recirculation wells. Several months after the initial lactate injection, the total organic carbon (TOC) levels decreased, and the slow release carbon substrate, EOS®, is planned for injection into groundwater using the recirculation wells. A detailed monitoring program, which included an evaluation of physical, chemical, geochemical and microbiological parameters, was conducted to assess the effectiveness of the in situ bioremediation field-scale study over time.

Results/Lessons Learned. This presentation will summarize the results of the biostimulation via lactate injection, bioaugmentation injection using *Dehalococcoides,* and biostimulation via the planned EOS® injection. The initial lactate injection led to a significant increase in the TOC, which corresponded to elevated levels of volatile fatty acids, including acetate, propionate and butyrate in downgradient field-study monitoring wells. Following the bioaugmentation injection, the *Dehalococcoides* population increased by three to five orders of magnitude in the field-study wells. A decrease in TCE and an increase in cis-1,2-DCE and VC was also observed, and the ethene concentrations increased by several orders of magnitude in the groundwater. The summary will address how the amendments impacted the chlorinated solvent concentrations, microbial community and chemistry of the groundwater in the area surrounding the recirculation wells and compare these results to wells outside the field-study area.

Substrate Delivery to Treat a Deep TCE Plume in a Highly Heterogeneous Unconsolidated Aquifer

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Background/Objectives. Successful bioremediation relies on the concurrent presence of substrates, target contaminants, and active contaminant-degrading microbial consortia. It is conceivable that different substrate delivery strategies may result in different degrees of mixing between substrates, contaminants, and active bioaugmentation cultures (if applicable). The current practice of substrate delivery often involves (but is not limited to) the following considerations: (1) substrate injection methods (e.g., using direct point injections or injection wells), (2) substrate types (soluble vs. slow releasing), (3) aquifer acidification, and (4) enhanced delivery methods (e.g., recirculation and/or vacuum-assisted pumping). The extent of the bioactive zone stimulated via substrate injection is known to relate to the transport behavior and biodegradability of the substrates, as well as injection methods and injection volumes. In many circumstances, the extent of the bioremediation treatment zone coincides with the extent of the substrate utilization zone. Therefore, it is important to understand what factors control the fate and transport of the substrates in order to increase the size of the bioactive treatment zone for treating a large plume.

Approach. For our evaluation, we plan to use a hypothetical heterogeneous aquifer system containing a complex paleo-channel network (based on actual project experiences) to provide the hydrogeological context. Trichloroethene (TCE) contamination will be assumed to be present at the depth intervals between 80 and 100 feet. The injected organic substrates used to stimulate microbially-mediated reductive dechlorination will be assumed to be well buffered, so it does not result in aquifer acidification. The following four substrate delivery approaches are evaluated: (1) direct point injections, (2) injection wells under gravity-fed conditions, (3) injection wells under moderate pressure, and (4) injection wells coupled with recirculation. The substrate degradation half-lives will be based on the literature data obtained from anaerobic digestion processes. Substrate injection via a well may gradually result in well clogging – an evidence of a highly concentrated bio-active zone in the vicinity of the well. To reduce the clogging potential and to help produce a larger bio-active zone, we will also evaluate how the distribution of highly concentrated substrate pulses (at the concentration level inhibitory to microbial growth in the vicinity of the injection well) will help spread substrate. The sizes of the substrate reaction zones potentially achievable will be estimated using fate and transport numerical simulations. The potential extent of the bio-active zone established by each approach will be used to evaluate the circumstances that are suitable to apply that approach.

Results/Lessons Learn. The pros and cons of the evaluated injection approaches will be compared. The potential remedial performance and cost effectiveness of individual approaches will be discussed. In addition, real-world project experiences related to difficulties and complications of various injection approaches will be presented.

Back to Contents

In Situ Microcosm Evaluation of Biostimulation and Bioaugmentation for Chlorinated Ethenes in Groundwater

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Background/Objectives. The purpose of the in situ microcosm (ISM) evaluation was to assess the potential for biostimulation and/or bioaugmentation of chlorinated ethenes in groundwater at a site in Pennsylvania. The groundwater contains elevated concentrations of the following chlorinated volatile organic compounds (cVOCs): tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), 1,1,1-trichloroethane and 1,1-dichloroethene. A preliminary natural attenuation evaluation indicated that reductive dechlorination was occurring in several of the on-site monitoring wells.

Approach/Activities. During the Phase I evaluation, Bio-Trap ISMs containing two to five different types of Bio-Trap ISMs were deployed in two monitoring wells at the site:. The Bio-Trap assemblies remained in the groundwater for 63 days. Bio-Trap ISMs included non-amended Bio-Trap ISM to evaluate the potential for natural attenuation; Bio-Trap ISMs amended with one of the following: AquaBupH, ABC (Anaerobic Biochem); ABC+ (ABC plus a zero valent iron [ZVI]) or EHC (composed or organic substrate and ZVI). In addition to the carbon and ZVI amendments, bioaugmentation was also evaluated in the Bio-Trap ISMs using the microbial consortium, SDC-9, which included *Dehalococcoides* sp. The effectiveness of the various amendments was evaluated by monitoring the impact of the amendments on the following parameters: anions, volatile fatty acids, microbial biomass, microbial populations, *Dehalococcoides* and key functional genes (tceA Reductase, bvcA Reductase and vcrA Reductase), cVOC concentrations and dissolved gasses in the various Bio-Trap ISMs.

Results/Lessons Learned. The results from the Bio-Trap ISM evaluation provided key information concerning which remedial approach would be most appropriate for site remediation. By comparing the results of the *Dehalococcoides* populations in the MNA and biostimulation Bio-Trap ISM units, it is apparent that the groundwater contains a significant population of *Dehalococcoides*. However, even after the indigenous *Dehalococcoides* population was provided with four different types of electron donors/carbon sources, the indigenous *Dehalococcoides* population did not significantly increase in comparison to the MNA microbial population. When the SDC-9 microbial consortia was added to the various Bio-Trap ISMs, there was at least a two to three order of magnitude increase in *Dahalococcoides* and five order of magnitude increase in the key functional gene vcrA Reductase, which is responsible for VC biodegradation. The VFA results indicate that the highest level of acetate production was observed in the bioaugmentation unit amended with AquaBupH and SDC-9. Significant levels of acetate were also observed in all of the carbon substrate/electron donor amended Bio-Trap ISMs, with the exception of the ABC+ amended Bio-Trap ISM.

The cVOC data demonstrate that the SDC-9 bioaugmented Bio-Trap ISMs showed the highest level of conversion of TCE to cis-1,2-DCE and that VC was only detected at elevated levels in the bioaugmented Bio-Trap ISMs. The dissolved gases results indicate that elevated levels of ethene production were observed in the Bio-Trap ISMs amended with SDC-9 and EHC or AquaBupH.

Laboratory Evaluation of Biostimulation to Treat Chlorinated Ethenes in Fractured Sandstone

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Background/Objectives. A fractured sandstone aquifer in southern California is contaminated with trichloroethene (TCE) to depths in excess of 244 m. Field data indicate that TCE is undergoing reduction to *cis*-1,2-dichloroethene (cDCE). Vinyl chloride (VC) and ethene have been detected, although not in significant amounts. The main objective of this study was to evaluate the effectiveness of biostimulation to enhance TCE and cDCE degradation within the sandstone matrix.

Approach. The first phase of research involved monitoring over 500 microcosms (50 mL of groundwater + 20 g of sandstone). Crushed sandstone was prepared from core samples; exposure to air was minimized by vacuum packing under a nitrogen atmosphere. Microcosm treatments included biostimulation with lactate, hydrogen release compound (HRC) and emulsified vegetable oil (EVO). Control treatments included unamended live microcosms, autoclaved bottles, and bottles with only distilled water and TCE or cDCE. Each treatment was prepared with and without ^{14}C-TCE or ^{14}C-cDCE; addition of ^{14}C permitted tracking of CO_2 and nonvolatile products, while microcosms without ^{14}C permitted analysis of δ^{13}C enrichment. The second phase was designed to simulate delivery of electron donor by diffusion into the sandstone, based on the use of unique intact rock core microcosms. These microcosms consist of a sandstone core (3" long, 2.375" diameter) sandwiched between stainless steel end caps. One of the caps was hollowed out and used to simulate groundwater flow along a fracture (i.e., at one end of the core). Each core was encased in heat-shrinkable Teflon and inserted in a stainless steel pipe, the ends of which were welded to the caps. Cores were initially saturated with TCE-containing groundwater while the chamber was filled with groundwater, with or without lactate. Mininert valves on the hollowed out end cap permitted weekly addition and extraction of groundwater. Bromide was added to the groundwater to serve as a conservative tracer.

Results. In the crushed rock microcosms, reductive dechlorination of TCE to cDCE was significantly enhanced by the addition of lactate (HRC and EVO were less effective). Lactate also stimulated reduction of cDCE to VC and ethene, achieving nearly complete dechlorination after two years. This result implies that *Dehalococcoides* exist within the rock matrix. Their presence was confirmed by qPCR; none were detected in microcosms without accumulation of VC or ethene. ^{14}C analysis revealed increases in CO_2 and soluble products in all microcosms, presumably produced at least in part via abiotic processes. Degradation of cDCE by pathways other than reductive dechlorination was consistent with enrichment in δ^{13}C in unamended microcosms and autoclaved controls. In the intact rock core microcosms, reductive dechlorination of TCE to cDCE is underway in 3 of the lactate-amended and 1 of the unamended units. TCE levels in microcosms without dechlorination are consistent with model predictions of diffusion using COMSOL, as are bromide levels. Addition of lactate stimulated sulfate reduction and created low redox conditions (based on resazurin).

This study has demonstrated the potential for biostimulation to enhance complete TCE dechlorination within fractured sandstone, based on the apparent presence of *Dehalococcoides* within the rock matrix. The magnitude of enhancement will depend on delivery of the electron donor, which is being evaluated with the intact rock core microcosms.

Enhanced Reductive Dechlorination of a TCE Bedrock Groundwater Plume, Northern New Jersey

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Background/Objectives. A site previously exhibiting the presence of TCE DNAPL has been addressed via groundwater pump and treat and direct recovery of DNAPL followed by Fentons Chemistry in-situ remediation. A pilot test for Enhanced Reductive Dechlorination (ERD) was performed to evaluate ERD as a remediation alternative to address residual TCE concentrations in the bedrock groundwater zone.

Approach/Activities. A pilot test was performed involving circulation of groundwater amended with sodium lactate to effect ERD of TCE in the bedrock groundwater zone. The groundwater circulation system consists of two bedrock groundwater recovery wells positioned on the down-gradient property boundary and one bedrock groundwater recharge well situated 100 feet up-gradient of the recovery wells and 100 feet down-gradient of the shallow overburden source area previously treated via ISCO. The circulation cell was designed consistent with geologic structure to favor delivery of amended groundwater toward the down-gradient recovery wells. The pilot test performed over the course of 6 months demonstrates ERD degradation of TCE to 1,2 dichloroethene (cisDCE), vinyl chloride (VC), and ethene.

Results/Lessons Learned. Field application results indicate the following:

- After approximately 3 months of recirculation, the lactate/TOC amendment reached the down-gradient well. Degradation of TCE was rapid with minimal accumulation of cis-dichloroethene/vinyl chloride. After six months of recirculation TCE concentrations were reduced by approximately 90% in the shallow bedrock aquifer
- Additionally, conditions at the site resulted in delivery of some of the substrate to the deep overburden resulting from shallow bedrock groundwater recirculation. Approximately two months of observing substrate in the deep overburden aquifer TCE concentrations have been reduced by approximately 60% with a molar equivalent of cis-DCE produced.
- Based on the successful pilot test results, a larger system is planned for installation with an anticipated five year run time to evaluate effect on the TCE plume.
- Currently full scale groundwater pumping and treatment at a recovery rate of up to 100 to 150 gallons per minute is being performed as a groundwater containment control. Application of full scale lactate groundwater circulation is likely to replace or reduce the scale of the groundwater pumping and treatment program, thus reducing energy demand (reduced carbon footprint) and hydrologic cycle impacts related to the recovery/treatment/discharge to surface water currently employed at the Site.

Back to Contents

Technology for Inhibiting Methanogenesis during In Situ Sediment Treatment

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Background/Objectives. In situ sediment capping remediation systems mitigate the migration of contaminants through sediments. Two generalized approaches are: (1) passive capping, which is the deployment of a barrier material that is relatively impermeable to both the water above and the contaminants below; and (2) active/reactive capping, which employs one or more additives or amendments to a relatively permeable barrier in an effort to bind up and/or destroy the contaminants as they migrate through the treatment area. One resulting complication of any sediment capping action or the addition of reactive agents is that the implementation/construction processes themselves typically create an initial spike of methanogenic activity because the sediment becomes disturbed and available carbon sources are more rapidly consumed. A second methane spike can occur later as oxygen is depleted from the remediated site, thus shifting the balance between aerobic biodegradation and anaerobic biodegradation in favor of methanogens. The production of methane is problematic from several perspectives, including: i) stimulation of anaerobic microbial activity can lead to methylation of mercury and other heavy metals, with many negative consequences, and; ii) the production of methane can create gas bubbles (ebullition) which can transport contaminants via surface tension phenomena through localized cap failures due to gas buildup, and sometimes produce a toxic sheen at the water surface.

Approach/Activities. AquaBlok™ technology supports the uniform and targeted placement of high-value/low concentration treatment amendments in sub-aqueous environments. These materials can be formulated with various remedial amendments to meet site-specific needs. For example, Provect-IR™ combines controlled-release particulate carbon material and micro-scale zero valent iron (ZVI) or other metals to yield in situ chemical reduction (ISCR). Provect-IRM™ is similar in composition, but it is designed to immobilize metals and other inorganic contaminants. Uniquely, these amendments also contain a number of natural statin compounds, including Monacolin K (also known as Lovastatin), that effectively inhibit methanogens while permitting other biodegradation processes to occur. AquaBlok-CH4™ offers the combined advantages of both technologies (Hull and Mueller, 2014). As described herein, the resulting cap will simultaneously treat contaminants, both in sediment and in pore water, while controlling methane production which manages several problems common to in situ sediment capping systems, namely: i) reduced ebullition of gases; and ii) reduced methylation of heavy metals.

Results/Lessons Learned. The presentation will provide an overview and update of current thin capping concepts and other subaqueous technology applications utilizing variable permeability materials. The antimethanogens can improve performance of active amendments/caps designed to address sorbed contaminants and/or contaminants that have partitioned into pore water, as either situation could lead to methylation. They can also be used as a pre-application to isolation capping and even sand capping. Data and modeling will be presented to support active capping designs/in situ funnel-and-gate systems for sediments illustrating the ability to perform treatment of subaqueous contaminants below a cap. For example, treatment of arsenic in an AquaBlok-CH4 zone involves the reduction of adsorbed arsenate [As(V)] anions to arsenite [As(III)] coupled with their long-term sequestration as solid arsenic species by means of reductive precipitation and adsorption onto the iron corrosion products with reduced production of methyl arsenic.

An In Situ Pilot Study Evaluating the Efficacy of Bioaugmentation for Treatment of PCB-Impacted Sediments in Abrahams Creek, Quantico, VA

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Background/Objectives. *In situ* treatment with granular activated carbon (GAC) has been used successfully to sequester aromatic POPs such as PCBs in sediments effectively minimizing their interaction with the biological food chain. The objective of this research is to develop and test the efficacy of a bioamended form of GAC embedded with microorganisms to sequester PCBs from the food chain and concurrently dechlorinate and degrade weathered PCBs in sediments. A pilot study was initiated in April 2015 to demonstrate and validate this environmentally sustainable technology at a PCB-impacted DoD field site. The project goal is to: 1) evaluate the efficacy of bioaugmentation for the complete degradation of highly chlorinated Aroclors *in situ*; and 2) evaluate the efficacy of a delivery system for deploying biocatalysts into PCB-impacted sediment through a water column, near obstacles and in environmentally sensitive areas.

Approach/Activities. The innovative aspect of the technology is the application of anaerobic organohalide respiring bacteria and aerobic PCB degrading bacteria with selected activities to sediments with a GAC agglomerate (SediMite^{TM}) as a delivery system. The bioamended SediMite serves as a solid substrate for: 1) delivery of microorganisms into sediments, 2) formation of microbial biofilms, and 3) sequestering and concentration of hydrophobic PCBs in close proximity to the biofilm of PCB transforming bacteria. Treatability tests conducted in mesocosms using sediment from Abrahams Creek in the Quantico Marine Base demonstrated that the approach reduced total PCB levels by 72% after only 120 days. Based on these results the pilot field study was initiated at the site in 0.1 acre plots. The effectiveness of the approach is being evaluated by monitoring changes in total PCB concentration and congener distribution, porewater concentrations with passive samplers, sustainability of the bioamendments and effect of treatment on the indigenous microbial community.

Results/Lessons Learned. Among the challenges for the pilot field study were development of methods for production level scale-up of the microorganisms without residual POPs, production of SediMite modified as a carrier for the bioamendments, development of an inoculation system to introduce active PCB-transforming microorganisms into SediMite pellets during deployment at the site, and maintaining viability of the anaerobes and aerobes during the deployment process. Methodology, challenges associated with deployment and initial results for the pilot study will be discussed. *In situ* treatment by bioaugmentation has the potential to significantly reduce the environmental impact compared with dredging by reducing the health risks associated with sediment disruption, reducing overall energy use, effectively negating the requirement for extensive waste management and substantial habitat restoration.

Exploration of Bauxaline, Bauxsol and Granulated Bauxlaine for the Stabilization of Trace Metals in Marine Dredged Sediments

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Background/Objectives. Management of sediments is a priority issue in the Mediterranean Sea due to the presence of high levels of contaminants. The present study investigated the possibility of using bauxite residue: bauxaline, graulated bauxaline and bauxsol as an amendment for the treatment of multi contaminated sediments. Bauxaline is the highly alkaline waste from bauxite extraction generally known as "red mud", granulated bauxaline is bauxaline neutralized with 5% of gypsum, and bauxsol is sea water neutralized bauxaline.

Approach/Activities. Pilot scale experiments with 5% and 20% of bauxaline, granulated bauxaline and bauxsol were conducted for the stabilization of dredged marine sediment. pH, ionic conductivity, and leached As, Cd, Cu, Mo, Ni, Cr and Zn concentrations were measured regularly during the experiment. Toxicity of sediment and stabilized sediments was also assessed.

Results/Lessons Learned. For the 5% bauxaline and bauxsol, the results showed that after 3 months of treatment, Cd, Cu, Zn and Ni can be effectively immobilized but increased leaching of As, Cr and Mo is observed as compared to control. Then the experiment were performed with 5% of granulated bauxaline and 20% of bauxaline, granulated bauxaline and bauxsol in order to evaluate the efficiency of (i) gypsum neutralization for immobilization of anionic species such as As, Cr, Mo, (ii) increased amount of additives to increase the overall immobilization rate (iii) decrease the toxicity of sediment.

RECOY—Green Soil Washing Technology

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Background/Objectives. Soil contaminated with hydrocarbons is indeed a big problem for the environment. We estimate that the global productive sector annually generates somewhere around 81 million tons of this material. Today, the technologies available for treatment can be divided into three main groups: thermal, biological and physical/chemical. For efficiency and agility of treatment, the most used technologies fall under thermal methods. These thermal methods, as well as the ones classified in the other groups, have difficulty in the treatment of clay material, which must be separated from the remainder of the material to be destroyed. With the goal of bringing a new technology for this purpose, the AMBIEVO toured companies in the TWM segment in order to discover how a disruptive technology for soil treatment should looks like. From these inputs, the RECOY process was developed. A green soil washing plant that aims to recover materials rather than destroying them. RECOY is a system that operates in a closed-loop concept without generating wastewater. Besides, it uses as the washing media a natural product from renewable sources. It is a mobile plant with high processing capacity - up to 20 tons/hour - and works at room temperature. This is a soil washing system with innovative concept

Approach/Activities. The system was developed over the last five years, having passed through the laboratory stage, pilot stage and industrial scale. The results in all phases were consistent, being that the industrial scale presented final results superior to those obtained in laboratory scale. The system consists of two stages: the first, the washing stage, is where the soil stays in contact with a natural product solution based on citrus terpenes. At this stage, the product removes the oil from the soil by creating an oil emulsion. The clean soil with large particles is removed from the system at this stage. The washing solution with oil and fine particulate proceeds to the second step. In the second stage is called recovery phase. The citrus terpene solution is separated from the oil and fine particulate. The oil is stored in an existing buffer tank in the trolley and then sent to the client's storage tank. The citrus terpenes solution is sent back to the process for washing a new portion of soil. The fines are recovered and removed from the circuit for mixing with the coarse fraction. The technologies involved in this system and with pending patents are: process for enhancement of orange peel oil's solvency, formulations for specific products for soil washing and soil washing process in closed loop. The project is already in industrial application phase and during 2014 the system was on trials for technology approval.

Results/Lessons Learned. Several trials were performed in lab, pilot and industrial scales. Pilot tests on contaminated soils with BTEX, PAH and SVOC obtained positive results, reducing the contaminants to a level below the detection level of the method. Pilot tests with benzoates and phthalates were also positive. Several industrial tests were performed with clayey soils contaminated with crude oil. Contamination levels of 12,642 mg/kg before treatment were reduced to levels of 329 mg/kg after green washing at an operational capacity of 5 tons/hour. The fine particulate, the clay part, gets to an even lower level of contamination than the coarse fraction, proving the efficiency of the system also for clayey soils. There is a white paper containing information about the system, laboratory, pilot and industrial trials with TPH analyzes performed by third party laboratories. This material will serve as a basis for the presentation of results as well as images of the samples before and after treatment.

Back to Contents

Cryogenic Dewatering of Dredged Sediments in Confined Spaces

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Background/Objectives. This paper discusses the use of a potentially cost-effective method to separate suspended solids in hydraulically dredged contaminated slurries in confined spaces through the use of cryogenics (super-cooling).

Currently, the most common method of dewatering hydraulically dredged contaminated sediments in confined spaces requires three steps: (1) The removal of the coarse and medium-sized solids (gravel and sand) through a desanding mechanical unit consisting of vibrating sieves and hydro-cyclones; (2) The subsequent removal of the fine-sized solids (silt and clay) through filter presses and/or dosed polymers (flocculants and coagulants) in retention tanks; and (3) The final filtering of the final effluent (for example, using geo-bags, reverse osmosis, etc.) to comply with EPA turbidity requirements. A vexing problem with this method in confined spaces is that it commonly generates a large bypass of the medium solids from the Step-1 effluent that often leads to the flow's slow-down or even shut-down.

Approach/Activities. An effective alternative is to super-cool the effluents from the desanded slurry. The cryogenic condition leads to an enhanced precipitation of the suspended clay-sized solids to such a degree that the use of flocculent polymers and/or filtration may be greatly reduced or eliminated.

This paper discusses experimental results of using the cryogenic (super-cooling) treatment of the dredged slurry (vg., cold mountain streams commonly have crystal clear carrier water in spite of their high turbulent flow and large volumes of solids, whereas warmer water exhibit higher turbidity under the same conditions). Super-cooling the slurry after the desanding phase is an attempt to imitate this natural phenomenon. The desanded slurry is spread as a thin film over a brine-cooled (< -15ºC) inclined metallic wire mesh filter plate.

Results/Lessons Learned. Preliminary results shows that the removal of up to 99% of the suspended solids is possible by controlling the filter plate geometry, the slurry flow rate, the upstream and downstream temperatures and pressures of the filter plate and the mesh filtration efficiency (grid spacing, thickness, etc.). The method's energy consumption appears to be equivalent to filter press processes.

Remediation of Dredged Marine Sediments Contaminated with PCBs by Separation and Washing Techniques

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Background/Objectives. Contaminated marine sediment with PCBs entered from various sources is a potential contamination source because those pollutants adsorbed on sediments can be taken up and bio-accumulated by sediment-dwelling organisms, transferred to high trophic levels and then cause toxic effect on terrestrial organism as well as marine organisms. Therefore it is necessary to remediate the marine sediment contaminated with PCBs either in situ and ex situ. Chemical oxidation processes have the potential to provide effects of quick destructing contaminated sediment with efficient process control.

Approach/Activities. In this study, some simultaneous effects on PCBs in the fine sediments, caused by Fenton oxidation with surfactant in contaminated marine sediments, were tested. Hydrogen peroxide was used as chemical oxidation regent for Fenton like reaction. Surfactants including Triton X-100, Tween-60 and Tween 80 were used to enhance the solubility of PCBs as washing reagent. A combination of using various concentrations of hydrogen peroxide and surfactants was evaluated to degrade PCBs in contaminated marine sediments. And time-dependent removal efficiencies of various concentrations of hydrogen peroxide were also tested.

Results/Lessons Learned. A washing treatment of using various concentrations of hydrogen peroxide and surfactants was evaluated to degrade PCBs in contaminated marine sediments and the mean removal efficiency of total PCBs were from 0 to 47 % in the sediment for 1 hour duration of the treatment. The highest removal efficiency was shown in the fine sediment (<32 µm) treated 15% hydrogen peroxide and 0.05% Tween 80 among various concentrations of hydrogen peroxide and surfactants. In case of 63-125 µm of the sediment size fraction, 1% hydrogen peroxide and 0.05% Tween 80 also showed the highest removal efficiency of total PCBs. Most of treatment conditions were tested for from 10 minutes to 24 hour and the sediments treated for 24 hour yielded the highest degradation rate of total PCBs in tested contaminated sediment. The level of tPCBs in treated marine sediment by the combination of hydrogen peroxide and Tween 80 satisfy the government regulatory limit of tPCBs for remediation of contaminated harbor marine sediments in South Korea. From these findings, we are currently designing bench scale pilot system to develop a commercial system to be used in harbors around the nation.

Back to Contents

Assessment of Secondary Organic Aerosol Formation by Bioremediation of Polycyclic Aromatic Hydrocarbons Contaminated Site

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Background/Objectives. Biodegradation pathways of polycyclic aromatic hydrocarbons (PAHs) generally obey the rules of converting refractory compounds to easily degradable ones, accompanying with fission and number reduction of rings due to responsible enzymes by specific bacteria. There is a serious concern of small organic compounds, usually volatile, during bioremediation of PAHs contaminated site. Some of these cannot be promptly degraded before releasing into atmosphere, leading to the formation of secondary organic aerosol. This would results in serious impacts on climate change and may also have potential risk to human health. The objective of this study is to discover the critical emission proportion of PAHs degradation byproducts during bioremediation and to assess the potential risk of secondary organic aerosol formation related with PAHs degradation byproducts.

Approach/Activities. Soil samples were taken from a typical PAHs contaminated site and the components of PAHs were quantified. Batch column tests for 90 days with corresponding supplement of two specific bacteria respectively were carried out. The volatile organic compounds (VOCs) were collected and analyzed by GC-FID and GC-MS methods. The emission proportion of PAHs degradation byproducts was calculated using carbon benchmark. The secondary organic aerosol formation from the VOCs during bioremediation of PAHs contaminated site was estimated applying a semi-empirical model. The contributions of each group of compounds identified to the total secondary organic aerosol formation were also estimated under different air pollution levels in correlated with NOx concentration.

Results/Lessons Learned. The results showed the significant emission proportion of PAHs degradation byproducts, summing up to 45% of original source according to carbon benchmark calculation. The VOCs can account for up to 52% of the total secondary organic aerosol from bioremediation of PAHs contaminated site, representing a potentially remarkable influence on climate change and human health. It should be notified the importance among the assessment of secondary organic aerosol when applying bioremediation measures.

The Influence of Climatic Uncertainty on Bioremedial Methods Intended to Protect and Restore Sensitive and Critical Water Resources

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Background/Objectives. The manifestation of climatic conditions, both short term and long term, will have an important strong influence on the design of reliable and protective contamination mitigation measures, and in particular, those mitigation measures such as bioremediation that rely on a relatively predictable and non-extreme environmental condition to be effective as intended. Predictions from leading national science affiliations, such as the U.S. National Oceanic and Atmospheric Administration (NOAA) and the Australian Commonwealth Scientific and Industrial Research Organization (CSIRO) are for a continuing trend of big heat events and big rain events as well as less total rainfall, more rain than snow, and longer dry periods in currently arid to semi-arid areas such as California, the entire U.S. West Coast and much of Australia. The conditions associated with these predictions will severely test our ability to develop effective and robust contaminant clean up and water resource protection measures. In particular will be challenges faced by remedial systems that are located in shoreline areas - including ocean, rivers, and lakes - where changes to the hydrologic system such as rising (e.g., ocean) or lowering (e.g., the Great Lakes) water levels will impact changes to the environmental conditions, including chemical make up, temperature, and water flow (rate and gradient) should be taken into account during the remedial design phase.

Approach/Activities. The challenge to assessing design aspects for bioremedial and other remediation systems that may be influenced by climate-induced hydrologic changes is to consider how the rate of hydrologic change may impact the long-term applicability and efficacy of the remedial methods. Challenges may be focused on (1) developing passive measures that can withstand moderate to high swings in the direction and rate of groundwater flow, as well as groundwater level; and, (2) developing measures that can tolerate gradual changes in geochemical conditions (e.g., salinity, dissolved solids, nitrate, dissolved oxygen, and, temperature conditions, etc.) that may accompany the hydraulic changes. Above ground and active treatment also may be stressed as hydraulic pumping regimes have to be robust enough to accompany higher or lower rates and volumes of groundwater flow within short operational time frames. From existing projects, as well as a survey of projects reported in the public domain, there is no clear path for which designers or regulators have followed. A review of the literature indicates that while some sites have acknowledged the potential for changing sea levels, for example, as a potential influence on remedial effectiveness, there does not appear to be a recognized technical approach applied to actually consider potential affects over the long term. Our work helps to elucidate the considerations important to assessing the relative stress that climate induced impacts, whether hydrologic, chemical, or biological, may have on the evential remedial effectiveness.

Results/Lessons Learned. This presentation aligns the dire predictions concerning the influence of changes in the total climatic sphere (i.e., both above and below ground) on our current state of environmental and water resource conditions with the reality and challenge of how we are changing our approach to protecting sensitive water resources in agricultural and urban landscapes by using science and principles of adaptive environmental engineering. Bioremediation applications are at the forefront of this attention as rising sea levels and salinity influences to groundwater conditions, changes in hydrologic flow rates and gradient directions, and the resultant changes to the biosphere important for bioremedial processes to proceed (including changes to dissolved oxygen content, temperature, and hydraulic flow rates) should be examined for both short- and long-term implementations of bioremedial approaches. Examples and discussions will utilize case studies and information from developing concepts.

Groundwater Flow and Remediation of Hydrocarbons in the Freeze/Thaw Zone of a Fractured Clay Till

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Background/Objectives. Remediation of petroleum hydrocarbons in fractured clay and clay till is a significant challenge. Sites dominated by clay are prominent across the Canadian prairie provinces, and many sites exhibit hydrocarbon impacts considerable distances from likely source areas that suggest fracture control of flow and mass transport. A former fuel retail site in Saskatoon is the subject of a research project by the Sustainable In Situ Remediation Cooperative Alliance (SIRCA) as well as an enhanced bioremediation program. The site is subject to seasonal climatic extremes that are expected to affect the hydraulic behaviour of the clay. In the frost-free months, fractures are expected to be open and hydraulically active. In the winter months, shallow fractures in the capillary fringe and near the water table are likely frozen. These conditions are expected to affect the flow of water and distribution of dissolved nutrients intended to augment natural biodegradation. It is critical to the success of the site remediation program to resolve hydraulic behaviour under both frozen and thawed conditions so the remediation system can be optimized. The objective is to determine whether the remedial approach is sufficiently effective to transition from pilot trial to full scale.

Approach/Activities. A 1 m diameter nutrient injector was installed in fractured clay to a depth of 5 m and backfilled with coarse silica sand. The injector was plumbed to a nutrient delivery system controlled by float switches that results in a pseudo-steady elevated hydraulic head in the injector to encourage outward radial flow and nutrient transport. Several transducers were installed at the site to characterize the hydraulic footprint of the nutrient injection during periods of deep frost (ice-blocked fractures) and thaw (open fractures) through a number of seasons. The nutrient system commenced operation in August 2014, during which approximately 2000 L of nutrient cocktail has been released. In addition, a bromide tracer test is planned to evaluate the relative contributions of fracture and matrix flow, as well as transport of hydrocarbons and the nutrient cocktail comprised of sulphate and nitrate salts and orthophosphate. The latter is theorized to be limiting sulphate reduction at the site. In subsequent seasons, other forms of phosphate will be evaluated.

Results/Lessons Learned. Based on the distribution of hydrocarbons extending a significant distance off-site, the system was expected to be more uniformly permeable. However, it appears that a few fracture zones have a notable influence on mass transport. Preliminary transducer data in monitoring wells close to the infiltrator appear to indicate a lag in response to nutrient pulses, suggestive of matrix buffering of flow and transport. Monitoring using high resolution multilevel devices may be considered to improve understanding of spatial flow characteristics.

Management Strategies to Achieve Remedy Complete When Groundwater Concentrations Fluctuate with Water Table Changes and Drought Conditions

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Background/Objectives. At several hazardous waste sites, Leidos has faced challenges in achieving remedy complete when volatile organic compound (VOC) concentrations have approached cleanup levels, but continued to fluctuate above and below the cleanup values for an extended period of time. In some instances, concentration fluctuations appear to be correlated with precipitation events, which may be either annual cyclic trends or extended drought interrupted by significant rainfall events. Such precipitation-correlated concentration fluctuations have been observed for chlorinated or petroleum VOCs at numerous hazardous waste sites, at locations such as former Brooks City-base, Memphis Air National Guard Base, an EPA led Superfund site in New Jersey, and an industrial site in Iowa. The challenge in these instances is predicting when a site is expected to attain remedy complete (that is, the termination of active remediation or monitored natural attenuation) and can then transition into long-term monitoring (LTM), when fluctuations that lead to cleanup standard exceedances are unpredictable. Many states require one to two years of quarterly or semi-annual monitoring with contaminant concentrations continually below respective cleanup levels for closure, however the above instances of contaminant fluctuation can upset an ongoing LTM period.

Approach/Activities. The conceptual site model that explains such fluctuations is residual contamination that is adsorbed to the vadose zone or adsorbed to the solid phase in the saturated zone or capillary fringe that is then released to the groundwater by leaching as a result of infiltration. An additional potential contributor is the creation of VOC exceedances by appearance of daughter products from degradation of the parent after instances of high water table or leaching from the vadose zone.

Leidos developed several different management strategies to address or overcome the unpredictable nature of precipitation that leads to these undesirable situations in LTM and closure. This included (a) performing chemical injection events coincident with a high water table so that the maximum aquifer saturated thickness is affected by the injection chemicals; (b) using biostimulation or chemical oxidation chemicals that react quickly rather than slowly so as to maximize the immediate effect under the current, as opposed to future unpredictable, water table conditions; (c) creating artificial infiltration and water table rise by irrigating the surface of the site to immediately promote leaching and in situ degradation; and (d) implementing a risk-based approach, such as a plume management zone, that allows a small residual level of contamination to be left behind as long as the point of exposure meets the cleanup level.

Results/Lessons Learned. Leidos has successfully implemented options (b) and (d) at select sites, and has negotiated to implement option (c) at a site where different levels of drought conditions have persisted for several years. The decrease in time to closure and the project savings are the metrics of greatest interest when implementing one of these approaches, however also of importance is whether the site is closed with or without land use controls. The implementation and outcome of these recommendations / approaches will be discussed in this presentation.

Back to Contents

Large Diameter Nutrient Delivery Systems for Enhanced Hydrocarbon Remediation in Cold Soils

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Background/Objectives. Federated Cooperatives Limited (FCL) has several fuel retail sites in western Canada that are impacted by petroleum hydrocarbons. While being fully committed to remediation or risk management of these sites, FCL is also keenly interested in novel approaches to remediation, including passive and semi-passive techniques designed to minimize energy demands, materials and time on site. A former fuel retail site in Saskatoon, SK is the subject of both a collaborative research project by the Sustainable In Situ Remediation Cooperative Alliance (SIRCA) and a pilot scale remediation trial of enhanced bioremediation. Groundwater in Saskatchewan often contains high sulphate concentrations (3,000 to 7,000 mg/L), but little evidence of active sulphate reducing bacteria. The hypothesis posed by the research team is that sulphate reduction is limited due to a source of bioavailable phosphorous, and that enhancing the bioavailability of phosphorous will in turn result in an increase in degradation by sulphate reducers. The project site is subject to seasonal temperature swings from -40C to +30C. Such extremes may stress indigenous bacteria, particularly near the water table.

Approach/Activities. Two 1 m diameter caissons were installed to a depth of 5 m, the soil within evacuated, instrumentation set in place and backfilled with coarse silica sand. The caissons were then removed to form nutrient infiltrators. Each infiltrator was plumbed to a separate clean UST where nutrient solutions were stored. Submersible pumps in the USTs transferred nutrient to the respective infiltrator, which was controlled by float switches in the infiltrators. The transfer of nutrients increased the head in the infiltrators, resulting in outward radial flow. One infiltrator was installed in contact with native sand and the other in clay. Initial nutrients consist of sulphate and nitrate salts and orthophosphate. In subsequent years, triethylphosphate and tripolyphosphate will be released to enhance bioavailability. In addition, low molecular weight organic acids will be included to further promote phosphorous bioavailability. Delivery commenced in August 2014 and will continue for the next 18-24 months.

Results/Lessons Learned. The two infiltrators exhibit markedly different hydraulic behaviour: over 40,000 L of nutrient has been released from the “sand” infiltrator and 2000 L from the “clay” infiltrator. Transducers are installed across the site to characterize seasonal flow changes and that associated with the injection process. The effects of frost on microbial activity and changes in flow characteristics induced by frozen fractures will also be assessed. The remediation performance of the infiltrators will determine whether additional systems will be installed at the site or modifications are indicated.

Back to Contents