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ABSTRACT BOOK

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Interlaboratory Study on PCB Analysis of Natural Waters by Method 1668A

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Method 1668, Revision A (1668A) for polychlorinated biphenyl (PCB) single congener analysis uses high resolution gas chromatography combined with high resolution mass spectrometry. Method 1668A includes estimated method detection limits as low as 4 pg/L for individual PCB congeners. Despite the reported increased sensitivity of Method 1668A with respect to previous PCB analytical methods, test results using independent laboratories are not available. The objective of this interlaboratory study is to provide estimates of measurement error for PCB analysis in natural waters using Method 1668A. Due to the widespread use of solid-phase-extraction (SPE) for field-concentrating high volumes of natural waters, the study included two applications: (a) analysis of grab samples, and (b) high volume field sampling using SPE with XAD resin. Samples were taken at two locations, where previously measured PCB concentrations differed by approximately two orders of magnitude. Grab-low volume (4L) and SPE-high volume (~1000 L water) samples were taken at the location where a higher concentration previously had been reported, while a SPE-high volume sample (~1000 L) was taken at the location where a lower concentration previously had been reported. Grab and SPE-high volume extract splits triplicates were sent to three commercial labs for analysis. Analysis of variance indicated that results by the three labs on the “higher concentration site” samples (both grab samples and split extracts) were significantly different (C.L. = 95%), while results for the “lower concentration site” split extracts were not. Reported lab-specific detection limits were different than those included in the method and varied widely among labs. None of the three labs met all the QA/QC method provisions (i.e., chromatographic resolution, internal standard recoveries, spikes recoveries). Laboratory and field blanks showed concentrations higher than the method detection limits.

An Assessment and Overview of PCB and Congener Specific PCB Testing Methodologies

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As the public health and ecological concerns surrounding PCBs in the environment grow and, as the extent of the problem becomes more apparent, efforts to identify and remediate sources of contamination take on greater significance. Both health and environmental professionals face a daunting array of situations in which proper identification of sources of contamination is critical to evaluating environmental impact and determining the appropriate cleanup and protection measures. The wide array of analytical tests available for PCB determination is not immediately apparent as many are not part of the formal EPA method system or are not widely used outside of specific regions or applications.

To help clarify the scope of methods available, an evaluation of all current PCB testing methodologies was undertaken. Specific attention was given to the following areas of interest; detection level capabilities, applicable matrices, ruggedness, cost, complexity, turnaround time, data format, data consistency, historical usage, current applications and regulatory considerations.

A brief overview of all current methodologies as well as the history of PCBs and PCB method development will be presented. The remaining discussion will delve into greater detail on the currently available PCB Congener methods. These represent the current state of the art and are some of the least understood of the methods available. Specific information will be presented on HRGC/HRMS (USEPA 1668/1668a), HRGC/ECD (USEPA 8082, Green Bay Congener) and HRGC/LRMS (USEPA 680, Lab Specific).

Compliant Analysis of Water, Wastes and Related Solid Environmental Samples Using Inductively Coupled Plasma Atomic Emission and Mass Spectrometry - a critical comparison of QA/QC requirements of EPA and Standard Method Procedures

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Inductively coupled plasma atomic emission and mass spectrometry (ICP-AES and ICP-MS) is widely employed for compliant determination of trace, minor, and major element constituents in all types of water, liquid and solid wastes - from natural surface and ground water to acid mine waters, to industrial effluents and hazardous solid wastes. As a result of their excellent analytical characteristics, these instrumental technologies and compliant and performance-based methods have been specified by regulatory agencies and adopted in commercial accredited and research laboratories.

However, there are several critical differences in QA/QC requirements for these analytical tasks using EPA 200.7, EPA 200.8, EPA 200.5 and SW 846 (6010C and 6020A) and SM ICP-AES and MS procedures. In this presentation, a comparison will be made of the contrasting differences in terms of sample throughput and accuracy. For example the following figures of merit will be addressed: range of elements, instrument and method limits of detection, minimum limits of determination, multielement calibration and calibration stabilities (CCV, ICV) linear dynamic ranges, compensation of spectroscopic and non spectroscopic interferences), and QA/QC and ISO 17025 requirements.

The Nylon Plasticizer, N-(*n*-butyl)benzenesulfonamide, Misidentified as Diesel Contamination in Groundwater

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During groundwater investigations at Lawrence Livermore National Laboratory (LLNL) Site 300, a previously unidentified chemical was discovered. Diesel range organic compounds were identified in 22 wells using EPA Method 8015. However, such widespread diesel contamination was not consistent with site data. Upon detailed examination of gas chromatograms and analyses using EPA Method 8270, it was determined that what had been interpreted as diesel fuel was predominantly N-(*n*-butyl)benzenesulfonamide (BBSA). BBSA, a plasticizer used in the manufacture of nylon tubing, has a retention time that overlaps with diesel range compounds. All wells in which BBSA was identified were equipped with dedicated pumps and nylon discharge/air-supply tubing. Following the discovery of BBSA, a new analytical method involving liquid chromatography/ tandem mass spectrometry (LC/MS/MS) was developed at LLNL to confidently identify and accurately quantify the BBSA in groundwater. The LC/MS/MS method allows direct injection of samples into the instrument and has a detection limit of <1 µg/L. Using the 8270 method, BBSA could be positively identified, but concentrations only estimated. All wells equipped with nylon tubing were re-sampled and analyzed by LC/MS/MS. BBSA concentrations ranged from 800 to 531,000 µg/L. Experiments conducted to determine the origin of the BBSA included: (1) time series sampling of two wells, and (2) recirculation testing to evaluate BBSA leaching potential. Both experiments indicated that the BBSA was indeed related to the equipment and was not a groundwater contaminant. The equipment supplier confirmed the nylon was the source of the BBSA through a leach test. Thus, we observed that non-diesel compounds can be erroneously identified as diesel fuel in routine analyses, and chemicals leaching from equipment may be incorrectly interpreted as groundwater contaminants.

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Low Thermal Mass Gas Chromatography – Analysis at MACH Speed

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Gas Chromatography (GC and GC/MS) analysis has been the mainstay for the analysis of regulated organic contaminates in the environmental field. Numerous advancements have occurred in GC instrumentation that include improvements for injectors, detectors, automation, software, and GC column choices. Although many advancements have been made in GC technology, very little has changed for column oven design and operation. Traditionally, GC column ovens are still large, with huge power requirements, limited temperature programming rates and long cool down times, dictating the overall speed of analysis.

Recently Low Thermal Mass (LTM™) technology, developed by RVM Scientific, has become commercially available from Gerstel as the Modular Accelerated Column Heater (MACH™). This new technology has dramatically increased the speed of analysis while still maintaining chromatographic resolution. Key to this new technology is that LTM™ hardware can be retrofitted to GCs currently in use, providing ultra fast temperature programming with unprecedented cool down time and extremely low power consumption.

This presentation will discuss data obtained from the MACH™ and lessons learned for dual column PCB and Pesticide analysis, column selection and optimization, and retrofitting MACH™ hardware to instrumentation not currently supported by the manufacturer. Several case studies will be discussed on how fast GC analysis can provide benefit to the contract lab industry as well as the environmental professional who utilizes lab services.

Lessons Learned on the Implementation of CRREL Multi-Increment Sampling (MIS) and Analysis by SW-846 Method 8330B

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A Multi-Increment Sampling (MIS) approach and modified analytical method 8330B have been recommended for sampling and analysis of explosive compounds by the U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL). This method was recently adopted by EPA in their Small Arms Range (SAR) Work Plans. The U.S. Army Corps of Engineers, New England District (NAE) has been working closely with CRREL, the Army Environmental Command Impact Area Groundwater Study Program (IAGWSP), MassDEP, EPA, Environmental Chemical Corporation (ECC), and TAL VTB (formerly STL-VT) on implementing the Multi-Increment Sampling (MIS) approach and modified analytical method at the Massachusetts Military Reservation (MMR), Camp Edwards, MA.

The MIS and Method 8330B have been implemented at Small Arms Ranges (SARs) and Gun and Motar (G&M) firing positions and target locations. The MIS approach has mainly been applied to explosives. The several different multi-increment sampling (MIS) and grinding techniques that were evaluated during implementation will be discussed.

Specific MMR project requirements were developed based on the MMR Program DQO's required. These DQO's included dual column confirmation using the Phenyl Hexyl confirmatory column, an extended target analyte list including NG, PETN, 2,4-DANT, 2,6-DANT, picric acid, as well as the RDX degradation by products, MNX, DNX and TNX. All 22 Target explosives and propellants have been resolved in one analysis run on both the primary C-18 and confirmatory phenyl hexyl analytical HPLC columns. STL-VT has also been using the Photo Diode Array (PDA) detector or UV spectral detection method for an additional level of confirmation. The closest matching concentration standard PDA spectra are compared to the sample PDA UV spectra for any dual column confirmed explosive target analyte HPLC peak.

Analysis

The main focus on this presentation will be on the lesson learned during the implementation of the CRREL Multi-increment Sampling and analysis by SW-846 Method 8330B. The analytical method development used to meet the MMR project specific DQO's will be discussed in detail. Also, the successes of the multi-increment sampling will be highlighted by review of actual SAR sampling and analysis data. The pros and cons encountered will be evaluated throughout the presentation.

Risk-Based Characterization of Extractable Petroleum Hydrocarbon Contamination Using Comprehensive Two-Dimensional Gas Chromatography with Dean's-Switch Modulation

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Approximately ten years have passed since the first generation of risk-based petroleum methods was developed and put into production in the environmental laboratory. However, the precise amounts of the several different solvents needed, in addition to variables affecting the fractionation medium often result in “breakthrough” of target compounds into the wrong fraction(s) and/or contamination of the final extract(s). Advances in gas chromatographic and flow control technologies can now be used to replace the tedious sample preparation techniques previously required to obtain the separate sample extracts (“fractions”) used for site characterization/assessment.

Soil/wastewater samples are extracted using methylene chloride. Extracts are dried with sodium sulfate, concentrated and treated with silica gel to remove polar, non-petroleum related compounds. The final extract is then analyzed using a two-dimensional gas chromatograph (2-D GC; GC x GC) designed to separate the aliphatic and aromatic species present in the extract using flame ionization detection (FID).

This new approach meets the original intent of the Massachusetts state and TPH Working Group methods to measure and quantitate collective aliphatic and aromatic hydrocarbon concentrations, as well as target polynuclear aromatic hydrocarbons (PAHs).

Bioremediation

Using Field Pilot-Testing Results to Design a Full-Scale Enhanced Bioremediation Approach to Remediate DNAPL TCE
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Use of Degradable Non-oxidizing Biocides and Biodispersants for Maintenance of Capacity in Nutrient Injection Wells
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Mechanisms and Kinetics of Extracellular Electron Shuttle Mediated Cyclic Nitramine (RDX and HMX) Biodegradation
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Influence of Carbon Source on Microbial Community in Passive ARD Treatment System
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Replacement of a Groundwater Extraction System with Bioremediation to Treat Trichloroethylene in Fractured Bedrock
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Transport of Lactate and in-situ Bioremediation of Tetrachloroethylene (PCE) under Direct Current
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Using Field Pilot-Testing Results to Design a Full-Scale Enhanced Bioremediation Approach to Remediate DNAPL TCE

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Several field pilot studies of enhanced bioremediation (reductive dechlorination) of trichloroethene (TCE) were conducted at a site located in western Connecticut. The concentration of TCE in the groundwater plume varied spatially, but was up to 768 mg/L (~ 70% solubility of TCE), indicating the presence of dense-non-aqueous-phase-liquid. At the source area and within the groundwater plume, emulsified soybean oil, amended with a bromide tracer, was injected into the subsurface, providing a slow-release source of carbon and reducing power for the naturally-occurring microbial populations. Reducing conditions, characterized by negative oxidation-reduction potential and decreased dissolved oxygen levels, were achieved within several weeks of the injection events. The distribution of the carbon substrate was evaluated using total organic carbon (TOC) and bromide concentrations. After operating the pilot tests for several months, bioaugmentation of dehalococcoides spp. bacteria was performed at each of the test locations. Chlorinated ethenes, TOC, geochemical parameters, and microbial populations were monitored to determine the effectiveness of the treatment.

The results of the pilot tests were utilized to design a full-scale enhanced bioremediation approach for the chlorinated solvent groundwater plume. A reaction and transport groundwater model was developed for the site and used in the design of the bioremediation approach. Biodegradation reaction rates were estimated and incorporated into the modeling. Injection radii of influence, and carbon substrate composition, quantities, and loading rates were determined. In addition, required biodegradation geochemistry, and carbon delivery locations, rates, and methods were incorporated into the design. The design also included a plan to monitor the performance of the enhanced bioremediation approach.

Use of Degradable Non-oxidizing Biocides and Biodispersants for Maintenance of Capacity in Nutrient Injection Wells

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Fouling of water supply wells is a common problem, dating from the time humans started using groundwater resources for water supply. In the groundwater remediation field, fouling of recovery and treatment systems has been a similarly common operating problem. Thus it is not surprising, with the increased use of in-situ remedial methods, that fouling of in-situ treatment units is becoming a major design concern. In-situ treatment units include recovery wells, injection wells, recirculating wells, flow-through treatment cells, and in some cases, geologic formations themselves. The very effectiveness of these units depends greatly upon retention of permeability or hydraulic capacity. Capacity can be dramatically reduced due to fouling by naturally occurring inorganic precipitates or by microbial deposits.

One of the least surprising instances of fouling of an in-situ treatment unit involves various bioenhancement techniques, where nutrients are injected with the intention of enhancing certain types of bioactivity and subsequent biodegradation of contamination. The data presented in this paper are derived from experience at remedial sites where bioenhancement activities have been self-defeating by causing a loss of permeability in injection wells, surrounding geological formations, or down-gradient recovery or recirculation wells. In these cases, non-oxidizing biocides, bio-dispersants, saponification agents or other additives have been applied to retain permeability in the hydraulic “bottlenecks” of these systems, such as injection wells and surrounding formations. Data collected from such applications shows that proper characterization of fouling mechanisms and subsequent application of well-designed deposit control programs can eliminate operational problems associated with fouling arising from bioenhancement.

This paper introduces the key concepts in deposit control practices as they apply to fouling of in-situ treatment units. It provides an overview of the various agents and techniques used in such deposit control programs. Regulatory and design issues are discussed, and subsequently illustrated by a series of brief case studies.

Mechanisms and Kinetics of Extracellular Electron Shuttle Mediated Cyclic Nitramine (RDX and HMX) Biodegradation

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Microbial enrichments were generated using RDX-contaminated aquifer material that was incubated under a variety of extracellular electron shuttle (EES)-amended conditions. Electron donors tested included H2, benzoate, formate, lactate, or acetate; electron acceptors included poorly crystalline Fe(III) oxide, AQDS, or RDX. Enriched cultures were sequentially transferred (10%) into new media containing the same electron donors and acceptors.

AQDS and Fe(III) reducing enrichments were developed with H2 or acetate as the sole electron donors. Although the enrichments have not reduced RDX directly, it is known that reduced EES and Fe(II) can reduce RDX by abiotic mechanisms. Lactate and RDX (15μM) were used to develop specific RDX-reducing enrichments and these microorganisms reduced RDX below the detection limit within 7 days suggesting enriched microorganisms can utilize RDX directly as the sole electron acceptor. Microorganisms grown in a medium containing lactate and RDX also grew with lactate and with quinone-based military smoke dye as the sole electron acceptor. Additional experiments with the resting cell suspensions of G. metallireducens indicated that RDX reduction rate was 8 times faster with military smoke dye (12 μM), suggesting that military smoke dye could be another optimal source of EES and applicable to RDX remediation in military areas. In addition, RDX ring cleavage was fastest and most complete in the presence of EES; approximately 70% of the available RDX carbon was recovered as formaldehyde (a labile compound) when EES were present versus 12% when the cultures received only an electron donor.

These results indicate that indigenous microorganisms in sediments can utilize EES to stimulate RDX biodegradation. EES-mediated RDX biodegradation is an effective remediation option in various environmental settings. Future study will identify the dominant microorganisms associated with EES-mediated RDX biotransformation by DNA quantification using real-time PCR and total microbial community analysis using amplified rDNA restriction analysis (ARDRA).

Influence of Carbon Source on Microbial Community in Passive ARD Treatment System

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Passive anaerobic remediation using bacterial sulfate reduction is a low-cost, effective, and long-term treatment option for acid rock drainage. This approach was used by Nature Works Remediation Corporation to build a six-stage treatment wetland system for removal of arsenic, cadmium and zinc from a waste pile leachate stream near Trail, British Columbia. The leachate flows through two anaerobic bioreactors filled with pulp mill biosolids as organic material and then through three cattails plant cells and a wetland pond. Over the five years of operation, the arsenic removal efficiency remained above 96.6%. However, it is not known how much carbon is left available for the microbial growth in the system, thus the long-term successful treatment cannot be predicted.

In this study, five different carbon sources: pulp mill biosolids, vegetable compost, silage, molasses, and composted cattails were compared in situ to determine the influence of organic material on the sulfate reducing bacteria (SRB) community and on the long-term treatment efficiency. Subsamples of the materials were removed from the system after 3 and 5 months to evaluate the carbon degradation kinetics. Rapid and reliable molecular techniques, such as quantitative polymerase chain reaction (q-PCR) was developed to specifically target and quantify SRB groups present.

The results of this study will bring new information on the relationship between carbon degradation and the microbial community for different commonly used carbon materials. This will potentially aid in design and choice of the most suitable material for new passive treatment systems, as well as estimate the time scale of efficient treatment for existing systems.

Replacement of a Groundwater Extraction System with Bioremediation to Treat Trichloroethylene in Fractured Bedrock

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Bioremediation was used to replace a 15-year old groundwater extraction and treatment system that had been installed to address trichloroethylene (TCE) and its daughter products at an active chemical manufacturing facility in Tennessee. Most of the TCE mass in the source area was detected in fractured limestone bedrock at depths of approximately 9 to 12 meters below ground surface. The groundwater extraction and treatment system had reached a point of diminishing returns, yielding less than 0.5 kg of TCE per year of operation even though average TCE concentrations in source area wells remained on the order of 5,000 ug/L. Bioremediation was implemented by adding emulsified soybean oil at a concentration of approximately 1% by volume into five source area wells. After achieving anaerobic and reducing conditions in the amended wells, 5 liters of a microbial culture (KB-1™) containing dehalococcoides bacteria was added to each well. Within six months after addition of the microbial culture, total chlorinated volatile organic compound (CVOC) concentrations decreased by approximately 85%. The estimated dissolved mass of TCE destroyed by bioremediation in the source area was approximately 6.7 kg; the total TCE mass destroyed is likely much greater due to biodegradation of CVOCs sorbed or trapped in the rock matrix. The cost of the bioremediation remedy was roughly equivalent to the cost of 18 months of operation of the groundwater extraction and treatment system. Based on the data obtained from bioremediation in the source area, a line of downgradient biobarrier wells was installed in December 2006 to mitigate offsite migration of the residual CVOC plume.

Transport of Lactate and in-situ Bioremediation of Tetrachloroethylene (PCE) under Direct Current

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Bioremediation of tetrachloroethylene (PCE) by reductive dechlorination has been successful when the microorganisms are supplied an additional electron donor such as lactate. However in heterogeneous PCE contaminated aquifers, uniform delivery and mixing of electron donor amendment have met limited success because the electron donors cannot be delivered into the low permeable zones. Electrochemical amendment injection provides an alternative to hydraulic methods by delivering the electron donor to microorganisms in the low permeable zones where hydraulic delivery fails. Lactate injection experiments were conducted in clay (kh = $2x10^{-7}$ cm s^{-1}) and heterogeneous soil under 1.2 A m^{-2} and 5.3 A m^{-2} current densities. Additional experiments mixed Dehalococcoides dechlorinator KB-1™ culture (SiREM, Ontario, Canada) with PCE (20 mg L^{-1} in the pore water) in a clay-water slurry and consolidated the slurry in a nitrogen filled anaerobic chamber. Electroosmotic and ion migration transport rates averaged 2.16 cm^2 $V^{-1}day^{-1}$ and 3.4 cm day^{-1}, respectively. Pore water lactate concentrations reached as high as 800 mg L^{-1}. The ion migration rate was more than 191 times faster than transport under a hydraulic gradient. No biological fouling was observed under the experiments using electrochemical injection. The PCE and the KB-1™ culture mixed (no electricity) with the clay resulted in partial dechlorination of PCE halting at cis-DCE presumably because of absence of an electron donor. The duplicate PCE and KB-1™ culture experiments with lactate injection by electrochemical means completely degraded PCE to ethene within 4 months across the 40 cm long silty clay medium. PCE was transformed to DCE following a zero order rate of 0.0063 to 0.027 mmol $L^{-1}\cdot day^{-1}$ and the transformation of DCE to ethane followed a first order specific remediation rate of 0.0577 to 0.254 day^{-1}. The soil pH remained between 7 and 7.5 throughout the experiment.

Biotechnology

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Advanced Diagnostic Tools and Applications to Site Design, Management and Closure
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Applying Environmental Biotechnology to a VCUP Program for the Remediation of a Mixed Chlorinated Solvent Plume
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Comparison of Sediment, Groundwater, and Bio-Trap Microbial Samples from a Biostimulation Study at Rifle, Colorado
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Combining Transcriptomic and Proteomic Methods to Develop Bioindicators of Chlorinated Solvent Bioremediation
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In-Situ Stable Isotope and Fluorinated Analog Probing to Evaluate Fate of cDCE via both Reductive Dechlorination and Anaerobic Oxidation
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Reductive Dechlorination of Chlorinated Solvents with Electrodes as the Electron Donor
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Advanced Diagnostic Tools and Applications to Site Design, Management and Closure

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Site remediation has evolved from energy intensive, mechanically driven remediation processes to more effective and cost efficient in situ processes. In many cases, in-situ remediation is best served if integrated with advanced diagnostics that employ molecular biological tools (MBTs) and compound specific isotope analysis (CSIA). Diagnostic protocols, taken alone or in combination, can help with site assessment and subsequently assure the best in-situ remedy from among the available options. As an extension of this, the diagnostics can further be used for optimization of on-going remedial operations.

While advanced diagnostics can assist in site assessment and the design and management of in situ remediation options, there are also important extensions of this work to site closure, with an emphasis on monitored natural attenuation (MNA). We have applied advanced diagnostics in ten remedial operations since March, 2006. In eight cases the diagnostics were used to help site assessment and/or remedy selection and these results will be summarized. In two cases, which will be discussed in detail, there was movement directly to an MNA status based on the use of MBTs.

The larger of the two sites that received and MNA ruling had soil and groundwater concentrations of chlorinated solvents greater than the Georgia Risk Reduction Standards (RRS). Applications of phospholipid fatty acid analysis (PLFA) and nucleic acid diagnostics were employed to assess the status of natural attenuation prepare a petition for MNA. With the results of these analyses the site was put into an MNA status. This ruling was in concert with excavation of the source and an ozone treatment of source groundwater. The MBT data was used to successfully establish that downgradient bioremediation barriers could be held in abeyance subject to the impacts of the source treatments and if permanently avoided an average cost savings of $1.2 MM will be realized.

Applying Environmental Biotechnology to a VCUP Program for the Remediation of a Mixed Chlorinated Solvent Plume

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Molecular diagnostics inconjunction with standard bioindicator parameters are becoming valuable tools for site evaluation, remedy selection and post remedial site evaluation. A former solvent recovery process at an industrial facility released chlorinated volatile organic compounds (CVOCs) to the groundwater. The major constituents exceeding Illinois Tier 1, Class 1 groundwater standards are; 1,1,1-Trichloroethane [TCA], 1,1-Dichloroethene (1,1-DCE), 1,1-Dichloroethane (1,1-DCA), Tetrachloroethene [PCE] and Trichloroethene [TCE]. Under a voluntary cleanup program a source area removal action was performed to remove soil impacts and a groundwater remediation program implemented. A supplemental site characterization was implemented to collect groundwater data on organic and inorganic bioindicator parameters. In addition microbial traps were emplaced in a series of wells throughout the plume to collect samples of the microbial community and analyze the community structure using molecular genomic tools. Specifically, the presence and response of dechlorinating microbes to stimulation with anaerobic aquifer conditioners was monitored. The objective was to use the molecular genomic tools and bioindicator parameter data to define and guide the remedial system design, and monitor remedial performance. Over a period eighteen months, six organic acid nutrient injection events were performed to stimulate anaerobic reductive dechlorination of the target contaminants. Transect mass flux analysis and spatial moments analyses were used for analyzing performance monitoring data and demonstrated complete remediation and retraction of the dissolved phase plume to the source area. Only two of eleven monitoring wells had impacts exceeding the regulatory limits. In the nine down gradient monitoring wells choroethenes were completely degraded to ethene and 1,1,1-TCA was transformed to ethane with transient accumulation of 1,1-DCA, and chloroethane. Analyses of microbial traps showed up to three orders of magnitude increases in the Dehalococcoides ethenogenes and Dehalobactor sp. subsequent to stimulation with organic nutrient supplementaton. In addition key reductive dehalogenase gene copies (TCE rd, BAV-1 VCrd and VCrd) were observed to increase during the treatment program.

Comparison of Sediment, Groundwater, and Bio-trap Microbial Samples from a Biostimulation Study at Rifle, Colorado

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In bioremediation, it is crucial to be able to monitor the subsurface microbial community in terms of its biomass, community composition, and activities. However, the subsurface is difficult to access and has large sample-to-sample variation. Sediment samples are the gold standard of subsurface conditions. However, the great expense of obtaining quality samples of subsurface sediments limits the number available. Also, due to technical or legal restrictions, the locations that can be sampled may be further limited. The high variation in the subsurface environment means that any one sample is not a very good indicator of subsurface conditions - several samples must be taken before reliable estimates can be made. Bioremedial treatments (for example, addition of carbon or oxygen) will affect a portion of the microbial community, and there may be another portion which is still present but unaffected. Groundwater samples are typically much more readily available. Since the goal is groundwater quality, wells have usually already been installed for groundwater sampling. These groundwater samples must either be filtered on-site, or chilled and shipped to a laboratory for analysis. Bio-traps are small perforated plastic cylinders packed with Bio-Sep beads, which are composed of the plastic Nomex and powdered activated carbon. The internal structure of the Bio-Sep provides a large surface area for bacterial colonization. Bio-traps are suspended in existing wells, for a period of time, and then retrieved and analyzed by methods appropriate for sediment samples including molecular, lipid, and microscopic techniques. In this study we compared sediment, groundwater and Bio-trap samples taken during a biostimulation event designed to reduce the amount of soluble Uranium in site groundwater. Results show the groundwater community reacts more strongly to subsurface treatments than the total subsurface community, while Bio-traps appear to capture just the active portion of the microbial community from the groundwater.

Combining Transcriptomic and Proteomic Methods to Develop Bioindicators of Chlorinated Solvent Bioremediation

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Molecular bioindicators (DNA, RNA, and protein) show promise for aiding bioremediation efforts at chloroethene-contaminated field sites. While DNA can be analyzed to show the presence of *Dehalococcoides* (DHC) populations, RNAs and enzymatic proteins serve as more appropriate bioindicators of instantaneous activity of those populations. In this study, we elucidate several RNA and protein bioindicators that are highly expressed during chloroethene dehalorespiration by DHC.

The genome of *Dehalococcoides ethenogenes* strain 195 was first screened for candidate bioindicator genes including a housekeeping gene (RNA polymerase), reductive dehalogenases (RDases), and other genes with potential roles in the dehalorespiration process. Expression of these genes was determined at the level of RNA via reverse transcription quantitative polymerase chain reaction (qRTPCR). To validate the RNA results and to develop protein-based bioindicators we also ran shotgun proteomics (via tandem mass spectrometry of digested proteins -GeLC/MS/MS) on proteins from these cultures. The most highly expressed RDases were TceA, PceA and two other putative RDases (DET gene numbers 1545 and 1559). Outside of the RDases, the most highly expressed candidates were the hydrogenase Hup and a gene annotated as formate dehydrogenase (“Fdh”).

The proteomic analyses were then extended to three other cultures containing DHC strains: pure culture strain CBDB1 (grown on trichlorophenol), the bioaugmentation culture KB1TM, and an uncharacterized PCE-to-ethene enrichment. Through these comparative proteomic studies, we detected several proteins (including "Fdh") in all cultures and on all substrates. As they are not strain-specific, such proteins might serve as good bioindicators of general DHC activity. In contrast, the suite of RDases detected varied considerably. Most notably, only cultures which respired vinyl chloride (VC) to ethene contained peptides matching VC RDases - suggesting that this protein is a specific bioindicator of VC-dechlorination activity. Our results have generated a suite of RNA and protein bioindicators that, with further development, should aid in situ bioremediation efforts.

In-Situ Stable Isotope and Fluorinated Analog Probing to Evaluate Fate of cDCE via both Reductive Dechlorination and Anaerobic Oxidation

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Anaerobic biostimulation and bioaugmentation techniques are now among the most widely used remedies for chloroethene-contaminated groundwater aquifers. Most of the literature and reports on field applications have focused on either biostimulation of reductive dechlorination or bioaugmentation with commercial cultures containing Dehalococcoides spp. whereas relatively little has been published concerning the anaerobic oxidation of chloroethenes. As cDCE is a potentially persistent daughter of PCE and TCE, bioremediation strategies that can simultaneously promote both reductive dechlorination and anaerobic oxidation processes may be more rapid and effective than reductive dechlorination alone. As reported by Paul Bradley (USGS) and his colleagues, anaerobic oxidation processes can be the dominant biodegradation pathways for partially reduced chloroethenes such as cDCE and vinyl chloride at some sites. Nitrate and Mn(IV) appears to provide sufficient energy as electron acceptors for the anaerobic oxidation of both cDCE and vinyl chloride, whereas Fe(III) reduction likely provides sufficient energy for oxidation of vinyl chloride but perhaps not cDCE.

This paper will provide a progress report on the use of Bio-trapTM samplers to investigate both in-situ reductive dechlorination and anaerobic oxidation processes at two different chloroethene contamination sites in the greater New York metropolitan area. Pairs of Bio-trapTM samplers have been designed and installed as follows: one sampler with Bio-sepTM beads loaded with 13C-labeled cDCE will be used to investigate the anaerobic oxidation pathway whereas the second sampler with Bio-sepTM beads loaded with DCFE (a fluorinated analog of cDCE) will be used as a tracer for reductive dechlorination. At one site in southern New York, complete reductive dechlorination is already occurring (prior to remediation) and a biostimulation demonstration program designed to promote simultaneous reductive dechlorination and anaerobic oxidation is underway. At a second site in northern New Jersey, nano-scale iron was injected into a TCE source area that resulted in a large decrease in TCE and large increases in the biological daughter cDCE and total inorganic carbon without appreciable increases in vinyl chloride. The available data from the NJ site suggests that the nano iron injection stimulated anaerobic oxidation and mineralization of cDCE to inorganic carbon.

Bio-trapsTM loaded with “normal” (12C) cDCE were installed and analyzed at both sites from June 2006 through January 2007 to investigate the relative rates of microbial biomass growth and cDCE degradation prior to the deployment of the 13C-labeled cDCE and DCFE loaded Bio-trapsTM. The initial results have shown considerable losses of cDCE and the collection of PLFA biomarkers mostly associated with the Proteobacteria, consistent with potential heterotrophic anaerobic oxidation of cDCE. The first 13C-labeled cDCE and DCFE loaded Bio-trapsTM were deployed at the NY demonstration site in January 2007. The Bio-trapsTM will periodically be retrieved for analysis and replaced with new sets of Bio-trapsTM. Bio-trapsTM will be analyzed for residual 13C-labeled cDCE, DCFE and the fluorinated daughters of DCFE to quantify cDCE degradation rates and for analysis via gas chromatography/isotope ratio-mass spectrometry (GC/IR-MS) to assess the incorporation of 13C into PLFA biomarkers. Analysis of inorganic carbon and the 13C/12C isotopic signature thereof will help quantify the respiratory (versus biomass) fraction of cDCE oxidized anaerobically. Quantitative PCR will be used to enumerate Dehalococcoides bacteria and the functional Rdase genes involved in reductive dechlorination and multi-color fluorescence in-situ hybridization (“FISH”) will be used to conduct co-localization studies of Dehalococcoides and other bacteria and to enumerate other important groups of anaerobic bacteria including Deltaproteobacteria and Firmicutes. A battery of biogeochemical species will be analyzed to evaluate and correlate changes in biogeochemistry with the SIP and molecular microbiological data collected.

Reductive Dechlorination of Chlorinated Solvents with Electrodes as the Electron Donor

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The addition of various electron donors to groundwater to promote reductive dechlorination of chlorinated solvents has proven to be an effective bioremediation strategy in many instances. However, adding the appropriate levels of electron donor that will stimulate reductive dechlorination, without unduly stimulating other forms of anaerobic respiration, can be problematic. Furthermore, it can be difficult to add organic electron donors exactly to the required site for the most strategic application, especially when bioremediating source zone contamination. Previous studies in our laboratory have demonstrated that *Geobacter* species can electrically interact with electrodes. For example, *Geobacter sulfurreducens* and *Geobacter metallireducens* can generate electricity by oxidizing a variety of organic compounds to carbon dioxide with electron transfer to the anodes of microbial fuel cells. When electrodes are poised at negative potentials *Geobacter* species can accept electrons, reducing contaminants such as nitrate and uranium. Previous studies in the laboratory of Frank Loeffler have demonstrated that *Geobacter lovleyi* can reduce the chlorinated solvents PCE and TCE to DCE with acetate serving as the electron donor. To determine whether an electrode might also serve as an electron donor for reductive dechlorination, *G. lovleyi* was pregrown on the graphite electrode surfaces with acetate as the electron donor and PCE as the electron acceptor. Once dechlorination of PCE to DCE was observed the medium was replaced with a medium that did not contain acetate and the electrode was poised at –500 mV versus a silver/silver chloride reference electrode. PCE was rapidly dechlorinated to DCE with the electrode serving as the sole electron donor. Repeated additions of PCE continued to be rapidly removed. Control electrodes, poised at –500 mV, but without a *G. lovleyi* biofilm, did not dechlorinate PCE. As in previous studies in which an electrode served as an electron donor for the reduction of various other electron acceptors, hydrogen produced as the result of proton reduction at the electrode surface could be ruled out as an important electron donor for reductive dechlorination. This is the first demonstration that electrodes can serve as an electron donor for microbially catalyzed reductive dechlorination. The possibility that other types of dechlorinating microorganisms, such has *Dehalococcoides* species, might also accept electrons from electrodes is currently under investigation. Using electrodes to supply electrons to the subsurface for reductive dechlorination may prove to be a beneficial bioremediation approach, especially for the treatment of source zones.

Brownfields

Database Analysis of State Surface Soil Regulatory Guidance Values

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Removal of Chlorinated DNAPL below the Water Table Using Thermal Conduction Heating

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Database Analysis of State Surface Soil Regulatory Guidance Values

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A 2001 study of Cleveland, Ohio Brownfield surface soil contamination led to the examination of state regulatory guidance values for soils. Surface soils were of particular interest since these generally pose the greatest risk to human health at Brownfield sites. This investigation initially focused on heavy metals, common contaminants at Cleveland Brownfields. However, the discovery of significant variability in guidance values applied to Cd, Cr, Cu, Pb, Ni, and Zn led to questions regarding all remaining state-regulated components. The state-by-state inconsistencies encountered led to an ongoing program of research that is examining the origins, magnitudes and explanations for guidance value variability.

The results presented here are based on the compilation of a 18,776 state surface soil guidance value database assembled from regulatory guidance available in 2006 for organic, inorganic and element contaminants. All guidance values were captured electronically from internet sources using procedures designed to preserve the original content of each standard. The structure of each guidance value set was then standardized to a database-compatible format. Chemical Abstract Service (CAS) registry numbers were added to each record if they were not provided by the regulatory agency. Identification of all records by CAS number resolves the problem of component synonyms. For example, Ethyl Chloride (CAS 75-00-3) also commonly identified as Chloroethane can be identified by as many as 33 other generic and product-specific names, so searching for it by name would not yield comprehensive results. All value sets were then assembled into an ACCESS database that may be interrogated for data about the current state of regulatory guidance values.

Statistical analysis will be presented to characterize the nature and extent of variability in state surface soil guidance values. For example, toluene is currently one of the most commonly regulated components in the United States. Residential surface soil guidance values for toluene range from 0.7 to 16000 mg/kg. The organics, inorganics and elements most and least commonly regulated and the range of guidance values are discussed. Explanations for the orders-of-magnitude variability observed for selected components are explored, and opportunities to reduce the observed variability are identified.

Removal of Chlorinated DNAPL below the Water Table Using Thermal Conduction Heating

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An In-Situ Thermal Desorption ISTD-system was used to remediate three separate source zones at the Midler Avenue Redevelopment Brownfield Cleanup Program BCP-Project in Syracuse, NY. The three CVOC source zones covered a total area of 22,300 square ft, and averaged a depth of 20 ft below the ground surface. A volume of 16,200 cubic yards was treated by thermal conduction heating. Ninety percent of the treated sediments were below the water table, located ~ 3 ft below grade. A significant mass of DNAPL constituents, primarily PCE was present within the treatment volume. To address these source areas, a thermal treatment system was installed, consisting of 211 heater wells and 17 horizontal vapor collection wells. Monitoring included temperature profiling using 30 thermocouple wells. A power supply of 2,500 KVA was used to raise the subsurface temperatures to an average of 100°C in approximately 150 days. Effluent vapors were treated using thermal oxidation and acid gas scrubbing to meet the air emissions standards. Interim and final confirmatory soil sampling was performed to demonstrate compliance with the stringent remedial objectives set by New York State Department of Environmental Conservation NYSDEC). This paper presents the subsurface design, remediation mechanisms utilized, implementation sequence, and the operational adjustments made to ensure effective treatment. A related paper by Vinci et al. presents the site background, regulatory framework, and overall remedial results.

Chemical Oxidation

Control of MnO_2 Particles during Permanganate-ISCO through Use of Chemical Stabilization Aids

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Treatment of Chlorinated Ethanes using In Situ Chemical Oxidation and In Situ Chemical Reduction Technologies

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Phase III ISCO with Catalyzed Persulfate of Chloro Benzenes in Glacial Till and Bedrock, Corinna, ME

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Chemical Oxidation of Sulfa Drugs, Barbiturates and Chlorinated Solvents in Groundwater: A Bench Test Evaluation

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Site Remediation of Chlorinated Solvent Contaminated Groundwater via In Situ Application of Activated Persulfate

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Treatment of Non-Aqueous Phase Liquids (NAPLs) using Surfactant-Enhanced In-Situ Oxidation (S-ISCO®)

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Control of MnO_2 Particles during Permanganate-ISCO through Use of Chemical Stabilization Aids

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In-situ chemical oxidation (ISCO) has been widely applied to remediate groundwater, soil, and sediment contaminated by organic compounds, such as PCE, TCE, BTEX, etc. Among various chemical oxidants, permanganate is relatively stable than other oxidants, thus, it has been successfully delivered to contact with contaminants in various subsurface environments. Interesting phenomenon associated with permanganate-ISCO is the formation of MnO_2 particles which can precipitate and accumulate in porous media, resulting in a loss of permeability and hydraulic conductivity and a reduction of organic compound degradation efficiency. In order to improve mass transfer and to prevent permeability reduction, it is necessary to control the excessive accumulation of MnO_2 particles in porous media.

The goal of this research is to understand the genesis and control of MnO_2 particles and to identify the MnO_2 particle stabilization aids that will allow for their transport in groundwater through porous media under a variety of reaction conditions. Bench-scale experimental studies using 12mL reaction vials were conducted to examine reaction conditions that affect the formation of MnO_2 particles. These conditions include (1) particle concentration, (2) pH, (3) ionic variation, (4) solid content, (5) redox conditions, and (6) stabilization aid types and concentrations. These conditions are evaluated through spectrophotometric analyses at wavelengths 418nm and 525nm; particle filtration at various membrane sizes; and optical measurements for particle size and zeta potential. 1-D transport experiments in column (2.5cm ID × 60cm) are in progress to study particle transport in varied porous media- (1) sand only, (2) sand + organic matter, (3) sand + clay, (4) sand + iron oxides, and (5) sand + organic matter + clay + iron oxides. This presentation will highlight results of the effectiveness of four chemical stabilization aids to control MnO_2 particles under various reaction conditions and particle transport studies in column.

Treatment of Chlorinated Ethanes using In Situ Chemical Oxidation and In Situ Chemical Reduction Technologies

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In situ chemical oxidation (ISCO) and reduction (ISCR) technologies are being employed on the bench and field scale to remediate organic contaminants found in soils and sediments. Oxidation processes take an electron away from the target compound, transforming the target compound by making it more oxidized. Reduction technologies donate an electron to the target compound making it more reduced. Common ISCO technologies are based on the oxidants hydrogen peroxide (Fenton's reagent, catalyzed hydrogen peroxide or catalyzed H2O2 propagations), sodium perusulfate (activated with iron, iron-chelates, heat or alkalinity), sodium or potassium permanganate and ozone. With the exception of permanganate, these technologies involve the creation of radical species, such as the hydroxyl radical, superoxide, and the sulfate radical. Recent research has shown that reductions can take place in technologies based on hydrogen peroxide. Field data indicates that the same is true with alkaline activated persulfate. Common reduction technologies include zero valent iron (ZVI) and different sulfur based technologies such as dithionate. The effectiveness of ISCO technologies with chlorinated ethenes, and reduced compounds such as petroleum hydrocarbons, is well established. Similarly, significant research and cases studies support the effectiveness of ISCR technologies with treating chlorinated ethenes. However, less data exists to define which technologies can effectively degraded chlorinated methanes and chlorinated ethanes. These types of compounds are not as readily degradable as they lack the double bond of chlorinated ethenes. A series of bench and field scale data recently conducted has illustrated the successful treatment of 1,1,1-trichloroethane (TCA) by catalyzed hydrogen peroxide and alkaline persulfate, of 1,2-dichloroethane by catalyzed hydrogen peroxide and of carbon tetrachloride by catalyzed hydrogen peroxide, alkaline activated persulfate and ZVI.

Phase III ISCO with Catalyzed Persulfate of Chloro Benzenes in Glacial Till and Bedrock, Corinna, ME

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Pilot and full scale ISCO tests were carried out at the former Eastland Woolen Mill, Corinna, ME in prior years as part of an overall program to reduce the residual contamination left after a large excavation and thermal treatment project was completed. Approximately 100,000 tons of soil were excavated and treated thermally to reduce the average concentration of tri-, di, and chlorobenzene to below 15 mg/kg prior to backfilling. Residual contamination existed in untreated soils on site adjacent to former USTs and a loading dock as well as the upper burden soils between the excavated materials and a state highway. A portion of the upper burden was treated in Phase II pilot and full scale tests after determining the most effective oxidant to use at this site. The residual contamination at the USTs and former loading dock were treated in a Phase I ISCO project. Residual contamination in the lower till burden and shallow weathered bedrock was subsequently addressed with catalyzed persulfate injection in Phase III. A unique aspect of this project was the bath tub shape which lies between the subsurface below an existing road way down to the upper bedrock and the face of the former excavation, now backfilled with the thermally treated soils. The lower soil and upper bedrock first had to be dewatered to allow the chemicals to be drawn into and flooding the shallow bedrock prior to completing the ISCO in the soils above. The results of this Phase III ISCO project are described in this presentation to potentially complete the ISCO remediation of chlorobenzenes at this site. Additional aspects of this ISCO project discuss the presence of chloromethanes and, as expected, acetone, etc. oxidation byproducts, and the determination of residual contaminant concentrations and/or rebound. Further ISCO work extending the Phase II and III projects is currently being considered and a fourth phase may be investigated if funding becomes available for the untreated, contaminated bedrock zones below.

Chemical Oxidation of Sulfa Drugs, Barbiturates and Chlorinated Solvents in Groundwater: A Bench Test Evaluation

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The Kærgård Plantage pharmaceutical waste disposal site represents one of the most complex remediation challenges in Denmark. The site groundwater is impacted with high concentrations of relatively rare contaminants, including sulfonamides, barbiturates, and aniline, as well as chlorinated solvents and fuel hydrocarbons. Fenton’s reagent (hydrogen peroxide + Fe2+), advanced oxidation processes (AOP [hydrogen peroxide + ozone]), and permanganate are three chemical oxidation technologies that may offer promise – to varying degrees - for remediation at Kærgård. Published literature suggests that sulfonamides and barbiturates can be at least partially treated by Fenton’s reagent, AOP, and permanganate; however, there is no published literature regarding the performance of these technologies for several of the primary sulfa drugs and barbiturates at the site. Bench tests were performed using soil and/or groundwater collected from the site to evaluate the treatment performance of Fenton’s reagent, AOP, and permanganate. Treatment was assessed through monitoring a variety of parameters, including changes in contaminant concentrations, detection of degradation intermediates, and groundwater toxicity (Microtox® bioassay) consequent to treatment. A subset of tests evaluated treatment and dissolution of chlorinated solvent dense-nonaqueous phase liquids (DNAPLs) in core material from the Site. The tests demonstrated that all the primary organic contaminants in Kærgård groundwater can be effectively treated by Fenton’s reagent and AOP. A 10-fold and 3-fold reduction in groundwater toxicity was achieved by the permanganate and Fenton’s reagent treatments, respectively. Permanganate effectively treated sulfonamides and aniline as well, but achieved only partial degradation of most barbiturates. Both Fenton’s reagent and permanganate effectively accelerated dissolution and treatment of DNAPLs. Collectively, the results of these tests demonstrate that certain chemical oxidation technologies are effective for treating the unique mixture of sulfa drugs, barbiturates and chlorinated solvents at the site.

Site Remediation of Chlorinated Solvent Contaminated Groundwater via In Situ Application of Activated Persulfate

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Activated Persulfate was utilized for the in situ chemical oxidation (ISCO) of a chlorinated solvent impacted site. The ISCO application reduced groundwater concentrations of the contaminants. Activated persulfate is a strong chemical oxidant that is capable of destroying a wide range of chemical contaminants, including chlorinated solvents. For this application, alkaline activation of the persulfate was accomplished through co-injection of sodium hydroxide. The site is a former industrial property located in the South San Francisco Bay area. Contaminants migrated from the primary site to an adjacent property that is under-going a property transaction. As a result, a rapid approach to site remediation is desired. Volatile Organic Compound (VOC) impacts were observed in groundwater from depths of 15 to 28 feet below ground surface (ft bgs). The site lithology at these depths is predominantly Bay Mud – silty clay formation. The remediation is driven by vinyl chloride. In late 2006, solutions of persulfate and sodium hydroxide were injected via hydraulic fracturing in 91 direct-push wells on approximately 15-foot centers due to the tight clay formation. A total of 150,000 lbs of persulfate were injected along with enough sodium hydroxide to reach a target pH of 11. Continuous electrical conductivity profile measurements were utilized to demonstrate the delivery of persulfate to the target zones. Post-injection sampling indicates a significant reduction in VOCs across the site. A second round of activated persulfate injection is planned for early 2007.

Treatment of Non-Aqueous Phase Liquids (NAPLs) using Surfactant-Enhanced In-Situ Oxidation (S-ISCO®)

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Traditional ISCO methods have had limited success in degrading non-aqueous phase liquids (NAPLs) because of mass transfer limitations controlling the rate of dissolution of NAPL constituents into groundwater. In Situ Chemical Oxidation (ISCO) reactions predominantly take place in the aqueous phase in the subsurface. Treatability studies and field verification pilot-studies have been conducted to evaluate the effectiveness of a new type of Coelution Technology®, Surfactant-Enhanced In-Situ Chemical Oxidation (S-ISCO®), in reducing the amount of non-aqueous phase liquids (NAPLs) in soils. The S-ISCO® technology, patent-pending by VeruTEK Technologies, Inc., uses biodegradable, food-grade cosolvents and surfactants (VeruSOL®) (for example, coconut oil, castor oil and citrus extracts) to solubilize immiscible phase organic compounds into groundwater. Application of S-ISCO with VeruSOL® destroys contaminants in-place using traditional ISCO processes, particularly activated persulfate. S-ISCO® involves coeluting both the cosolvent-surfactant mixture with the oxidant enabling simultaneous dissolution and oxidation. Selection of the specific VeruSOL® mixture is dependent on the nature of the NAPL components, particularly, the mol fractions and octanol-water partition coefficients (K_{ow}) of the individual organic compounds. The coelution involves the controlling the rate of NAPL compound dissolution and the oxidation reaction rates. Laboratory treatability studies demonstrate that the solubilization reaction by surfactant and surfactant/cosolvent mixtures resulted in significant increases in dissolved phased COCs without mobilizing NAPL. Winsor Type I solubilization was observed; Winsor Type II and Winsor Type III behaviors were not observed. Laboratory and field pilot test results for both chlorinated solvent mixtures of DNAPLs and Former Manufactured Gas Plant (DNAPLs) demonstrate that the dissolution and oxidation reactions can be beneficially controlled.

Coated and Uncoated Microbubble Ozone Remediation Projects

Sponsored by Kerfoot Technologies, Inc.

Managing Uncertainty: Perozone Sparging Under a Fixed-Price Contract
Christopher J. Watt, LACO Associates-Consulting Engineers, CA
Franziska von Herrath, LACO Associates-Consulting Engineers, CA

In-Situ Remediation of Hydrocarbons and MTBE in a Low-Yielding Aquifer - A Practical Approach
Daniel P. Cusick, Conestoga-Rovers & Associates, Inc., Pittsburg, PA

Source Area Control Using Peroxzide-Coated Ozone Microbubbles - A Key Component to Whole Site Cleanup
Matthew Burns, WSP Environmental Strategies LLC, Boxborough, MA
Stephen Koenigsberg, WSP Environmental Strategies LLC, Irvine, CA

Source Reduction at a Former Wood-Treating Site by Coated Microbubble Injection
J. Geoffrey Gay, MACTEC Engineering and Consulting, Inc., Kennesaw, GA
Andrew Brolowski, Kerfoot Technologies, Inc., Mashpee, MA

Effective Removal of Recalcitrant Contaminants Using Peroxide-Coated Ozone Microbubbles
William B. Kerfoot, Kerfoot Technologies, Inc., Mashpee, MA
A.M. Scheffer, Verhoeve Milieu bv, Hummelo, The Netherlands
Edward van de Ven, Verhoeve Milieu bv, Dordrecht, The Netherlands

Managing Uncertainty: Perozone Sparging Under a Fixed-Price Contract

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Characterization of hazardous material releases has historically been performed with the purpose of developing a conceptual model of the hydrogeologic, chemical, and physical parameters of a site area. More recently, an approach is being used which incorporates an assessment of parameters which affect remediation design (EPA Triad). In general, for remediation designs to be implemented successfully they must account for the inherent uncertainty the site conceptual model. It is our claim that the development and commitment to a fixed-price performance-based contract requires tools to manage uncertainty: these tools are pilot studies, flexible design, and process optimization.

A pilot study can be used evaluate the performance of several remedial methodologies which can be used to develop a remediation conceptual model. Flexibility in system design allows for multiple remediation technologies to be exchanged in order to maintain cost effective mass removal rates as removal rates decrease over time. When combined with acquisition of real-time performance data acquisition to optimize system performance, the uncertainty around maintaining cost effective operations is managed. This opens the opportunity for a remediation practitioner to enter into a fixed-price performance-based contract with a greater degree of certainty to achieve project results on time and within budget.

We will discuss the advantages and risks associated with fixed-price performance-based contracts and explain the application of tools to manage uncertainty as part of several case studies.

In-Situ Remediation of Hydrocarbons and MTBE in a Low-Yielding Aquifer - A Practical Approach

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A subsurface release of unleaded gasoline was discovered at an operating retail gasoline station in southwestern Pennsylvania during due diligence activities conducted in September 2003. Site characterization activities concluded that dissolved phase unleaded gasoline constituents (specifically benzene, ethylbenzene, naphthalene, and methyl tertiary-butyl ether [MTBE]) were present at concentrations above the Pennsylvania Statewide Health Standards (SHS) Medium-Specific Concentrations (MSC) in the uppermost water-bearing unit underlying the property. Based on pilot testing results and aquifer characterization properties, traditional remediation techniques (i.e., vacuum extraction, pump & treat, etc.) with ex-situ treatment were determined not to be feasible for this low-yielding unconsolidated aquifer. Supporting evidence of biodegradation was present; however, anoxic conditions (i.e., oxygen depleted) were present in the aquifer, and the availability of electron acceptors was limited in areas of constituent impact. Ozone sparging with enhanced bioremediation was determined to be a practical, cost-effective remedial technique for the site conditions. The ozone sparging treatment process consists of a combination of chemical oxidation destruction (primary remedial mechanism), followed by enhanced natural bioremediation (secondary remedial mechanism). A Kerfoot Technologies, Inc. C-Sparger® unit was installed with ozone distributed through seven spargepoints that began operations in July 2005. Reductions in benzene concentrations from a maximum of 4,400 micrograms per liter (μg/L) to less than the SHS MSC (5 μg/L) have been achieved for groundwater within approximately 19 months. MTBE (maximum 2,600 μg/L), ethylbenzene (maximum 3,000 μg/L), and naphthalene (maximum 840 μg/L) have all been reduced to concentrations below the SHS MSC or laboratory detection limits within approximately 12 months of system operation. The project is approaching closure through a risk-based approach with an active remediation life cycle of only approximately two years with minimal operations and maintenance.

Securing MNA with Perozone®-Mediated Source Control Combined with Molecular Diagnostics

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A historic release of coolant containing chlorinated solvent has lead to a 1200-foot long dissolved volatile organic compound (VOC) plume at central Georgia manufacturing facility. Site characterization showed a continuing vadose zone source, elevated dissolved VOC concentrations in the source area (50 mg/l), temporally decreasing VOC concentrations, and evidence of chlororespiration. Application of molecular biological tools (MBTs), primarily the use of quantitative polymerase chain reaction (qPCR) taxonomic and functional gene analysis conclusively demonstrated that Dehalococcoides spp (DHC) and key dechlorinating enzymes were present at the site. This provided evidence to the fact that the plume was stable as a result of natural attenuation.

To minimize the remedial timeframe and gain regulatory approval for monitored natural attenuation (MNA) source area soils and source area groundwater containing VOC concentrations greater than 0.5 mg/l were targeted for active remediation. Source area soil excavation and groundwater chemical oxidation were the technologies selected for these areas of concern. Perozone® was selected as the chemical oxidant because it does not leave a footprint of oxidized inorganic species that could inhibit chlororespiration such as manganese. Also, site conditions provided advantages regarding the greater radius of influence of Perozone® as compared to aqueous-phase oxidants.

The integrated remediation approach, defined as source treatment plus MNA, was approved by the Georgia Environmental Protection Division (EPD). This integrated remediation approach holds in abeyance the additional application of downgradient in-situ bioremediation operations. The cost of implementing such additional steps is estimated to be anywhere from $700,000 and $1,700,000 depending on the final configuration of in-situ barriers and arrays, should those steps ever be necessary.

Source Reduction at a Former Wood-Treating Site by Coated Microbubble Injection

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This former wood treating RCRA site has been involved with an extensive source control/remediation pump and treat approach that involves a system of shallow and deep slurry walls, groundwater collection trenches, and numerous recovery wells. Raw wood at the site was treated with a combination of creosote, pentachlorophenol (PCP) and other preserving chemicals. In an effort to reduce long-term pumping and discharge costs, a decision was made to evaluate in-situ oxidation of source areas with an ozone/peroxide (Perozone®). The site is located in the southeast region just south of the Fall Line which separates the Piedmont from the Atlantic Coastal Plane physiographic provinces with soils consisting of alluvium and sand deposits with isolated clay lenses. The targeted treatment zone was comprised of a 45-foot sand formation underlying a partially confining unit consisting of soft brown silty clay with peat.

Impacted soil and groundwater in source areas at the site exhibit concentrations ranging up to 1,000 mg/kg total polycyclic aromatic hydrocarbons (PAHs) and 14 mg/L, respectively. A bench-scale study was initially conducted to evaluate the ability of the oxidants to treat the target contaminants from a source area. The study found that the most effective mass removal occurred with the coupled addition of ozone and hydrogen peroxide.

Hydrogen peroxide (17.5%) and ozone (2,500 ppmv) were injected over a two month period into four multi-level spargepoints at an approximate 3.3:1 molar ratio (H2O2:O3). Seven monitoring wells were located at varying offset radial distances from spargepoints ranging from 11 to 30 feet. Four groundwater monitoring events were conducted to evaluate the redox condition of the groundwater and PAH degradation.

The aquifer responded efficiently to the injected oxidant as evidenced in the redox probe data and rapid contaminant reduction. Dissolved PAH removal greater than 97 percent occurred in six of the seven monitoring points with half lives ranging from 7 - 17 days.

Effective Removal of Recalcitrant Contaminants Using Peroxide-Coated Ozone Microbubbles

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Chloroalkanes like dichloroethane (DCA) and chloroform (CF) and also pesticides are normally considered as reluctant to recalcitrant contaminants for treatment by ISCO. This presentation shows two case studies about the effective treatment with the Perozone®-system of the apparently recalcitrant contaminants.

The chloroalkanes (mainly chloromethanes and chloroethanes) were present on a industrial site together with chloroethenes, xylenes and monochlorobenzene. Prior to the application of Perozone®, excavation and P&T were used for removal of the contaminants. After about six years of P&T the remediation stagnated in 2001 probably due to sorbed fractions or through slow mass delivery from a humic intervening layer. After some investigations Perozone® was selected to treat the remaining contamination and was started in September 2005. Upon start DCA and CF were found in maximum concentrations of 1,900 and 2,200 µg/l, respectively. The groundwater concentrations are lowered to about 150 µg/l and 20 µg/l after 9 months of treatment, i.e. efficiencies of respectively 92 and 99%.

Perozone® is also used on a other industrial site where MCPP, a organic herbicide (common name: Mecoprop) was found in groundwater. A bench-scale test showed that MCPP was treated succesfully using a combination of ozone and hydrogen peroxide. A 9-week pilot test was done to study the possibilities of Perozone® for in-situ treatment of MCPP in groundwater. The pilot test was set up with a 3-well system in triangular setup. As common for pesticides the groundwater concentrations were low, 55 µg/l of MCPP at the start of the pilot test. After startup of the pilot test mobilization was found and the concentrations raised to a maximum of 170 µg/l. In the most monitoring wells within the “injection triangular” the concentrations decreased to below 0.5 µg/l (the regulatory MCL) and resulted in a overall removal of 87% in 9 weeks of treatment, representing quick and effective removal of an uncommon organic pesticide.

Combining Chemical and Biological Technologies for Soil and Groundwater Remediation

Sponsored by Regenesis

Integration Chemical and Biological Technologies for Remediation of Contaminated Soil and Groundwater
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Combined Physical and Biological Processes for Remediation of Contaminated Sites
Maureen Dooley, Regenesis, Wakefield, MA
Bob Kelley, Regenesis, San Clemente, CA

Former Manufactured Gas Plant (MGP) Remediation using Surfactant-Enhanced In-Situ Chemical Oxidation (S-ISCO®)
John Collins, VeruTEK Technologies, Inc., Glastonbury, CT
George E. Hoag, VeruTEK Technologies, Inc., Glastonbury, CT

Evaluation of In-Situ Biostimulation Effects Related to Sodium Persulfate Injections
Edward Sullivan, The Whitman Companies, Inc., East Brunswick, NJ
Eric C. Hince, Geovation Consultants, Inc., Florida, NY,
Greg Davis, Microbial Insights, Inc., Rockford, TN
Dora Ogles, Microbial Insights, Inc., Rockford, TN
Kerry Sublette, University of Tulsa, Tulsa, OK
Jennifer Busch-Harris, University of Tulsa, Tulsa, OK
Eleanor Jennings, University of Tulsa, Tulsa, OK

Bioremediation of TCE and TCA using SDC-9TM after Sodium Permanganate Treatment
Raymond J. Cadorette, Shaw Environmental, Inc., Hopkinton, MA
Lawrence Nesbitt, Shaw Environmental, Inc., Hopkinton, MA
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Integration Chemical and Biological Technologies for Remediation of Contaminated Soil and Groundwater

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While environmental remediation literature has contained references to 'treatment trains' for decades, the last 3-5 years have seen a significant increase in actual field deployments to address contaminated groundwater. ISCO and enhanced bioremediation are promising technologies for the treatment of source areas. Several field demonstrations were recently completed to demonstrate the efficacy of coupling in situ chemical oxidation (ISCO) to rapidly remove accessible mass with in situ enhanced bioremediation to degrade and contain the remaining mass.

Two case studies will be discussed in detail. The first was a former retail gasoline station in which chemical oxidation (RegenOx™) was followed sequentially with enhanced bioremediation (ORC-Advanced®) were used to remediate BTEX contamination in and round a excavation resulting from a tank removal. The initial concentrations were in the 50ppm range, and treatment goals were achieved within 2 months. Mass flux calculations based on groundwater measurement indicate significant reduction in contaminant mass. In a second field demonstration, similar BTEX removal (96%) was seen with a simultaneous application of RegenOx™ and ORC Advanced®. Treatment goals were reached in 4 months

This presentation will provide an overview of the results from these field demonstrations, draw conclusions for the applicability of the technology for groundwater remediation and provide recommendations for a best-practice approach for future work with the combined chemical oxidation and enhanced bioremediation technologies.

Combined Physical and Biological Processes for Remediation of Contaminated Sites

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Distribution of electron donor substrates is a key factor in the successful *in situ* reductive dechlorination of contaminants in aquifers. Transport in the subsurface is governed by hydrogeologic characteristics of the aquifer under treatment and, equally important, by the characteristics of the electron donor substrate itself.

As electron donor technology has evolved away from simple sugar substrates that rapidly ferment and require continuous application, complex electron donor substrates have emerged allowing for a range of hydrogen release rates from a single application. Many of these products contain slower releasing components of very low solubility. The aqueous solubility and oil/water partitioning of substrates is governed by the specific hydrophile/lipophile balance index (HLB) of the compound considered.

The HLB of the electron donor substrate governs its ability to form emulsions when preparing the material for subsurface application, as well as the requirement for chemical emulsifiers to aid in stabilization of the product. Additionally, and perhaps most importantly, the HLB indicates the propensity for the substrate to spontaneously form micelles (sub-micron size colloids) that advance the forward movement of the substrate through the contaminated aquifer.

This paper reviews the impact of substrate HLB on subsurface adhesion to aquifer matrices, micro-emulsion formation, and micro-emulsion/micelle movement in the subsurface. Data is presented from laboratory studies involving aquifer simulation columns (20' in length) which demonstrate the positive impact of spontaneous micelle formation on the advancement of electron donors in aquifer materials. Data is also presented from full-scale field applications of an electron donor substrate designed to cost effectively achieve broad aquifer distribution through micellar transport.

Data is presented from full-scale projects in the field where HRC Advanced has been applied for the treatment of the DNAPLcomtaminant showing wide distribution compared to typical controlled release electron donors and excellent biostimulation. Results from a variety of geologic conditions where chlorinated ethenes have been treated indicate performance. Cost data is presented and compared with the use of other commercially available controlled release electron donors indicating the wide cost advantage of employing this state-of-the-art product.

Former Manufactured Gas Plant (MGP) Remediation using Surfactant-Enhanced In-Situ Chemical Oxidation (S-ISCO®)

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A treatability study and a field verification pilot study were conducted to test the efficiency of a new type of Coelution Technology®, Surfactant-Enhanced In-Situ Chemical Oxidation (S-ISCO®), in reducing the amount of source coal tar DNAPL in soils and reducing the flux of groundwater constituents associated with a former Manufactured Gas Plant Site (MGP).

Both laboratory column studies and a large field pilot test confirm that the S-ISCO® process effectively degrades MGP tar-saturated soils without any significant increases of groundwater contaminant flux. Persulfate-Fe-EDTA mixtures persisted in solution and effectively destroyed solubilized COCs in laboratory column tests. Batch tests revealed that VeruSOL®-3, a proprietary cosolvent/surfactant mixture of FDA approved chemicals, was able to resist activated persulfate oxidation and maintain low IFT conditions while maintaining the ability to dissolve COC from coal tar saturated soils. The Pilot Test consisted of four injection phases and three post-injection monitoring Phases. A total of 72,674 kg persulfate, 475 kg Fe(II)-EDTA, and 3,314 kg of VeruSOL®-3) were injected during the Pilot Test. Both the field and laboratory treatability studies found that VeruSOL®-3 treatment was able to solubilize both high and low molecular weight PAHs. Soils mass destruction analysis from more than 50 soil sampling locations collected before and after the S-ISCO® Pilot Test indicates that at least 954 kg of polycyclic aromatic hydrocarbons (PAHs) and at least 3,636 kg of medium weight petroleum hydrocarbons (MPH) were removed in the Pilot Test area. Thirty days after the termination of S-ISCO® injection and 75 feet downgradient of injection wells, the mass flux was less than the pre-Pilot Test mass flux for PAH and MPH compounds and slightly greater for BTEX compounds.

Evaluation of In-Situ Biostimulation Effects Related to Sodium Persulfate Injections

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In recent years there has been increased interest in combined chemical oxidation and bioremediation approaches to site remediation. At a site contaminated with 1,2-dichlorobenzene DCB), a chemical oxidation remedy was implemented in the fall of 2006 using sodium persulfate persulfate). Geochemical parameter and DAPI cell count data were collected prior to the initial persulfate injection and approximately one month post-injection. DAPI cell counts one month after the first injection indicated microbial counts had not decreased, which was contrary to expectations. Post-injection cell counts ranged from 3 x 105 to over 2.5 x 107 cells/ml. The highest cell counts were observed in the most highly contaminated source area well. This unexpected trend in cell counts prompted the additional investigations outlined herein.

Dissolution of injected sodium persulfate Na2S2O8-results in the formation of sulfate ions SO4--upon reaction. Additional oxidation and decomposition reactions could result in the formation of bioavailable ferric iron and oxygen. All of the above could theoretically be used by native microbes as electron acceptors.

Subsequently, DGGE and mFISH data was collected to identify and quantify the important microbial consortia that had developed in response to the persulfate injections. Prior to the 2nd injection planned for late February-and at various post-injection intervals, additional data will be collected including an expanded list of geochemical parameters, DAPI cell counts and mFISH. In addition, Bio-trap^{TM} samplers supplied by Microbial Insights, Inc., will be installed in the source area well. The Bio-trap^{TM} samplers will contain Bio-sep^{TM} beads loaded with 13C labeled chlorobenzene and DCFB a fluorinated analog of DCB). Stable carbon isotope profiles 13C/12C-of the phospholipid fatty acid PLFA-biomarkers from the microbial biomass will be measured to quantify approximate DCB aerobic/anaerobic oxidation biodegradation rates. DCFB will be used to evaluate the reductive dechlorination pathway. The combined geochemical and microbiological data will be used to compare 1-the amount of DCB mass reduction achieved by the direct chemical oxidation and secondary biodegradation and 2-the relative rates of anaerobic oxidation and reductive dechlorination to determine which biological process is dominant.

Bioremediation of TCE and TCA using SDC-9TM after Sodium Permanganate Treatment

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Shaw has conducted a highly successful sodium permanganate treatment program at a manufacturing site in New England. The permanganate treatment program involved the injection of over 177,000 gallons of a 20% sodium permanganate solution into the shallow overburden, deep overburden and bedrock aquifers at the site over four years. The sodium permanganate applications have resulted in significant reductions in TCE concentrations across the site.

Subsequent to the sodium permanganate treatment, an enhanced bioaugmentation treatment program was conducted using sodium lactate, Shaw's SDC-9TM culture and a TCA reducing bacteria also developed by Shaw. The bioremediation program targeted TCE contamination adjacent to an on-site stream where permanganate injection was not feasible, and residual TCA impacts in the deep overburden that are not amenable to treatment via permanganate. This presentation will discuss the additional steps needed to successfully complete an enhanced bioaugmentation program following permanganate treatment and will provide results of the initial application. In particular, the presentation will focus on the technical aspects of implementing bioaugmentation in an area previously targeted with permanganate, such as the quenching of residual permanganate concentrations with lactate, the potential for solubilizing manganese under reducing conditions, and the ability to achieve complete dechlorination of TCE and TCA via bioaugmentation.

Environmental Fate

Characteristics of a Plume of Extremely High pH Groundwater

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Transport of Testosterone, Androstenedione and Estrogen in the Vadose Zone Underlying a Dairy Waste Lagoon

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Characteristics of a Plume of Extremely High pH Groundwater

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A historic release of a sodium hydroxide solution occurred at an industrial site in the New England area. The resultant pH of the groundwater was found to be as high as 14 standard units (s.u.), with a plume of groundwater with a pH greater than 10 s.u. extending from the source area to a wetland discharge point approximately 500 feet away. The source of high pH has remained in place within soils and shallow bedrock for over 20 years – its persistence due in part to density and viscosity differences that cause the sodium hydroxide to act as a dense aqueous phase liquid (DAPL). This paper will discuss the hydrogeologic and geochemical findings resulting from the extreme pH conditions.

The transport and fate of the DAPL is governed by both fluid properties and the site hydrogeology. Density and viscosity contrasts between ambient groundwater and DAPL likely inhibit mixing of DAPL and ambient groundwater in a manner similar to that of a salt water / fresh water interface in costal aquifers. The bulk of the DAPL occurs in a glacial till of low hydraulic conductivity, further contributing to the DAPL's persistence in the subsurface.
The chemistry of the high pH groundwater is characterized by strong correlations between various metals (some anthropogenic and others naturally-occurring) concentrations and pH, as well as a relative absence in biodegradation of organic contaminants. Possible geochemical reactions/mechanisms responsible for the elevated metals concentrations will be discussed.

Transport of Testosterone, Androstenedione and Estrogen in the Vadose Zone Underlying a Dairy Waste Lagoon

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Testosterone, androstenedione and estrogen are present in animal manures and are constantly excreted into the environment. Previous reports have indicated the inter-convertible estrogens, estradiol and estrone, are immobile in soil while, of the two androgens, - testosterone is mobile and reaches the groundwater and androstenedione is partially mobile. To study the transport of these compounds in the vadose over long time exposure (30 yr), we studied a dairy barn with 50 dairy cattle. This was calculated as a load of 36 kg estrogens and 7 kg androgens. All of the effluent was released into 15 x 10 m lagoon, which drained toward a dry creek, creating a constant overflow of about 300 meters long and 1-4 meters wide. The lithology under the waste lagoon consists of 8 m of clay layer on top of sand and calcareous formation and the water table was at a depth of 47 m. Soil samples (5 g) were extracted with organic solvents and analyzed using radioimmunoassay or Elisa. Groundwater samples (500 ml; after pumping four well volumes) were extracted on C-18 solid extract columns and similarly analyzed. It was found that testosterone and estrogen were present in the clay zone at concentrations of greater than 500 ng/kg) and <100 ng/kg in the sandy zone while androstenedione <100 ng/kg was present only in the clay zone. Testosterone and estrogen, but not androstenedione, were present in the groundwater (3 ng/l). The level of the steroids in control soils and groundwater taken 1 km upstream from the site were below the limit of detection. We conclude that unlike previous reported, estrogen can be transported in the vadose zone and can reach the groundwater after long time exposure to dairy barn effluents. The concentrations of estrogen observed were above the amount known to affect soil bacteria and aquatic fauna.

Environmental Forensics

Identification of Natural Gas Sources Using Geochemical Forensic Tools

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PCB Source and Dechlorination Fingerprinting

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Forensic Analysis and PCB Fingerprinting in Sediments Using Congener Data and Multiple Statistical Evaluation Methods

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Fact or Fiction: The Source of Perchloroethylene Contamination in Groundwater is a Manufacturing Impurity in Chlorinated Solvents

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Thoughts on Manufacturing Changes in the US Petroleum Industry: Implications for Age-dating, Calculating Weathering Indices and Hydrocarbon Fingerprinting

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Age-Dating Diesel Fuel: A Case Study Averse to the Christensen and Larsen Method

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Identification of Natural Gas Sources Using Geochemical Forensic Tools

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Processed natural gas (storage gas) from a number of states has been transported to the permitted storage facility and injected in an underground formation 900 ft below ground surface. The formation is surrounded by geologic divides initially thought to be preventing gas from escaping the storage formation (storage field) boundaries. Recently, pressure monitoring in observation wells around the storage field indicated that the southern divide is leaking storage gas. In addition, property owners south of the field have begun producing natural gas and claim that the natural gas they are extracting is native gas from the area and not storage gas escaping the field. The objective of this work was to apply knowledge of oil and natural gas geochemistry and geochemical fingerprinting techniques to determine if storage gas is escaping the southern divide; to determine the extent of storage gas migration beyond the divide; and to determine if the other companies are extracting storage or native gas. A field investigation was conducted where gas samples were collected from the storage field and from observation wells located outside (south of) the field. Samples were analyzed for gas hydrocarbons and nonhydrocarbons, and stable isotope compositions (carbon for methane and ethane). Using double ratio analysis (hydrocarbons represented by C1/C2+), tracers (helium), and carbon isotope ratio of ethane, the different fingerprints of native and storage gases were identified. The analysis determined that gas in the observation wells across the southern divide is storage gas indicating that the divide is in fact leaking. This work showed that storage gas is migrating beyond the storage field boundary and that property owners adjacent to the field are extracting storage gas escaping the field.

PCB Source and Dechlorination Fingerprinting

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Detailed chemical forensic analyses were conducted to characterize source and chemical alteration congener compositions in lake sediments. At the Lake Hartwell Superfund Site (Pickens County, SC), surface sediments resembled a 50/50 mixture of Aroclors 1248 and 1254. Congeners became increasingly dominated by lower chlorinated congeners with sediment depth and corresponding age, resulting in a relative accumulation of ortho chlorines and loss of meta and para chlorines; ortho chlorines were highly conserved.

This study presents a quantitative approach used to measure dechlorination processes in situ. The conservation of ortho chlorines with depth allowed the use of ortho chlorines to serve as a unique fingerprint of the original source material and dechlorination byproducts. Toxic equivalencies were calculated using Toxic Equivalency Factors listed by the World Health Organization (WHO). WHO congeners were preferentially removed under natural conditions resulting in an apparent reduction in toxicity relative to total PCB mass.

Forensic Analysis and PCB Fingerprinting in Sediments Using Congener Data and Multiple Statistical Evaluation Methods

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A study was performed to determine the PCB sources and fate processes affecting congener compositions in an estuarine contaminated sediment site in New Jersey. PCB contamination of sediments can originate from different sources and Aroclor mixtures, and fate processes can modify congener signatures. Such signatures can help identify Aroclor mixtures, their sources and relevant fate processes. Multivariate statistical evaluation of PCB congener patterns in sediment samples, compared to known signatures, allows identification of Aroclor fingerprints, chemical alteration processes, spatial distribution of Aroclors and alteration patterns, and a refined understanding of processes responsible for transporting solids/contaminants across the site. Multivariate analysis depends on incomplete mixing within the sediment environment, preserving various degrees of statistically detectable 'signals' of the original mixtures (Aroclors) in each sample. Three levels of statistical analysis were used to identify Aroclor fingerprints, and formulate hypotheses about source identities and fate processes. The congener composition of individual samples, the spatial pattern of sample compositions, and the correlation patterns of congeners indicated the presence of more than one distinctive pattern at the site. Principal component analysis (PCA) confirmed this interpretation, and polytopic vector analysis (PVA) was performed to determine their compositions and relative importance. PVA "unmixes" congener distributions within samples and predicts congener distributions of candidate source fingerprints. PVA is based on traditional PCA and subsequent rotation of principal component axes until all PC compositions and their sample loadings are positive. Results point to both on-site and potential off-site sources of PCB impacts. PCB contamination is dominated by Aroclor 1248, and congener patterns in buried sediments have been altered by dechlorination processes over time. Results also allowed for evaluation of Aroclor concentration gradients across the system, and clarified the major sediment transport processes operative at the site.

Fact or Fiction: The Source of Perchloroethylene Contamination in Groundwater is a Manufacturing Impurity in Chlorinated Solvents

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Manufacturing impurities in chlorinated solvents have been considered to be sources of contamination in groundwater. Chlorinated solvents are manufactured in a variety of grades; the technical grade is used at many industrial and manufacturing facilities. Compounds present as manufacturing impurities in technical grade chlorinated solvents vary, and their quantity is extremely small or not measurable, because chlorinated solvents historically have been manufactured to a high degree of purity. The purity of currently manufactured TCE ranges from 99.9% for reagent grade to 98.0% for the technical grade. Impurities in technical grade 1,2-dichloroethane, also known as ethylene dichloride (EDC), manufactured within the last 10 years with purities of 99.9991% and 99.9955% included PCE between about 0.0001% and 0.0006%, respectively.

In a number of litigation cases where TCE released from a vapor degreaser is the major contaminant in groundwater, there is an accompanying minor concentration of PCE. The assumption made in these cases is that the PCE impurity in technical grades of TCE is the source of the PCE in groundwater. This assumption is based on the release of these two compounds together from a distillation bottom residue where PCE is concentrated, relative to the TCE, because of its much higher boiling point at atmospheric pressure.
There is no peer reviewed literature that can be cited to prove that PCE is a significant impurity in either the distillation bottoms produced from a vapor degreaser or technical grade TCE. PCE, if present as a manufacturing impurity, is present in such small amounts that significant concentrations would not be generated in groundwater. When PCE and TCE are present together in groundwater, the source of the PCE is likely not an impurity in the manufactured TCE.

Thoughts on Manufacturing Changes in the US Petroleum Industry: Implications for Age-dating, Calculating Weathering Indices and Hydrocarbon Fingerprinting

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Techniques for the aging of petroleum contamination in environmental matrices are undergoing major revision in the environmental forensic community at the present time. Techniques that were reliable in the past to age-date gasoline may not be that reliable in the reality of today's modern refinery practices. Age-dating of distillate fuels is undergoing a major debate in the forensics community at the present time. Forces working to expand the use of hydrocarbon degradation models from soils to other matrices may have pushed the most widely-used weathering approach too far, creating a two-sided debate which has not been settled in the peer reviewed literature as of now. Problems with numerous approaches to age-date gasoline and distillate fuel contamination will be outlined, and discussed. Both the positive and negative aspects of numerous common approaches will be discussed. Recommendations for cautiously age-dating petroleum in the environment will be presented.

Age-Dating Diesel Fuel: A Case Study Averse to the Christensen and Larsen Method

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Age dating petroleum products is a valuable forensic tool because it can be used to determine the time of release (i.e., ownership) and subsequent liability for site clean up costs. Diesel fuels necessarily contain abundant normal alkanes, i.e., the class of hydrocarbons that most easily ignite under compression, and numerous iso-paraffins within the same boiling ranges as the normal alkanes. It has been long recognized that comparably boiling normal alkanes are more susceptible to biodegradation in the environment than iso-paraffins.

Investigators have used the ratio(s) between selected normal alkanes (e.g., n-C17) and iso-paraffins (e.g., pristine) to compare the extent of biodegradation among diesel fuel residues in environmental samples. Christensen and Larsen (1993) reviewed data for soils from several European sites with documented release histories and concluded that the ratio of n-C17/Pr in soil extracts could be used to estimate the length of time (up to 20 years ± 2.1 years) that diesel fuel had been in the environment, so long as certain conditions were met. Although the universal validity of the Christensen and Larsen Method has been debated, one particular condition – a single release of diesel fuel at a particular point in time – is extremely rare and/or difficult to prove at most petroleum handling facilities. Consequently, subsequent testing of the Christensen and Larsen Method has been extremely rare.

In this case study, a catastrophic release of approximately 6000 gallons of on-road diesel fuel #2 occurred when an underground storage tank (UST) was accidentally punctured during drilling in February 1991. When “fresh” NAPL appeared in 2002, the issue of its “age” was of paramount importance since the property had changed ownership. In 2003, NAPLs and impacted soils throughout the study area were collected and analyzed using detailed chemical fingerprinting as a means of assessing the “age” of the contamination. The NAPLs were minimally biodegraded (n-C17/Pr ~ 1.6), exhibited a consistent “genetic’ character (e.g., sesquiterpane and methyl-phenanthene patterns and relative S-PAH abundance), and contained 1870 to 2500 ppm total sulfur, which according to the Federal On-Road Diesel Fuel Sulfur Reduction Act of 1993 indicated the NAPLs’ parent fuel was used/released before November 1993. The soils collected in 2003 met the aforementioned conditions of the Christensen and Larsen Model, yet despite exhibiting consistent genetic features with each other and with the NAPLs, exhibited a wide range of n-C17/Pr ratios (0.0 to 1.8) which would imply “ages” between 20+ and ~4.5 years. These results argue that despite a one-time release of a particular type of diesel fuel in 1991, the rates of normal alkane biodegradation within this site’s soils were sufficiently variable to confound the application of Christensen and Larsen Model. The high sulfur contents of the NAPLs and the “genetic” comparability to the soils provided a defensible basis to attribute both the NAPL and soil contamination to the 1991 catastrophic release – and not a new release(s). The “sudden” appearance of NAPL in 2002, which promulgated this study, occurred after a marked drop in groundwater elevation due to drought – and not a new release(s). This case study serves to emphasize the imprecision of the Christensen and Larsen Method for age-dating diesel fuel residues in soils and, certainly its inappropriateness for age-dating NAPLs.

Ethics in Environmental Practice: Responsibilities, Benefits & Case Examples

In Defense of the Earth: Considering the Rationales
Lisa H. Newton, Fairfield University, Fairfield, CT

Ethical Assessment at the Limits of the Risk Assessment Process: Uncertainty Perchlorate and Societal Consequences
David R. Brown, Fairfield University, Fairfield, CT
Lisa H. Newton, Fairfield University, Fairfield, CT

Consequences of Non-compliance in Production of Commercial Products
Clifford Chanler, Chanler Law Group, New Canaan, CT

The Public Trust and Air Quality
Norman Anderson, American Lung Association of Maine, Augusta, ME

Ethics in Technical Publications: How Can the System Identify and Address Scientific Fraud?
Christopher M. Teaf, Florida State University, Tallahassee, FL
Barry L. Johnson, Emory University, Atlanta, GA

In Defense of the Earth: Considering the Rationales

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What's wrong with pollution? The rationale for laws forbidding the pollution of soils (or water or air) tends to turn on actual or potential harm to humans, e.g. from cancer caused by carcinogenic substances dumped in the soil. But then, is a demonstration that no conceivable harm could come to humans from a given instance of use or disposal of waste substances in the soil, sufficient to defeat opposition to such use or disposal? In the literature of environmental ethics, can we find other rationales that might be deployed in defense of the earth? What philosophical grounds support these rationales?

Ethical Assessment at the Limits of the Risk Assessment Process: Uncertainty Perchlorate and Societal Consequences

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Presently the regulatory process is dependent on performance of Quantitative or Qualitative Risk Assessments. The limitations to each assessment are developed in the discussions of uncertainty. In the presence of incomplete, conflicting or ambiguous findings the usefulness of a risk assessment as a quantitative regulatory tool begins to fail. This failure is frequently based in the uncertainty of the research studies. Some procedures such as ecological and epidemiological studies have less statistical power than others. Thus they can increase the uncertainty in the process.

In such cases, the weight of evidence is often applied. Studies with low statistical power tend to magnify the uncertainty in the process. That limits to usefulness of all of the scientific information in the assessment. In those cases the usefulness of risk assessment to the protection of public health is compromised. Examples are found in the arsenic in water literature, the perchlorate in drinking water literature, particulate matter in ambient air literature and several others.

When viewed from an ethical perspective there are consequences to the failure or limitation of public health processes. Ethical reasoning is based on the development of philosophical principles that began with the Greek civilization and before. It is that line of reasoning that holds societies together. Ethical analysis is based on a trilogy of obligations and the structure of theories such as Deontology, Utilitarianism and Ontological Reasoning. Ethics presumes a systematic and fair process for resolution of issues. These principles provide a framework for identification actions appropriate when risk assessments are unable to provide quantitative guidance. The position of waiting to act until absolutely definitive information is found fails to meet the ethical standard of fairness. However delay and inaction is often the result of emphasis on risk assessment uncertainty. Moreover the delay in the process tends to in appropriately encourage those studies and analysis that increase uncertainty over those that explain the differences. In the face of increasing uncertainty does one act or does one wait? The answer to this question will define our society.

Consequences of Non-compliance in Production of Commercial Products

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California's Proposition 65 is one of the first attempts to reduce the health risk from consumer products through labeling. Enforcement is extended to the general public through a litigation option. Products that do not meet the levels of exposure that prevents health threats must be have a warning label. Although commercial products are regulated by the CPSC, toxins have been found in unacceptable levels in many products. For example, lead was detected in glassware and ceramics that could be used to deliver such low pH liquids as wine. This would allow the lead component to leach and contaminate the food or drink ingested. In addition, bottles of cola were found to contain lead concentrations on the decal decorating the bottle causing a potential for hand to mouth exposure.

The consequences of such contamination are to human health primarily and, financially, to the companies selling such a product. In California, lawsuits are brought against these companies because of stringent laws protecting the consumer. This talk will examine the cases where such products were found to be defective.

The Public Trust and Air Quality

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As we approach the fortieth anniversary of the Clean Air Act, it is worthwhile to review the basic philosophical underpinnings that place limits on private ownership for the public good. This presentation will examine the Public Trust Doctrine, which dates back to the time of the Emperor Justinian, in relationship to protecting the public from the harmful effects of air pollution. It will focus on issues that have emerged since the 1970 Clean Air Act, such as exposures to environmental tobacco smoke. It will also focus localized situations in which significant exposures can occur in the surrounding population, such as the emerging health threat of outdoor wood boilers. A central concern in all these instances is what the primary responsibility of government should be as the keeper of the public trust.

Ethics in Technical Publications: How Can the System Identify and Address Scientific Fraud?

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Well-publicized events in Norway, South Korea and elsewhere in recent years have refocused the scientific community on historical issues of whether, and how, continued integrity of our technical literature can be assured. Solutions to this thorny problem are neither simple nor certain. Many professional societies in our field have addressed scientific misconduct, and effective responses by the research community will require cooperation of scientific publications worldwide. While no one argues that the practice of scientific fraud is common, recent cases beg attention from editorial boards. The peer review system serves the valuable function of examination and critique by scientists in relevant disciplines, for the purpose of assessing submitted papers prior to publication. Implicit in that process is the fundamental assumption that data are real and that research actually occurred. Typically, the process is “blind” in both directions, with neither author nor reviewer aware of the other’s identity, although some journals permit “author-directed” reviews under specified conditions. A reviewer’s responsibilities include ensuring that text properly reflects the data, that tables and figures are necessary and appropriate, and that conclusions fairly and reasonably reflect analytical results and the body of information available on the subject. Thus, the existing system probably is not capable of detecting anything but the most egregious fraud. In addition to imposing or perpetuating stringent review protocols, journals also can amend author guidelines to speak explicitly about publishing requirements. Cases of properly documented fraudulent research warrant immediate public announcement, to be followed by official withdrawal or retraction of the article(s). Reflection on these difficult issues led the editors of one journal to institute changes in editorial policies and develop a code of ethics for editors, authors and reviewers. While acknowledging that prevention of dishonest research is a daunting proposition, we should make it as difficult as possible to publish fraudulent science. Editors should commit reviewers and authors to ethical conduct in technical publications.

Fisherville Mill: Assessment and Cleanup of a Brownfields Site on the Blackstone River

Fisherville Mill: Site History and the Initial Conceptual Model

Paul Ollila, MassDEP, Worcester, MA
Janis Tsang, USEPA, Boston, MA
Dean Brammer, Weston Solutions, Inc., Manchester, NH
Bette Nowack, Weston Solutions, Inc., Manchester, NH
Jim Soukup, Weston Solutions, Inc., Manchester, NH

Fisherville Mill: Risk Reduction and Source Cleanup

Jim Soukup, Weston Solutions, Inc., Manchester, NH
Dean Brammer, Weston Solutions, Inc., Manchester, NH
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Fisherville Mill: Cost Effective Remediation through Collaboration

Eugene Bernat, Fisherville Redevelopment Corporation, Springfield, MA
Eric Hultstrom, Woodard & Curran, Inc., Dedham, MA

Fisherville Mill: Site History and the Initial Conceptual Model

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The Fisherville Mill site is located on the Blackstone River in Grafton, MA. Soil and groundwater are contaminated with chlorinated VOCs and petroleum. The mill and a groundwater recovery system designed to prevent VOCs from migrating to a nearby public water supply well were destroyed by fire in August 1999. Immediately after the fire, remediation efforts focused on removal of asbestos contaminated debris, removal of lead contaminated ash, and monitoring the VOC plume. A passive vapor diffusion sampler (PVDS) study identified locations where contaminated water was discharging to the Blackstone River and Canal and the PVDS results were used to select vertical profiling locations. In November 2000, the South Grafton Water District (SGWD) reported that 0.7 ug/l of TCE was present in a sample collected from a public water supply well (Well #3) located approximately 1000 feet southwest of the site. After notification the USEPA, MassDEP and SGWD collaborated on efforts to define the migration pathway and establish safe operating parameters for Well # 3. Pumping test and monitoring data was consistent with a model where the VOC plume shifts south and west towards Well #3 during low water conditions in the fall. Based on the conceptual model, initial risk reduction measures involved installation of a temporary dam to raise water levels in a portion of the former Blackstone Canal. Subsequent monitoring refined and verified the conceptual model for the downgradient part of the site, and increased water levels in the canal allowed continued use of Well #3 during remediation of the VOC source area.

Fisherville Mill: Risk Reduction and Source Cleanup

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The US EPA, MassDEP, and Weston Solutions, Inc. collaborated to devise and implement a removal action to protect municipal water supply wells from groundwater contamination emanating from the Fisherville Mill Site (Site). A hydrogeologic investigation showed that extended pumping of the well field under drought conditions could draw contamination from the Site beneath the Blackstone Canal and toward the supply wells. A temporary dam was installed on the Blackstone Canal to impound water thereby creating a hydraulic barrier to contaminant migration while source area treatment technologies were evaluated.

In June 2000, an in-situ bioremediation technology demonstration project utilizing Hydrogen Release Compound (HRC®) to treat chlorinated VOC contamination was conducted under the EPA Superfund Innovative Technology Evaluation (SITE) Program. However, after 18 months of monitoring it was uncertain whether the dechlorination/degradation process would proceed to completion. As a result, evaluation of an alternate remedial technology began in January 2002.

In 2002, after bench-scale testing and on-site injection tests, In Situ Chemical Oxidation (ISCO) using sodium permanganate was selected as the preferred alternative. The cleanup objective was to decrease TCE concentrations in the source area by two orders of magnitude, thereby reducing the size of the contaminant plume, and the risk of drawing TCE into the downgradient water supply wells. Three rounds of permanganate injections into a grid of approximately 100 wells were conducted. Performance monitoring including pre-injection and post-injection groundwater VOC and permanganate monitoring and groundwater profile sampling upgradient of the injection grid was implemented. Re-circulation of permanganate in selected grid/areas was conducted twice to ensure optimal distribution of permanganate. The post-removal groundwater VOC sampling confirmed that the cleanup objective was achieved.

Fisherville Mill: Cost Effective Remediation through Collaboration

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Fisherville Redevelopment Company was formed by the principals of Cover Technologies, Inc as a special purpose entity in 2004 to undertake the remediation and redevelopment of the Fisherville Mill site. The principals of Cover Technologies undertook the remediation and redevelopment of the Fisherville Mill site believing that they could utilize the knowledge, expertise and experience accumulated during its thirteen year history to cost effectively convert the contaminated Fisherville Mill site into a valuable asset.

A collaborative approach and strategy was developed between FRC and our environmental engineers (Woodard & Curran), MassDEP and the Town of Grafton that would encourage significant remedial actions while environmental assessment and engineering activities were ongoing. The tangible out come of this approach allowed FRC to remove and dispose of visible uncontaminated solid waste debris including bricks, steel and wood, install a # 6 oil interception and collection infrastructure, clean up and partially restore a portion of the historic Blackstone canal, remove and dispose of contaminated soil, recover and inventory historic and architecturally valuable cut granite elements of the original mill building, encapsulate 100% of the asbestos impacted debris and lead containing soil present at the site in flowable fill, partially restore Fisherville Dam, and re-grade, seed and prepare the site for future construction. The interim result of the approach is an engaged and enthusiastic public and vastly improved site both environmentally and visually.

Additional site assessment activities focused on developing an accurate understanding of subsurface soil conditions in the VOC source area and concluded that remediation will require a combination of SVE systems and in situ treatment. A pilot project is underway to evaluate use of fungi and higher plants to remediate oil contaminated sediments. A remedial alternative analysis will be completed by the Fall of 2007.

Gasoline Oxygenates I

Sponsored by American Petroleum Institute

Gasoline Oxygenate Use, Groundwater Issues and Related Research

Bruce Bauman, American Petroleum Institute, Washington, DC

Trends in the Occurrence of MTBE in Drinking Water in the Northeast United States

Michael Moran, U.S. Geological Survey, Rapid City, SD

3D Expedited Characterization Methodology for MTBE Contamination Impacting Deep Public Drinking Water Supply Wells

Joselph E. Haas II, New York State Department of Environmental Conservation, Stony Brook, NY
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Behavior of Ethanol and Aromatic Hydrocarbons from Two Gasoline Releases and One Natural Gradient Experiment, CFB Borden

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Field Performance Comparison of Three Oxygen Distribution Technologies

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Results and Lessons Learned from Field Applications of Oxygen Distribution Technologies

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Gasoline Oxygenate Use, Ground Water Issues and Related Research

Bruce Bauman, API, Washington DC

Conventional gasoline (CG) and Reformulated Gasoline (RFG) are the two basic types of gasoline used in the United States to meet federal and state regulatory requirements. There has been a virtual national phase-out of MTBE from all US gasoline over the last several years, and EPA no longer requires a minimum oxygen content in RFG. However, federal and some state regulations require the use of ethanol in gasoline, and currently about 50% of the gasoline blended in the US contains ethanol, usually at 10% volume. Domestic production and use of ethanol is predicted to double within the next several years from its current (2007 estimate) 6 billion gallons, and EPA is currently developing regulations to implement the Bush administration “20 in 10” initiative that would replace 20% of US gasoline (~ 30 billion gallons) with alternative fuels within 10 years. Language in current 2007 federal Energy Bill legislation would require 35 billion gallons by 2022, so it is highly likely that ethanol gasolines of varying blends will become even more prevalent. Except for specialty fuels like E85 (~81% ethanol), EPA regulations prohibit >10% ethanol in gasoline, but there are also initiatives to allow ethanol blends of 11-20% for use in all gasoline motor vehicles. E85 blends are already widely available in the Midwest and heavily promoted by US auto makers. This broad-scale transition means that all parts of the US are likely to have ethanol present in gasoline, and all spill response personnel will need to develop a thorough understanding of how releases of these fuels might behave differently than gasolines without ethanol. It will become necessary to catalog all known release scenarios (e.g., small chronic releases, sudden large releases) and receptors (e.g., ground water, surface water, utilities) for these different types of gasolines. Existing conceptual models for spill response and corrective action require should be reviewed to determine if any modifications might be helpful to fully account for all important direct and indirect effects. API research has been developing some of this information over the last several years, and will continue to focus on key fate and transport issues as well as corrective action technologies.

Trends in the Occurrence of MTBE in Drinking Water in the Northeast United States

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Public water systems in Connecticut, Maine, Maryland, New Hampshire, New Jersey, and Rhode Island sampled treated drinking water from 1990-2006 and analyzed the samples for methyl tert-butyl ether (MTBE). The U.S. Geological Survey examined trends in the occurrence of MTBE in drinking water from these public water systems in the Northeast United States.

MTBE was detected in 15% of drinking water samples collected in 1990-1999 and in 21% of drinking water samples collected from the same systems in 2000-2006. The difference in occurrence of MTBE between these two time periods is statistically significant; however, a significant increase in the occurrence of MTBE was observed in only three individual States: Maryland, New Jersey, and Rhode Island. Trends in MTBE occurrence by year in each State were less informative because of the inconsistent number of systems sampled in each year. Nonetheless, significant positive trends in the occurrence of MTBE by year were identified in Connecticut and Maryland.

Most concentrations of MTBE in drinking water from public water systems were low and median concentrations by State were less than 2 micrograms per liter. Using paired data for drinking water from ground water sources, significant trends in MTBE concentrations were observed in Maryland and Rhode Island. Concentrations of MTBE increased in both States from 1990-1999 to 2000-2006.

Water that is contaminated by MTBE is increasingly being captured by public water supplies in the Northeast and transmitted to consumers, although most concentrations are considerably less than those that might cause taste and odor concerns. As a result of the Energy Policy Act of 2005 the use of MTBE in gasoline has significantly declined. Future trends in the occurrence of MTBE in public water systems supplied from ground water in the Northeast are uncertain due to many potential controlling factors such as the continued decline in use of MTBE, recharge, pumpage, and geology.

3D Expedited Characterization Methodology for MTBE Contamination Impacting Deep Public Drinking Water Supply Wells

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The production, distribution and utilization of MTBE as a component of motor fuels has resulted in widespread impacts to ground water quality and has resulted in significant impacts upon public drinking water supply wells. MTBE contamination has forced the temporary closure of wells supplying the localities of Santa Monica, CA, South Lake Tahoe, CA, Pascoag, RI, Liberty, NY, Cambria Heights, NY, Riverhead, NY, and West Hempstead, NY. Despite MTBE bans enacted by many states MTBE, detections in public drinking water supply wells continue. Past MTBE impacts to drinking water supply wells in New York prompted the development of three dimensional (3D) expedited site characterization (ESC) techniques to rapidly back-track the path of contamination. However, the effective depth for application of the ESC techniques has been limited to approximately 40 meters by the depth capabilities of direct push sampling devices and hollow stem auger drilling equipment. Recent MTBE impacts to deeper public drinking water supply wells has catalyzed efforts to identify sampling and drilling techniques with greater depth capabilities that could be integrated in to the ESC methodology.

The feasibility of integrating rotosonic drilling into the ESC was evaluated via the pilot installation of two multi-level nested well bundles (MLNWBs) by rotosonic methods. The MLNWBs were installed adjacent to the intake screens of two deep public drinking water supply wells (approximately of 100 meters) that were exhibiting MTBE impacts. The installations of the MLNWBs were without incident, demonstrating the technical viability of the rotosonic techniques as a component of a deep ESC methodology.

MTBE contamination detected in the West Hempstead Water District Birch Street Well Field at a concentration of 154 micrograms per liter (µg/L) at depths of approximately 60 meters was defined utilizing a modified ESC for deep MTBE contamination. In this case the dynamic installation of MLNWBs was via cased hole drilling methods, which coupled with immediate field analysis of environmental samples successfully defined the MTBE contamination in 3D to depths of 60 meters. The experience gained at the West Hempstead site in combination with data obtained from the rotosonic pilot study indicates that 3D ESC definition of groundwater contamination to depths of 100 meters can be accomplished in “real-time” when required.

Behavior of Ethanol and Aromatic Hydrocarbons from Two Gasoline Releases and One Natural Gradient Experiment, CFB Borden

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The development and fate of groundwater plumes derived from two emplaced oxygenate-gasoline residuals in the Borden Research Aquifer were recently monitored. One fuel contains 90% gasoline and 10% ethanol (E10); the second contains denatured ethanol with 95% ethanol and 5% gasoline (E95). Ethanol from both E10 and E95 sources dissolved quickly into the flowing groundwater and, in both cases, > 60% of the ethanol was biotransformed during the 15 m (150 days) downgradient transport. Laboratory studies suggest that the maximum ethanol levels in groundwater at the E95 source (about 7000 mg/L) were not likely inhibitory to aquifer BTEX-degrading microorganisms, but that ethanol and its metabolites such as acetate would be preferred substrates compared to BTEX in the competition for electron acceptors. Essentially all aromatic hydrocarbons were leached from the E95 source while only benzene has been completely leached from the E10 source after 600 days. Ethanol cosolvency may have caused unexpectedly high fluxes of benzene and toluene from the E95 source. The presence of significant dissolved ethanol seems to have essentially stopped benzene and toluene degradation in the E95 plume for at least the 15m section that was monitored. Ethanol may have also reduced the biotransformation rate of benzene and toluene in the E10 plume , but had little effect on the persistence of less-mobile o-xylene and 1,2,3-trimethylbenzene, perhaps because the ethanol plume moves faster than the xylene and trimethylbenzenes. This is consistent with a previous natural gradient experiment at Borden in which two slugs of groundwater, one amended with about 15 mg/L BTEX and the other with about 6000 mg/L methanol added as well, were followed for 376 days. The methanol degraded with an apparent first order rate constant of 0.019 day-1 and the methanol caused significantly slower rates of benzene biodegradation (apparent first order rate constants of 0.001 day-1 and 0.004 day-1 with and without methanol respectively).

Numerical modeling using BIONAPL demonstrates that ethanol in gasoline does have the potential to create longer-than-anticipated benzene plumes in groundwater. At later time, the residual hydrocarbon source will likely behave as a non-oxygenate source and so subsequent source and plume management by MNA should continue to be the preferred remedial response.

Field Performance Comparison of Three Oxygen Distribution Technologies

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There is keen interest in oxygen injection systems owing to the increased evidence of in situ aerobic biodegradation of potentially recalcitrant gasoline constituents. Significant remediation cost reductions are possible by stimulating indigenous microorganisms to degrade contaminants of concern by adding oxygen. Various commercial oxygen injection approaches are being marketed with little credible evidence supporting their claims.

A field demonstration of 3 oxygen distribution technologies was performed in side-by-side test cells at the Port Hueneme NETTS field site. Each test cell measured 50-ft by 50-ft and was instrumented with 60 to 80 monitoring wells. These wells were sampled at 4 to 6 week intervals in order to evaluate the extent of oxygen distribution to a medium-sand aquifer. After 1 month of operation, the pulsed oxygen injection test cell showed a 10 to 20-ft oxygen-enriched (dissolved oxygen > 4 ppm) ROI, the low-flow, microbubble test cell showed a 5 to 15-ft oxygen-enriched ROI, and the diffusion-based test cell showed no influence outside the injection well (less than 1.5-ft ROI). After 1 month, each test cell showed essentially stable dissolved oxygen signatures.

This presentation will also illustrate the stability of the oxygen plumes in the diffusion and low-flow, microbubble test cells by mapping dissolved oxygen concentrations at 6, 12, and 18 weeks after cessation of oxygen injection.

Results and Lessons Learned from Field Applications of Oxygen Distribution Technologies

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Remediating oxygenate plumes by stimulating indigenous aerobic microorganisms is a proven technology. Oxygen distribution is essential for the technology to be effective. Unfortunately, oxygen distribution is difficult in many geologic environments.

Oxygen Pulsed Injection Systems (OPIS) use discrete volume injections of nearly pure oxygen to increase the DO of the groundwater. Distribution around the injection well is achieved by relatively high (>10 scfm) flow rates for discrete and short (~60 seconds) time intervals. Systems of this design have been installed at several retail and former retail sites in a variety of geologic settings. Experiences using this technology and site data will be presented.

Gasoline Oxygenates II

Sponsored by American Petroleum Institute

Predicting MTBE Legacy Impacts to the Sole Source Aquifer of Long Island, NY
Kristy A. Salafrio, New York State Department of Environmental Conservation, Stony Brook, NY
Joseph E. Haas, II, New York State Department of Environmental Conservation, Stony Brook, NY

Microbial Production and Consumption of *tertiary* Butyl Alcohol
Michael Hyman, North Carolina State University, Raleigh, NC

Anaerobic MTBE & TBA Biodegradation – Microbial Respiratory Processes versus Extent of Biodegradation
Kevin T. Finneran, University of Illinois at Urbana/Champaign, Urbana, IL

Stable Isotope Probing with 13C-MTBE-amended Bio-Sep® Beads in MTBE-degrading Microcosms
Xiaomin Yang, BP Corporation North America, Warrenville, IL
John Wilson and Cherri Adair, U.S. EPA, Ada, OK
Jennifer Busch-Harris, Kerry Sublette and Eleanor Jennings, University of Tulsa, Tulsa, OK
Tomasz Kuder and Paul Philp, University of Oklahoma, Norman, OK
Greg Davis, Microbial Insights, Inc., Rockford, TN
William E. Holmes, University of California, Davis, CA

Stable Isotope Fractionation Resulting from Biotic and Abiotic MTBE Attenuation Processes
Tomasz Kuder, University of Oklahoma, Norman, OK
Paul Philp, University of Oklahoma, Norman, OK
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Predicting MTBE Legacy Impacts to the Sole Source Aquifer of Long Island, NY

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The New York State Department of Environmental Conservation (NYSDEC) conducted a pilot study to better define the extent of MTBE contamination stemming from previously unidentified and/or unreported MTBE blended gasoline releases throughout the Long Island aquifer system. The study yielded sufficient data to project the potential MTBE impacts upon the sole source of drinking water for the residents of Nassau and Suffolk Counties. The study also yielded information that provided insight into the potential costs and work load associated with managing the MTBE legacy impacts to Long Island's drinking water supply.

During the study, 52 gasoline retail stations in Nassau and Suffolk Counties (approximately 4.7% of the total number of stations) that had no known prior release of oxygenated gasoline underwent petroleum bulk storage inspections and fuel oxygenates water quality impact assessments. The study found that MTBE was non-detect or less than 10 micrograms/liter (µg/L) at approximately 60% of sites investigated and that the MTBE concentrations in groundwater ranged from non-detect up to 240,000 µg/L in Nassau County and up to 63,000 µg/L in Suffolk County. Additionally, MTBE was found to have exceeded the drinking and groundwater standards of 10 µg/L at 34% and 53% of sites investigated in Suffolk and Nassau Counties, respectively.

Based upon the study findings, the per site costs of the study, and the estimated potential average per site costs at the projected MTBE impact sites, projections of the scope of the regional environmental contamination and its potential remedial costs were possible. Numerous projections stemming from the data collected are presented, including the estimated range of potential remedial costs associated with the MTBE legacy in Long Island, New York.

Microbial Production and Consumption of *tertiary* Butyl Alcohol

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Identifying the sources and sinks of *tertiary* butyl alcohol (TBA) is key to any comprehensive understanding of the environmental impacts of fuel oxygenates. Our recent studies have focused on several aspects of the microbial production and consumption of TBA. In one study we examined the potential for TBA production from other important gasoline components besides ether oxygenates. Isobutane (2-methylpropane) is a universal gasoline component found at its highest concentrations (~4% v/v) in gasoline used in colder climates. Aerobic metabolism and cometabolism of isobutane by pure and mixed hydrocarbon-oxidizing microorganism consistently leads to substantial TBA accumulation. Production of TBA during isobutane metabolism is strongly favored under the O_2-limited conditions typically encountered in gasoline-impacted environments. These results suggest microbial production of TBA might occur even during the biodegradation of gasoline that does not contain ether oxygenates such as MTBE or ETBE. In our studies of TBA consumption we have also isolated two organisms that appear to have different TBA-oxidizing pathways. One organism, strain S1B1, does not grow on n-alkanes and oxidizes TBA through a conventional pathway involving 2-methyl-1,2-propanediol and 2-hydroxyisobutyric acid. Rapid growth of this strain has been achieved in a mixed culture with the alkane-dependent, MTBE-cometabolizing, TBA-generating strain, *Pseudomonas mendocina* KR1. In the presence of n-octane and MTBE both organisms grow and full mineralization of MTBE is achieved even though neither organism can grow on MTBE alone as a sole source of carbon and energy. Our most recent studies have been directed at identifying the key enzymes responsible for TBA oxidation in strain S1B1 and other TBA-utilizing strains. The most current results of our various studies on microbial TBA production and consumption will be presented and their significance will be discussed.

Anaerobic MTBE & TBA Biodegradation – Microbial Respiratory Processes versus Extent of Biodegradation

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Methyl tert butyl ether (MTBE) and tert-butyl alcohol (TBA) are groundwater contaminants of concern arising from use in fuel as oxygenates. TBA is also problematic because it can accumulate during MTBE biodegradation. These compounds are often contaminants in anaerobic subsurface environments, where degradation rate and extent are influenced by different microbial processes and shifting microbial communities. Unlike aerobic respiration which is limited to oxygen, numerous anaerobic electron acceptors can be present simultaneously, which alters MTBE and TBA biodegradation in a positive or negative manner. The data to date have been primarily empirical, and this has led to great variability amongst the data sets. The major issue arising is "what conditions lead to TBA degradation versus accumulation"? The research presented here describes MTBE and TBA biodegradation studies in contaminated sediment under shifting electron accepting processes. In addition, we describe the first anaerobic, Fe(III)-reducing enrichment culture that degrades MTBE, strain NW1.

Sediment incubations were constructed with MTBE- and/or TBA-contaminated aquifer material from several sites located throughout the U.S. The dominant terminal electron accepting process (TEAP) was identified for each site, which was the starting or baseline condition for the experiment. Electron acceptors (nitrate, Fe(III), electron shuttles to promote Fe(III) reduction, fumarate, or sulfate) were added depending on the initial conditions at concentrations that would allow multiple TEAPs to overlap. This was to create what we refer to as "shifting" TEAP conditions. We compared this to conditions in which the TEAP was stable over time. Uniformly radiolabeled [^{14}C]-MTBE or [^{14}C]-TBA were added and $^{14}CO_2$ and/or $^{14}CH_4$ were quantified over time. Liquid enrichment cultures were also initiated in freshwater media with the same electron acceptors and MTBE or TBA as the sole electron donors.

While degradation was site specific the greatest extent of mineralization has been quantified in sediment amended with Fe(III) or Fe(III) plus electron shuttles, despite the initial conditions. Nearly 80% of TBA has been mineralized to CO_2 in Fe(III) plus AQDS amended sediment. Approximately 25% has been mineralized in sulfate amended sediment. Interestingly, MTBE is not oxidized at all at this site, which is unique. Microbial community composition will be monitored to determine why MTBE is not degraded while TBA is. Fumarate has promoted MTBE and TBA degradation in a variety of incubations; fumarate is an alternate electron acceptor for Fe(III)-reducing microbes. Shifting conditions to higher redox processes such as nitrate did not stimulate activity. In fact – all TBA degradation ceased when nitrate was added. This argues against broad assumptions that "higher redox potential" acceptors stimulate activity. Finally, a liquid enrichment culture, strain NW1, was obtained from one site. This culture oxidizes MTBE as the sole carbon and energy source coupled to Fe(III) and AQDS reduction. It accumulates stoichiometric TBA, but MTBE is completely degraded. This culture is critical as it provides the first Fe(III)-reducing model culture to investigate MTBE degradation (and TBA accumulation) at the cellular level.

Stable Isotope Probing with 13C-MTBE-amended Bio-Sep® Beads in MTBE-degrading Microcosms

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The relative concentrations of tert-butyl alcohol (TBA) and methyl tert-butyl ether (MTBE) in groundwater samples from a gasoline spill site in Orange County, CA suggested that MTBE was being transformed to TBA. Stable carbon isotope ratio analysis of MTBE in groundwater also indicated that MTBE had been biologically degraded. Sediment was collected from the site for an anaerobic microcosm studies. The removal of MTBE in the microcosms was rapid. The initial concentration of MTBE (1300 μg/L) was depleted to the analytical detection limit (<3 μg/L) within three months. MTBE removal was accompanied by a stoichiometric accumulation of TBA. The first-order rate constant for MTBE biodegradation was 25 ± 4 per year at 95% confidence. As MTBE was removed during the incubation, ^{13}C was enriched in the remaining MTBE with $\delta^{13}C$ values increasing from -29.7‰ to +40 ‰.

MTBE biodegradation was also observed in microcosms that were amended with $^{13}C_5$-MTBE-loaded Bio-Sep beads using either recycled or original sediments from the study referenced above. ^{13}C-labeling of specific phospholipids indicated that sulfate-reducing bacteria (SRB) played a major role in MTBE biodegradation in these microcosms. However, these microcosms were severely sulfate limited and Fe(III) reduction may well have been a significant, and possibly limiting, electron acceptor for the SRB. To our knowledge this is the first demonstration of a direct linkage between MTBE biodegradation and a specific group of bacteria. A mass balance in these microcosms suggested that some TBA degradation may have occurred in that the TBA inventory at the conclusion of the experiment was significantly lower than the amount of MTBE degraded.

Stable Isotope Fractionation Resulting from Biotic and Abiotic MTBE Attenuation Processes

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This presentation will discuss the application of compound-specific isotope analysis (CSIA) to MTBE attenuation studies. Results published to date indicate that: (i) it is practical to distinguish between the effects of aerobic and anaerobic MTBE biodegradation by combined carbon + hydrogen CSIA; (ii) the magnitude of carbon isotopic fractionation in the anaerobic process is large and consistent among different anaerobic microbial cultures (carbon isotope enrichment factors reported in literature for three different cultures are between -9.2 ± 5.0 and -15.6 ± 4.1) and (iii) there is little evidence of mineralization of the tert-butyl group of MTBE (tert-butyl alcohol accumulates upon MTBE degradation). This presentation will show new data from anaerobic, MTBE-degrading microcosms, aiming at accurate determination of carbon and hydrogen isotope effects. The values of carbon isotope enrichment factor were obtained from six different methanogenic and sulfate reducing cultures grown in agitated soil to assure uniform medium distribution. The resulting carbon isotope enrichment factors are similar to each other and higher than the previously reported ones, clustering between –17 and –20. It is proposed that calculation of anaerobic biodegradation progress based on Rayleigh model should use the latter value for conservative estimate of the extent of biodegradation. Hydrogen isotope data are consistent with the previously published results obtained from field samples. Hydrogen enrichment factor interpolated from the 2D-CSIA data is approximately –30 (i.e., the net hydrogen effect is similar to that of aerobic MTBE biodegradation). Abiotic in-situ degradation of MTBE is possible either at sites treated by chemical oxidation remedies or due to spontaneous acid hydrolysis. Examples of isotope fractionation will be shown for laboratory experiments on Fenton reagent degradation and acid hydrolysis of MTBE. In both cases, isotope effects are in agreement with the proposed reaction mechanisms. 2D-CSIA trends resulting from both reaction types are identical to those resulting from biological aerobic MTBE degradation. Published data on isotope effects upon phase partitioning, volatilization etc. suggest that these processes result with minor isotope fractionation and should not interfere with the studies of biodegradation. It will be shown that under certain environmental conditions, measurable changes of carbon and hydrogen isotope ratios are likely due to MTBE volatilization from aqueous or hydrocarbon phase. While the magnitude of those changes is low in comparison with those due to anaerobic biodegradation, volatilization and aerobic biodegradation can be difficult to distinguish from each other.

Heavy Metals

Lead in Soil by Field Portable X-Ray Fluorescence Spectrometry - An Examination of Paired In-Situ and Laboratory ICP-AES Results
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Soil-Lead Partitioning in Southern and Northern Hemisphere: A Comparative Evaluation
Maria Marin, Wayne State University, Detroit, MI
Carol J. Miller, Wayne State University, Detroit, MI

In-Situ Stabilization of Metals Contaminated Soils Using Phosphate Based Admixture
Rick Greiner, Conoco Phillips Company, Houston, TX
Gary M. Garfield, URS Corporation, Salem, NH
Michael Stiller, URS Corporation, Boston, MA
Russ Wilder, URS Corporation, Salem, NH

In-situ Remediation of Chromium with Nanoiron
David Henderson, New Jersey Department of Environmental Protection, Hamilton, NJ
Harch S. Gill, PARS Environmental, Inc., Robbinsville, NJ

Boston Mine: Cleanup of Mercury at an Abandoned Placer Gold Mine
David Lawler, US Department of the Interior Bureau of Land Management, Sacramento, CA
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Restoring Silver Bow Creek in the Upper Clark Fork River Basin in Western Montana
Gregory J. Mullen, Natural Resource Damage Program, Helena, Montana

Lead in Soil by Field Portable X-Ray Fluorescence Spectrometry - An Examination of Paired In-Situ and Laboratory ICP-AES Results

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RTI has conducted a study to compare the performance of field-portable X-ray fluorescence (FPXRF) with lab-based ICP-AES. The study was designed to produce paired ICP-FPXRF measurements from soil samples collected at multiple locations within each of nine geographically remote study sites. Soil samples tested in the field by FPXRF were returned to the laboratory for confirmatory lead analysis by ICP-AES. Evaluation of study data revealed the following: ICP-AES soil lead measurements were systematically higher than the paired FPXRF measurements and the degree of correspondence between ICP-AES and FPXRF measurements on the same soil sample is a function of a variety of factors, including soil moisture and particle size, specific to a particular location or site. In order to minimize the differences between field and laboratory results, RTI has developed a new protocol for field-drying and sieving of collected samples and measurement by FPXRF. In order to evaluate this protocol, composite samples were collected following both HUD Guideline and ASTM protocols, measured following drying by FPXRF, and returned to the laboratory for confirmatory ICP-AES analysis. Evaluation of study data from several diverse sites revealed no statistical difference between paired FPXRF and ICP measurements following the new method. A simple, cost-effective in-situ soil lead measurement is now available.

Soil-Lead Partitioning in Southern and Northern Hemisphere: A Comparative Evaluation

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An investigation was completed to determine soil-lead content and chemical partitioning of lead in soil samples from two different climatic zones (Maracaibo, Venezuela and Detroit, Michigan, USA). Various studies have demonstrated the great incidence of soil-lead contamination in metropolitan areas with a high traffic density. The Detroit Metropolitan area exhibits the same trend, having elevated soil-lead concentrations in the central part of the city, with levels decreasing with increasing distance from the inner-city area. There are no records of soil-lead contamination or lead poisoning prevalence in Maracaibo, Venezuela, but a study performed in Valencia, Venezuela found elevated blood lead levels in children, most of them above the threshold value of 10 µg/dL. The median of blood lead levels in children in this study was 11.6±5.5 µg/dL. Elevated blood lead levels have been found throughout Detroit.

The present investigation involved the collection of surficial soil samples, soil characterization, and analytical determination of soil-lead content in these two metropolitan areas. In addition, other tasks included the sequential extraction analysis of soil samples, to determine the chemical partitioning of Pb in different phases of soil. An additional step is added to the sequential extraction procedure to further break down the organic phase into humic and fulvic acids. A chelating agent (NTA) is added in each step of the sequential extraction procedure, to prevent readsorption of Pb into the soil, an issue that has been documented extensively.
There are several important differences between Maracaibo and Detroit that may impact the observed soil-lead partitioning. Certainly, the two cities are located in very different climatic zones. Venezuela is a tropical country and is very close to the equator, so there is no snow in Maracaibo and, therefore, no road salt application. It has been suggested that road salt can mobilize Pb through soil through complexation reactions. Another difference between the two cities is the amount of precipitation, the average annual precipitation in Maracaibo is 57.7 cm, and the average annual precipitation in Detroit is 80 cm of rain and 115 cm of snow.

Regarding the sources of Pb, in Venezuela leaded gasoline and leaded paint are still in use, so contamination of the soil with Pb has continued for almost 20 years after leaded gasoline was banned in the US.

In-Situ Stabilization of Metals Contaminated Soils Using Phosphate Based Admixture

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Historic operations of a former fertilizer manufacturing company have resulted in heavy metals contamination in surficial soils above the Massachusetts Contingency plan Upper Concentration Levels (UCLs). From 1860 to the 1960s, The American Agricultural Chemical Company manufactured phosphate type fertilizers at their Weymouth Neck, Massachusetts facility. The site is situated on the Weymouth Neck peninsula. Since the 1960s residential development consisting of high rise condominiums has occurred in and around the 25 acre site.

The results of initial site characterization conducted on a 2.5 acre portion of the site indicated that approximately 90,000 tons of soil had been impacted. Concentrations of arsenic and lead were present in surficial soils at concentrations up to 5,000 mg/kg and 12,000 mg/kg respectively. An evaluation of remedial response actions indicated that due to the high population density, the shallow water table (~7 feet), and the volume of soil requiring remediation in-situ soil stabilization was the most feasible remedial alternative.

Bench scale testing indicated that the most effective stabilization admixtures were phosphate based stabilization agents. Bench scale testing was completed on soils obtained from the site in July 2005. In October 2005, pilot scale testing was conducted and included the in-situ stabilization of six cells using three different chemical providers. Soils were stabilized above and below the water table using a rotary head mixer. Treated soils were sampled for TCLP metals, SPLP metals, pH phosphate, sulfate, and sulfide immediately after stabilization, after 21 days and after 4 months. In addition, selected samples were analyzed using a multiple SPLP methodology. The results of the pilot scale testing indicated that the impacted soils could be stabilized and that leaching of the soil would not result in a significant risk to human health and the environment.

Nearly 3,000 tons of admixtures were used to stabilize approximately 90,000 tons of soil. Soil stabilization was conducted in 40 by 15 foot cells between September and December 2006. Approximately 250 cells were stabilized from the ground surface to six feet (Upper Lift) and from six feet to twelve to thirteen feet (Lower Lift). Results of analytical analyses conducted on treated soils indicated that only 5 of the 250 cells required retreatment. TCLP and SPLP testing indicated successful treatment of the metals impacted soil was achieved within 4 days. The work was conducted in close proximity to condominium residents and adjacent to a salt marsh.

In-situ Remediation of Chromium with Nanoiron

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From 1905 to 1971, three major facilities in New Jersey were involved in the extraction of chromium from mineral chromite. In this period, over 2,000,000 tons of chromite ore processing residue (COPR) was produced. This waste product was used by the construction industry for various purposes such as grading material for roadways and as fill material in residential, industrial and commercial construction. The New Jersey Department of Environmental Protection (NJDEP) has classified over 150 sites in Hudson County as chromium-contaminated areas. These sites have chromium concentrations ranging from a few parts per million (mg/kg) to over 5 percent by weight.

The remediation of chromium-contaminates sites presents a technological and economic challenge; none of the currently available treatment methods have been effective and/or cost-effective. Recent research and development has demonstrated that hexavalent chromium can be rapidly reduced and immobilized at the surface of nanoscale zero-valent iron particles. Characterizations with High-Resolution X-ray Photoelectron Spectroscopy (HR-XPS) indicates that Cr(VI) is rapidly reduced to Cr(III), which is subsequently incorporated into the iron oxide shell of the nanoiron and forms an alloy-like Cr-Fe hydroxide which is stable and serves as a sink for Cr(VI). Due to the fast reaction kinetics and high chromium removal capacity, nanoiron is an effective reagent for in-situ immobilization of chromium contaminated soil and groundwater.

In the Fall of 2006, the NJDEP funded a comprehensive technology demonstration project in Jersey City in Hudson County to evaluate the in-situ remediation of chromium-contaminated soils and groundwater using zerovalent nanoiron. Tests were done in both the saturated zone as well as the vadoze zone. This paper presents the results of the comprehensive demonstration project and discusses the methodology for injecting the nanoiron to achieve optimum results.

Boston Mine: Cleanup of Mercury at an Abandoned Placer Gold Mine

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Elemental mercury was widely used at hundreds of placer mines in the Western Sierra Nevada to recover fine gold. Estimated losses of mercury to the environment during historical gold mining range from 10 to 30 percent. Much of this elemental mercury remains within the western Sierra watersheds. Regional studies of watersheds on the west slope of the Sierra Nevada Mountains in California have identified elevated levels of mercury in water, sediment and biota. In response to these observations, fish consumption advisories were issued by public health organizations. Agencies that administer public lands, including the BLM, are responsible for the control and cleanup of mercury from legacy mines under their jurisdiction. Regional sampling identified the drain tunnel outlet at the Boston Mine as a site of significant bioaccumulation in comparison to other placer mines that were sampled. Site specific investigations identified up to 45 grams of mercury per kilogram of sediment at the site. In addition, mercury in water from the drain tunnel outlet exceeded water quality standards. BLM determined that the drain tunnel at the Boston Mine represented an ideal opportunity to evaluate removal of mercury from sediment at these legacy mines. Successful implementation of on-site sediment processing resulted in cleanup of the drain tunnel and recovery of 1,162 grams of elemental mercury, 264 grams of amalgam, and lead and gold from site sediment. Washed sediment was suitable for burial on site without additional stabilization; heavy mineral concentrates were stabilized with cement prior to burial on site. The recovered mercury was recycled. Post removal monitoring is ongoing.

Restoring Silver Bow Creek in the Upper Clark Fork River Basin in Western Montana

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Decades of mining and mineral processing operation in and around Butte and Anaconda released substantial quantities of hazardous substances into the Upper Clark Fork River Basin between Butte and Milltown in western Montana, which now is the largest Superfund complex in the U.S. These hazardous substances extensively injured the area's natural resources including Silver Bow Creek, which extends from Butte approximately 23 miles to the Warm Springs Ponds, a four square mile water treatment facility located near the headwater of the Clark Fork River. Since the late 1880's, toxic discharges produced a metals-impacted floodplain and streambed and virtually eliminated aquatic life in Silver Bow Creek.

Using part of a $215 million partial settlement in 1999 with Atlantic Richfield Company, the State of Montana's Department of Environmental Quality (DEQ) and Natural Resource Damage Program, through a grant to the local Greenway Service District, are conducting an integrated remediation and restoration, respectively, of Silver Bow Creek. Since work began in 1999, three million cubic yards of tailings have been removed, 10 miles of stream reconstructed, and 850 acres of floodplain have been restored to productive wildlife habitat. Together these agencies are expediting and economizing by using the same contractors and contracts for the remediation and restoration effort, which is most likely the largest such integrated effort in the country. Recent monitoring of the State's injured resources along Silver Bow Creek has shown dramatic improvements to water quality, streamside soils and wildlife habitat. The state is over half done with this estimated $80 million integrated remedy/restoration effort, which is expected to be complete by 2011. The Greenway Service District is acquiring public ownership and developing a recreational greenway trail corridor along the restored creek corridor.

Innovative Technologies

Contaminant Removal during Large-Scale Experiments of Thermal Remediation of DNAPL Sources in Aquifers

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High Mass Delivery Gas Infusion Systems for Active Bioremediation, Modification of Groundwater Geochemistry and NAPL Removal

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Real-Time Contaminated Soil & Groundwater Remediation Optimization via the Information Superhighway

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Fluorescent Dyes Define Ground Water Flow Paths in Unconsolidated Aquifers

Edward Hinchey, ERM-Northeast, Inc., Syracuse, NY
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Innovative Groundwater Imaging Technology

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Innovative Off-Gas Treatment Technology Allows Recycling of Extracted Soil Vapor

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Contaminant Removal during Large-Scale Experiments of Thermal Remediation of DNAPL Sources in Aquifers

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At the core of a three-year SERDP-funded research project, two large-scale (75m³ and 150m³) 3-D remediation experiments, with controlled release of DNAPL into a lower-permeability layer beneath the water table are being conducted at the facilities of VEGAS - the Research Facility for Subsurface Remediation at the Univ. of Stuttgart, Germany. The purpose of these experiments is to better understand the principal mechanisms that control the performance of thermal conduction heating (TCH) and vapor recovery of DNAPL in the saturated zone, at field-relevant scales and under well-controlled conditions. In parallel, a numerical model was optimized based on earlier experiments, enabling numerical simulations to be used to design the controlled release experiments. During the experiments, the progression of heating to 100°C and accompanying desaturation are monitored using 300 temperature sensors and 35 time domain reflectometry probes, respectively, allowing comparisons of the physical conditions and accompanying numerical simulations. In addition, numerous solution and vapor samplers enable monitoring of contaminant concentrations at various locations within the containers over the course of the heating.

High Mass Delivery Gas Infusion Systems for Active Bioremediation, Modification of Groundwater Geochemistry and NAPL Removal

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High mass delivery rate gas infusions systems have been developed as new tools for site remediation. These systems transfer dissolved gasses including oxygen, hydrogen and cometabolic substrates to groundwater for active in situ bioremediation and optimization of extraction, treatment and reinjection systems. Additional applications include pH and redox adjustment and enhancement of NAPL recovery with CO_2 Saturated Water Injection. Laboratory scale technology development and field trial systems data for multiple applications will be presented.

Real-Time Contaminated Soil & Groundwater Remediation Optimization via the Information Superhighway

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An innovative engineering control system has been developed to optimize the process of activating sodium persulfate used to oxidize organic contaminants in soil & groundwater. This in-situ chemical treatment remediation process can be continuously optimized using an innovative web-based Smart Data^{SM} software information package that provides via the information superhighway three-dimensional images of real time data, which is readily accessible in the field.

Activated persulfate is a much more robust chemical oxidant than “unactivated” persulfate. Thus, the real-time field optimization of the techniques used to activate persulfate has significant process safety and economic value. Persulfate can be activated by a combination of the following: hydrogen peroxide injection, pH manipulation, transition metal catalyst application, and exceeding the minimum activation temperature threshold which can be achieved by exothermic chemical reactions generated by the application of catalyzed hydrogen peroxide.

The installation of a thermocouple in every chemical injection well and monitoring well can provide useful chemical oxidation process control data. Wireless radio frequency transmitters can be used to collect the real-time temperature data from the thermocouples on-site. A laptop computer equipped with a wireless modem on-site can then transmit this data electronically via the information superhighway to an off-site computer equipped with a web-based Smart Data^{SM} software information package to provide three-dimensional images of the data in a timely manner thus allowing efficient and effective field optimization of the chemical oxidation treatment process. Three-dimensional images enable the field technicians to adjust chemical oxidant and conditioning reagent injection flow rates. Groundwater temperature can be continuously optimized. If appropriate, dual phase extraction and off-gassing rates can also be readily controlled.

Key benefits include process safety management via the avoidance of potential run away exothermic reactions, reduction in chemical and in-situ groundwater heating costs and of course the minimization of field technician labor.

Fluorescent Dyes Define Ground Water Flow Paths in Unconsolidated Aquifers

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Organic fluorescent dyes are rarely used in organic-rich environments because most dissolved organic substances fluoresce thus camouflaging the fluorescent dyes. In this paper, we report the results of the successful application of ultra-high resolution dye tracing experiments in unconsolidated aquifers at multiple sites affected with organic contaminants. ERM and Nanotrace Technologies have developed continuous synchronous spectrofluorometric scanning techniques to characterize background water that allows us to identify the fluorescent fingerprint of ground water affected by organic contaminants. Dyes are then chosen with a specific spectral signature and dominant wavelength peak that does not overlap with the background fluorescence allowing tracer detection in the part per trillion range. The combined background identification techniques and ultra-low detection limits provide a cost effective and “ground truthed” method of empirically determining actual subsurface flow paths.

We will present the results from a site contaminated for over 50 years with chlorinated solvents, cutting oils and heating fuel. We injected low concentrations of the fluorescent dyes uranine and sulforhodamine B in monitoring wells at opposite ends of the site to determine the direction and velocity of ground water flow, and to evaluate matrix effects to dye transport. Within 12 days, the uranine dye reached an onsite ground water recovery system identifying the major flow paths across the site. The observed velocity and flow differed widely from multiple observations via ground water gauging and aquifer testing. At a second site, ultra-low detection limits allowed for the conducting of dye tracing close to potential sensitive receptors in a populated area. The dye tracer study successfully identified actual cross-gradient limits of ground water flow which will be used to direct the precise application of in-situ oxidation chemicals.

The fluorescent dye techniques developed provide a degree of accuracy to flow path and aquifer analysis that was not previously available to investigators of contaminated ground water in unconsolidated formations.

Innovative Groundwater Imaging Technology

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Groundwater contamination is perhaps the most troubling aspect of a brownfields site. The diffusion of pollutants into the aqueous networks lying beneath such a site not only adds to the difficulties of local remediation, it also threatens the drinking water of a much larger area. The greatest challenge in addressing groundwater contamination is gaining an accurate understanding of the complex web of channels and reservoirs which lie hidden below the surface. Unfortunately, traditional methods for determining the potential flow paths of subsurface pollution require extensive drilling—a time-consuming and expensive process which could result in significant environmental harm such as formation caving or slumping in loose sands. The electromagnetic imaging procedure detailed in this presentation provides exceptionally accurate groundwater maps but requires significantly less drilling. As a result, this method entails fewer costs in terms of time, money and ecological disruption. This rapid and minimally invasive technique may be particularly well suited to the task of environmental cleanup.

In this procedure, electrodes are used to charge the groundwater in question with a low voltage, low amperage, high frequency electrical current. As the current moves through the water between the electrodes, it induces a magnetic field whose size, shape, magnitude and direction are characteristic of the surrounding aqueous system. This field is then read at the surface by a specially tuned receiver. The data thus generated can be used to create maps indicating the attributes of the subsurface water network, including potential flow paths. Such information is of tremendous value in the difficult effort to remediate groundwater pollution.

This technology has recently been deployed in a variety of projects involving subsurface contamination. This presentation will discuss the science behind the methodology and the lessons learned from its recent applications.

Innovative Off-Gas Treatment Technology Allows Recycling of Extracted Soil Vapor

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There is increasing demand internationally for green technologies, including within the hazardous waste industry. An emerging technology[1] within soil vapor treatment field allows recovery and recycling of the extracted off-gases without potential generation of hazardous air toxins associated with incineration. This technology, referred to vapor condensation, recovers extracted solvents or petroleum compounds in a liquid form that can be recycled. This provides an additional cost-effective technology to use in conjunction with soil vapor extraction (SVE), commonly accepted as the most effective technology for remediating volatile organic compounds (VOCs) from soils. Within the past 5 years, vapor condensation technology has proven cost-effective at various industrial sites within the United States. This innovative, cryogenic technology uses compressors to extract VOCs from the ground and then condenses the VOCs to form recoverable product. Ideal sites for application of vapor condensation technology include those with high initial VOC concentrations (e.g., >4,000 parts per million by volume [ppmv]), or sites with recalcitrant compounds including fluorinated compounds (e.g., chlorofluorocarbons [CFCs]) or methylene chloride. Key advantages include rapid mobilization and short cleanup timeframes, potential recycling of the recovered chemicals, and elimination of potential generation of dioxins and furans. For example, at one industrial site, initial concentrations of tetrachloroethene (PCE) and trichloroethene (TCE) exceeded 10,000 ppmv. Treatment with only minimal dilution air allowed high mass-removal (over 10,700 pounds of chlorinated VOCs) and concentrations to decrease below 500 ppmv within 9 months, at which time the system was cost-effectively switched to GAC. The authors draw on their hands-on project experience, lessons learned, and rough costs incurred with regards to designing, operating, optimizing, and recovering solvents using the innovative vapor condensation off-gas treatment system at various sites.

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[1] United States Environmental Protection Agency, 2006. *Off-Gas Treatment Technologies for Soil Vapor Extraction Systems: State of the Practice.* EPA-542-R-05-028. March.

Modeling

A Spreadsheet-Based Multi-Layer Vadose Zone Leaching Model
Phillip C. de Blanc, Groundwater Services, Inc., Houston, TX

Use of SEVIEW Software in Determining Groundwater Impacts at POCs
Michael R. Kulbersh, U.S. Army Corp of Engineers, Concord, MA

A Permanganate Natural Oxidant Demand Kinetic Model
Laura Jones, University of Waterloo, Waterloo, ON, Canada
Xiuyuan Xu, University of Waterloo, Waterloo, ON, Canada
Neil R. Thomson, University of Waterloo, Waterloo, ON, Canada

A Proposal for a Quantitative Petroleum Weathering Model to Replace Today's Qualitative or Descriptive Categories
Michael J. Wade, Wade Research, Inc., Marshfield, MA

Evaluating the Impacts of Uncertainty in Geomorphic Channel Changes on Predicting Mercury Transport and Fate it the Carson River System, Nevada
John J. Warwick, Desert Research Institute, Reno, NV
Rosemary Carroll, Desert Research Institute, Reno, NV

BIOSCREEN, AT123D, and MODFLOW/MT3D, a Comprehensive Review of Model Results
Robert A. Schneiker, Environmental Software Consultants, Inc., Madison, WI
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A Spreadsheet-Based Multi-Layer Vadose Zone Leaching Model

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Environmental professionals routinely use one-dimensional models to simulate the leaching of contaminants from vadose zone soils to underlying groundwater. These models solve the one-dimensional form of the advection-dispersion-reaction (ADR) equation to determine the concentration of a constituent as a function of time and depth within the soil column. Many commonly-used models of contaminant leaching from vadose zone soils are numerical models that require an input file and post-processing. While these models are flexible and accurate, they require training for the user to take full advantage of the model capabilities, even if the user possesses all of the knowledge of the underlying physical principles. An alternative to numerical leaching models is to solve the ADR equation analytically. Because the ADR equation is linear, superposition can be used to simulate leaching from multiple layers by adding the solutions for each individual layer. By specifying the correct boundary conditions for each layer, leaching from any number of layers can be simulated without having to resort to numerical models. Because the analytical solutions are exact, time-step limitations and numerical dispersion are eliminated. In addition, because all calculations are performed in a spreadsheet, there is no need for qualified professionals to learn how to use new software; their knowledge can be applied directly with a tool that is nearly universally used by environmental practitioners. Currently, the leaching model simulates the processes of liquid phase advection, liquid and air phase diffusion, liquid phase dispersion, and first-order reactions. Each layer can have a different thickness and initial concentration of a single constituent. Breakthrough curves and concentration profiles computed by the model match those computed by a popular numerical model. The capability of simulating layers with different physical properties by using dimensionless scaling factors is in progress.

Use of SEVIEW Software in Determining Groundwater Impacts at POCs

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As part of soil and groundwater investigations at hazardous waste sites across the country organic and inorganic compounds are readily detected in surface soils. At many of these sites the current protocol is to use readily available soil impact to groundwater standards or use the SESOIL model coupled with the Summers dilution model to determine impacts at points of compliance (POCs). However, the Summers model cannot address multiple areas of discrete (patch) sources or contiguous areas of contamination not aligned parallel to groundwater flow.

SESOIL in combination with AT123D, a 3-D analytical transport model may be used to simulate impacts from either a patch or contiguous sources and can account for contaminants loading to groundwater not parallel to groundwater flow. Unfortunately neither SEVIEW nor RiskPro software packages that run SESOIL/AT123D in a GUI environment presently simulate impacts from multiple sources arrayed in various configurations as part of a single run.

USACE worked with the SEVIEW developer, Environmental Software Consultants, Inc. to modify the existing version of SEVIEW to be able to pull in multiple loads from SESOIL (presently 15) into one AT123D run. A beta version was developed and tested extensively by USACE and the developer. The benefits of being able to pull the SESOIL loads into a single run will reduce model runs/contractor costs. The beta version of SEVIEW now allows a user to toggle on/off a SESOIL load and immediately determine its impact on the POC. The user can view the soil loads impact to groundwater in both an areal view (2D array graphic) and through a time concentration plot at the POC for all loads. The net result is that at a site only certain areas may require soil remediation/excavation in order to be protective of groundwater standards.

A Permanganate Natural Oxidant Demand Kinetic Model

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The presence of naturally occurring reduced species associated with aquifer materials exerts a significant permanganate demand thereby reducing the mass of oxidant available for the destruction of the contaminant(s) of concern as well as reducing the oxidation rate. Recent laboratory efforts indicate that this demand is not a single-valued quantity, but is kinetically controlled and depends on the parameters of the test system and type of reduced aquifer material species present. A comprehensive model that captures the kinetic behaviour of permanganate consumption by aquifer materials was formulated by using data collected from well-mixed batch reactor and column systems. The batch experiments were based on the theoretical derivation of the stoichiometric reaction of permanganate with bulk aquifer material reductive components, and consisted of excess permanganate mass experiments and excess aquifer material mass experiments. A typical experimental column trial consisted of flushing an aquifer-material packed column with the permanganate source solution until sufficient permanganate breakthrough was observed. Aquifer material from several representative sites across North America was used. We assumed that the dichromate chemical oxygen test results could serve as a surrogate for the overall aquifer material reduction capacity. The developed kinetic model consists of three reactive components associated with the aquifer material: a fast component, an intermediate component, and a slow component. The fast and intermediate components were observed in the batch experiments, while the slow component was observed in the column breakthrough curves. Evidence of passivation was apparent in the data and confirmed by manganese oxide coating on grains. This presentation will include a discussion of the underlying processes, and a description of the experimental data and aspects of the developed kinetic model. In addition, the impact of permanganate consumption kinetics on source zone treatment will be demonstrated.

A Proposal for a Quantitative Petroleum Weathering Model to Replace Today's Qualitative or Descriptive Categories

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Assessment of the extent of petroleum weathering in today's environmental forensics community can be described as qualitative at best and at worst as slipshod. Descriptive determinations of chemical analysis results such as "moderately weathered" or "extensively weathered" are routine. Up until now there has been no quantitative model proposed to actually measure the various stages of natural weathering of petroleum products such as gasolines and distillate fuels.

Such a quantitative weathering model is proposed to the forensics community. The model is based upon today's analytical ability to accurately quantify numerous different types of petroleum hydrocarbons, such as paraffins isoparaffins, alkylaromatics and the like in gasolines and distillate fuels. Following the progress of natural environmental weathering by measuring the changes in selected alkylaromatics and paraffins, for example, will allow an accurate (quantitative) assessment of the progress of environmental weathering in modern gasolines and distillate fuels.

Illustrations of how to calculate quantitative indices of today's contemporary gasolines and distillate fuels are provided. Specific project examples where such calculated values have been used to distinguish among the different weathering stages of petroleum products are presented.

It is proposed that such quantitative descriptions of environmental weathering of petroleum products should replace today's much more vague and descriptive approach in common use today.

Evaluating the Impacts of Uncertainty in Geomorphic Channel Changes on Predicting Mercury Transport and Fate it the Carson River System, Nevada

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The Carson River is one of the most mercury contaminated fluvial systems in North America. Most of its mercury is affiliated with channel bank material and floodplain deposits, with the movement of mercury through this system being highly dependent on bank erosion and sediment transport processes. Mercury transport is simulated using three computer models: RIVMOD, WASP5, and MERC4. Model improvements include the addition of a bank package that accounts for flow history. The rates at which river stages are rising or falling will, in turn, impart time-dependant and vertically variable MeHg concentrations within the channel banks along the Carson River. Also, Lahontan Reservoir's geomorphic characteristics have been refined along with the explicit tracking of a temporally and spatially varying colloidal fraction. The augmented and refined modeling approach results in more accurate and realistic simulation of mercury transport and fate. An extensive uncertainty analysis, involving characterizing the co-variance of two calibration parameters used to define bank erosion and overbank deposition, will define the degree of expected variation in model predictions relative to limitations posed by available field data.

BIOSCREEN, AT123D, and MODFLOW/MT3D, a Comprehensive Review of Model Results

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The Domenico equation is commonly used to evaluate risks associated with contaminated groundwater. Numerous groundwater models are based on it, including BIOSCREEN and BIOCHLOR. Results from such Domenico equation based models are considered conservative and are readily accepted by most regulatory agencies. In fact many regulatory agencies even require that Domenico equation based methods be used.

This paper compares the results from the BIOSCREEN, AT123D and MODFLOW/MT3D groundwater models, and shows that there is little correlation between BIOSCREEN and the other models. As expected the BIOSCREEN model consistently produced the highest peak groundwater concentration. However these peak concentrations are identical for everything from benzene to polycyclic aromatic hydrocarbons. Although all the predicted concentrations produced by BIOSCREEN are identical, contaminant mobility varies significantly. Travel times discrepancies between BIOSCREEN and the other models increased as hydraulic conductivity is reduced. These travel time discrepancies range from insignificant to almost 40,000 years for benzene in a clay aquifer. The influence of biodegradation is also evaluated. The amount of biodegradation is controlled by the time it takes to reach a point of compliance. As such, inclusion of biodegradation further increases discrepancies between BIOSCREEN and the other models. Discrepancies in contaminant concentrations increased as hydraulic conductivities are reduced, reaching many orders of magnitude for benzene in a clay aquifer.

Correlation between the AT123D and MODFLOW/MT3D models is very good in that they produce nearly identical peak concentrations and travel times. Unlike BIOSCREEN, results vary significantly based on contaminant and aquifer properties as should be expected.

Although BIOSCREEN produces the highest maximum concentration, it underestimates consistently the mobility of the contaminant, and thus exposure. Inclusion of biodegradation only increases discrepancies between BIOSCREEN and the other models, thus making BIOSCREEN the least conservative model tested. Given that AT123D and BIOSCREEN use almost identical input parameters it is difficult to explain the use of BIOSCREEN and other Domenico equation based models.

Perchlorate/MECs

Containment of a Perchlorate Plume from the use of Road Flares in a Wellhead Protection Area

Thomas C Cambareri, Cape Cod Commission, Barnstable, MA
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Perchlorate Remediation using a Novel Autotrophic, Perchlorate-Reducing Microbial Community

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Effects of Reducing Conditions on the Fate and Transport of RDX in Groundwater

Michael W. Morris, Jacobs Engineering, Bourne, MA
Lonnie Fallin, Jacobs Engineering, Bourne, MA

Rejuvenation of Biowalls Used to Treat Perchlorate in Groundwater

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Field Evaluation of Release of Explosives Compounds from a Cracked UXO Item Using a Pan Lysimeter

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Grenade Range Management Using Lime for Dual Role of Metals Immobilization and Explosives Transformation Treatability Study

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Military Munitions Response Program Site Inspections for Formerly Used Defense Sites – Munitions Constituents Sampling

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Containment of a Perchlorate Plume from the use of Road Flares in a Wellhead Protection Area

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The Barnstable Fire Training Academy is a multi-purpose training facility for public safety officials serving Cape Cod and southeast Mass. The site has been in operation since the 1950s. The facility has been the site of chronic releases of petroleum hydrocarbons during fire training activities. Use of petroleum was ceased in 1986 when significant hydrocarbon pollution was discovered. Clean-up activities consisted of an extensive monitoring network, soil removals, vapor extraction, 18 years of pump and treat and recently a C-Sparge Perozone® system. Fire training activities have continued with the burning of straw. Expired marine and road flares are typically brought to local Cape Cod fire departments for disposal and collected at the training facility. The practice of using road and marine flares to ignite the straw was discovered at the site as the Mass DEP was promulgating a maximum contaminant level of 2 ppb, the strictest standards for perchlorate in groundwater in the nation. Groundwater sampled from the existing monitoring network revealed perchlorate concentrations ranging from trace levels to 50 ppb in a plume extending 1500 feet downgradient to public water supplies. Diluted levels of perchlorate below 1 ppb are observed in the water supplies. An Immediate Response Action is being conducted to assess and model the contaminant/water supply interactions and to recover and treat perchlorate-contaminated groundwater with a perchlorate-selective resin before it is returned to the aquifer. The IRA results will be presented along with appropriate practices for disposal of expired flares collected by public safety officials.

Perchlorate Remediation using a Novel Autotrophic, Perchlorate-Reducing Microbial Community

STUDENT PRESENTER

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Perchlorate contamination of groundwater can be hazardous to human health. Bioremediation is an economical method for perchlorate reduction. A novel microbial community that autotrophically reduces perchlorate using perchlorate as an electron acceptor and elemental sulfur (S0) pellets as an electron donor was investigated. Benefits of using S0 pellets are: the pellets are inexpensive, readily available, a versatile packing material for ex-situ and in-situ applications and the pellets serve as an excellent electron donor since bacteria grown autotrophically produce low levels of biomass, thus, reducing system maintenance. In a packed-bed bioreactor, filled with S0 pellet and oyster shell and using an enrichment culture of denitrifying sludge from a wastewater treatment plant as the microbial inoculum, perchlorate is reduced to below detection limits. We investigated the Sulfur Utilizing Perchlorate-Reducing Bacteria (SUPeRB); samples of the bioreactor packing material and the perchlorate treatment feed were examined using culture dependent and culture independent techniques. Phylogenetic analysis, using the 16S rRNA gene sequence, showed that the microbial community was predominantly composed of members of the beta-proteobacteria. Upon comparison to the GenBank DNA sequence database sequences were found to be similar to those of sulfur-oxidizing bacteria and potential perchlorate-reducing bacteria. The detection of the chlorite dismutase (cld) gene in these samples further supports the presence of perchlorate-reducing bacteria. Also, using a fluorescent in situ hybridization (FISH) probe for members of a known perchlorate-reducing bacteria genus, Dechloromonas, it was shown that Dechloromonas spp. were present in the bioreactor. Samples were diluted to extinction in broth culture to ensure isolation of perchlorate-reducing strains. Isolated strains will be grown in pure culture for further study.

Effects of Reducing Conditions on the Fate and Transport of RDX in Groundwater

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Groundwater investigations conducted at the Massachusetts Military Reservation show the impact of historic range activities on the development of groundwater contaminant plumes emanating from military ranges. Several of the plumes, located on the southeastern side of the Reservation, contain elevated concentrations of RDX. In most cases, these plumes show continuity from the source to the leading edge, indicating very little attenuation of RDX is occurring in the aquifer. An interesting exception to this trend are the plumes consisting of RDX and perchlorate which intercept part of the aquifer that has been previously impacted by a fuel spill, where reducing conditions due to biological activity persist. Whereas perchlorate shows no significant correlation with any groundwater physiocochemical parameter, RDX shows a significant correlation with oxidation-reduction potential and a significant negative correlation with specific conductance. The distribution of RDX is more consistent upgradient of the oxygen depleted zone and implies that RDX (and HMX) are degrading in the aquifer in the vicinity of the fuel spill. Possible explanations for this pattern include 1) lack of a consistent source, 2) smearing of the plume due to shifts in the apex of the aquifer, 3) biodegradation, 4) dispersion, and 5) attenuation of RDX due to reducing conditions in the aquifer. The mechanism for RDX attenuation could be explained by the reduction of nitro aromatic compounds to primary amines by an oxidation-reduction reaction.

Rejuvenation of Biowalls Used to Treat Perchlorate in Groundwater

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Biowalls are permeable reactive barriers (PRBs) that use organic media (e.g., mulch, compost, or wood chips) to provide a long-term carbon source to facilitate enhanced anaerobic biodegradation of chlorinated volatile organic compounds (CVOCs) and perchlorate. More than 13,000 feet of biowalls were installed from 2002 to 2005 in shallow weathered limestone at Naval Weapons Industrial Reserve Plant (NWIRP) McGregor, Texas to (1) reduce "source area" perchlorate plume mass, (2) remediate perchlorate-contaminated groundwater before it seeps into streams, and (3) expedite offsite property clean-up. Thirty-four biowall segments were excavated with a hydraulic excavator or rock-trencher, depending on the site geology, and backfilled with a mixture of mushroom compost, pine wood chips, soybean oil, and limestone aggregate. Diffuser pipes were installed on the bottom of each trench to allow for future injections of soybean oil or other carbon substrates as needed. Rows of bioborings, which comprise multiple, closely-spaced 12-inch diameter soil borings backfilled with the PRB media, were installed in a few locations where biowall construction was challenging due to surface conditions and an increased risk of forming a groundwater seep following trench construction.

Monitoring results indicated that the biowalls and bioborings rapidly reduced perchlorate groundwater concentrations from 1 mg/L (milligrams per liter) to below the laboratory detection limit. However, in fall 2006, after four years of operation, decreasing total organic carbon (TOC) concentrations, increasing levels of perchlorate, dissolved oxygen (DO), and nitrate, and rising oxidation-reduction potentials indicated that rejuvenation was required. Nearly 22,000 pounds of emulsified edible oil substrate (EOS®598 from EOS Remediation, Inc. of Raleigh, North Carolina) were injected using a purpose-made injection trailer to restore the treatment capacity of 15 of the biowalls that were installed in 2002.

The impact of the supplemental substrate injection on biowall effectiveness is currently being evaluated. This presentation will discuss biowall design, construction, and carbon substrate rejuvenation, and groundwater sampling results before and after the EOS® was injected.

Field Evaluation of Release of Explosives Compounds from a Cracked UXO Item Using a Pan Lysimeter

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At the Massachusetts Military Reservation (MMR) particulate residues of explosive filler and broken open unexploded ordnance (UXO) have been observed. Field investigations confirm that releases of explosive compounds such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) have resulted in groundwater plumes. Characterizing the release of these compounds is critical in evaluating future impacts to groundwater and the need for soil/UXO remediation.

Several field and laboratory studies have addressed explosives released from particulates (Lever et al 2005, Lynch et al 2002), however, few have addressed UXO. Thus, a pan lysimeter system was installed in the shallow subsurface and a cracked 155-mm munition was placed above it and exposed to the natural environment for several months. Soil porewater was collected from this apparatus periodically (the frequency dictated by precipitation events) and analyzed for RDX, 2,4,6-trinitrotoluene (TNT), and other explosives compounds. In addition, measurements of precipitation, volume of porewater collected, filler surface area exposed, and other environmental parameters were recorded.

To date, porewater from 13 sampling events have been analyzed. Observed RDX concentrations ranged from 0.4 to 8.9 ppm and TNT concentrations ranged from 0.13 to 11 ppm. Preliminary results suggest that: 1) the volume of porewater collected is typically 60% of precipitation (indicating 40% evaporation/specific retention), 2) the compounds principally being released are RDX and TNT, 3) the cumulative mass released correlates to surface area of exposed filler and "weathering" of the surface, and 4) the ratio of RDX to TNT also correlates to the degree of weathering, indicating the more soluble TNT is depleted from weathered explosive filler. Results will be compared to theoretical estimates of explosives release from perforated UXO (Praxis, 2004, Lever et al. 2005) and, ultimately, should contribute to an improvement in the ability to predict potential future release of RDX to groundwater and thereby assist in defining any required remedial actions.

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Grenade Range Management Using Lime for Dual Role of Metals Immobilization and Explosives Transformation Treatability Study

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The importance of live fire training for US forces cannot be overestimated. The success of our armed forces depends upon realistic training utilizing the actual weapons and munitions that will be used in theatre during strategic and tactical operations. However, a drawback of this type of realistic training is the potential contamination of firing ranges. Most munitions-contaminated soils found on training ranges contain a mixture of compounds. For hand grenade ranges (HGRs), the prevalent munitions used are the fragmentation grenade, typically composed of an iron shell and Composition B explosive material. Hand grenades can deposit trace amounts of both RDX and TNT at the range. The concentrations of RDX found on hand grenade ranges can pose significant health and environmental concerns depending on the range use. Metals such as zinc, iron, manganese, calcium, lead, chromium, copper, nickel, molybdenum, and vanadium are also present. Studies performed on ranges in both the United States and Canada have shown that there is a large degree of variability in munitions constituent type, concentration, size, and spatial distribution occurring on ranges. The application of hydrated lime is a useful and cost effective technology to reduce explosives from leaving live fire ranges. Under experimental conditions, the alkaline hydrolysis degraded the explosives before they left the top 15 cm of treated HGR soils. Lime application as a range management technology is currently being demonstrated at active HGRs. The field demonstration results from these ranges will be used to develop a guidance document on lime application for the dual role of metals immobilization and explosives transformation at active HGRs. As a result, U.S. military forces can continue to take advantage of large scale live fire training to support world wide operations, without significant environmental limitations imposed as a result of munitions use at ranges.

Military Munitions Response Program Site Inspections for Formerly Used Defense Sites – Munitions Constituents Sampling

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The June 2004 Department of Defense Financial Management Regulation added a new cleanup performance goal for the Defense Environmental Restoration Program. This goal is "Complete site inspections or equivalent for 100% of all munitions response sites by the end of 2010". In 2005, the US Army Corps of Engineers (USACE) initiated a programmatic Site Inspection (SI) effort under the Military Munitions Response Program (MMRP) for Formerly Used Defense Sites (FUDS) on behalf of the US Army. As of 1Q07, approximately 330 SIs have been funded and are underway throughout the US states and territories. This presentation will provide a status update of the program with a focus on the results to date of munitions constituents sampling efforts. It is anticipated that data for more than 100 sites will be available by summer 2007.

Pesticides

Abiotic and Biotic Approaches to Remediating Pesticide and Fertilizer-Contaminated Soil and Water

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Field-Scale Cleanup of a Pesticide-Contaminated Soil with a Combined Chemical-Biological Approach

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Abiotic and Biotic Approaches to Remediating Pesticide and Fertilizer-Contaminated Soil and Water

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Spills and inadvertent discharges of agrichemicals at formulating and retail facilities have contaminated soil and water. Impacted soils often contain numerous contaminants (pesticides and inorganic fertilizers), necessitating the need for multiple remedial treatments. This presentation will provide an overview of various abiotic and biotic approaches for degrading pesticides and fertilizers in soil and water. Examples of abiotic approaches include the use of chemical reductants like dithionite, dithionite-reduced sediments, and zerovalent iron (Fe^0) to transform pesticides. Biotic approaches involve the additions of carbon amendments such as sugar, peat moss and emulsified oils to stimulate biodegradation in contaminated soils. Results from our abiotic approaches indicate that dithionite rapidly transforms chlorinated pesticides in water with a stoichiometric release of chloride. Reducing aquifer and surface soils with dithionite produced reduced solids capable of dechlorinating pesticides and producing more biodegradable products. Laboratory experiments also confirmed that Fe0 could dechlorinate pesticides (metolachlor, atrazine and DDT) and reduce nitrate in aqueous solutions and that this process could be enhanced by adding small additions of $Al_2(SO_4)_3$, $FeSO_4$, or acetic acid (CH_3COOH). Field-scale application of zerovalent iron was also attempted and found to successfully remove metolachlor and nitrate but atrazine was more recalcitrant and not completely degraded by Fe^0. Combining Fe^0 (abiotic) with various organic amendments (biotic) more effectively degraded atrazine. Results from other previously completed field projects will also be presented.

Field-Scale Cleanup of a Pesticide-Contaminated Soil with a Combined Chemical-Biological Approach

STUDENT PRESENTER

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A former agrichemical dealership in North Platte, NE was suspected of having contaminated soil from multiple work-related spills. Dealership property was grid sampled and found to contain high concentrations of atrazine (>300 mg/kg) and cyanazine (>500 mg/kg). The top 60-cm of soil was removed, placed in windrows, and thoroughly mixed with a mechanical high-speed mixer. Mixing homogenized the contaminated soil and lowered pesticide concentrations via dilution. Laboratory investigations were then initiated to determine optimum treatments for pesticide destruction. Using zerovalent iron (Fe^0) as a chemical reductant along with ferrous sulfate ($FeSO_4 \cdot 7H_2O$), we observed greater than 70% destruction of both pesticides within 14 d. We also evaluated emulsified soybean oil (EOS® concentrate 598B42) as a carbon source to stimulate biodegradation and found it was also effective in degrading atrazine and cyanazine (~75%). Combining soybean oil with the chemical amendments resulted in higher destruction efficiencies (80-85 %) and reduced the percentage of $FeSO_4$ needed. Field treatments were applied (2.5 % Fe^0 + 1% $FeSO_4 \cdot 7H_20$ and Oil) to ~360 yd^3 of contaminated soil, water was added (0.30 kg water kg^{-1} soil) and soil windrows were covered with clear plastic to reduce loss of soil moisture. Temporal sampling through 60 days showed destruction of 75 to 80% for both atrazine and cyanazine. These results provide evidence that both chemical and biological approaches can be used for on-site, field-scale treatment of pesticide-contaminated soil. Investigation of pesticide degradation products are ongoing and will also be presented.

Phytoremediation

Phytoextraction of Arsenic in the Mid-Atlantic Area Using *Pteris* Ferns
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The Effects of Cyperus esculentus on the Phytoremediation of Contaminated Range Soils
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Concurrent Uptake of Semivolatile Organic Compounds and Metals by Desert Plants
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Plant Organic Matter Deposition Alters Sedimentary Organic Matter Composition and PAH Desorption
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Jennifer Musella, North Carolina State University, Raleigh, NC

Engineering Non-Food Plants for Phytoremediation of Heavy Metals and Metalloids
Om Parkash, University of Massachusetts, Amherst, MA

Investigation of Fluoride Distribution in Deciduous Trees at a Hazardous Waste Landfill
Fan Wang-Cahill, Parsons, Cincinnati, OH
Karen Fields, Parsons, Cincinnati, OH

Phytoextraction of Arsenic in the Mid-Atlantic Area Using *Pteris* Ferns

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Arsenic has been identified as a significant soil contaminant as a result of industrial applications, and its use in pesticides and herbicides in the United States and other countries, posing significant health risks to humans and animals. Because of its past wide-spread use, many large areas exist with elevated arsenic concentrations in the surface soil. Currently, there is no cost-effective method to clean large acreages of arsenic-contaminated soils. Phytoremediation has developed as a promising alternative to excavation and replacement of arsenic-contaminated soil to address some of these areas.

Selection of an appropriate plant species for arsenic phytoremediation is currently limited to ferns belonging to the Pteris genus. These ferns have shown a remarkable ability to tolerate and accumulate high concentrations of arsenic in their fronds. Although naturally adapted to a subtropical climate, these ferns can be grown in phytoremediation systems as annuals in cooler climates to remove arsenic from the soil. From 2004 to 2006 Pteris ferns were used to assist in removing arsenic from targeted residential soils in the Spring Valley area of Washington DC, resulting in more than fifteen properties requiring no further action. Phytoremediation activities at selected properties in Spring Valley will be continued in 2007.

In addition to the work being continued in Washington DC, the largest arsenic phytoremediation project to date was initiated in central Virginia in 2007 with over 20,000 fern plants being used to assist in removing arsenic from soils with elevated arsenic from arsenical pesticide applications.

This paper will present the application of phytoremediation in these two projects and discuss the benefits and challenges of implementing phytoremediation in these areas.

The Effects of *Cyperus esculentus* on the Phytoremediation of Contaminated Range Soils

STUDENT PRESENTER

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Range contamination is an issue that challenges the United States Military. Testing and training are essential elements to maintaining readiness for our armed forces. During these tactical and strategic operations, weapons and munitions are utilized to practice live-firing. Because of incomplete combustion and detonation, explosive contamination has documented at some ranges and has resulted in restriction of training activities.

Explosives, particularly hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and trinitrotoluene (TNT), have contributed to the contamination of soil and groundwater on and nearby firing range sites. Because live ammunition training is still needed, the cleanup of these contaminants may prove to be expensive. Also, the application of environmental maintenance designed to support other uses could interfere with routine testing and training operations. To avoid high cost and site interferences, an alternative being considered is the use of grasses to manage military firing ranges through phytoremediation. This technology uses vegetation to remediate contaminated soil, sludges, sediments and groundwater. Research studies have indicated that phytoremediation is effective which concludes that it could be a useful approach at active firing ranges.
This research study was conducted to evaluate the biological removal and physical stabilization of RDX and TNT range contaminated soil with the addition of *Cyperus esculentus* (Yellow Nutsedge) grass. Lysimeters were designed to assimilate natural rainfall to allow for the collection of leachate flowing through the soil as well as runoff from the soil surface. A vegetated (grass) vs. non-vegetated (control) cell was used in this study. The initial concentrations for RDX and TNT were 94mg/kg and 137 mg/kg respectively. After 15 weeks, results showed that vegetation was a factor in stabilizing RDX and TNT leachate concentrations compared to that of the control. Biological degradation accounted for 73% RDX and 23% TNT removal. Decreases in mobility indicate that this technique may stabilize explosive concentrations in addition to increasing degradation rates.

Keywords: Phytoremediation, *Cyperus esculentus*, RDX, TNT, leachate, stabilization, and degradation

Concurrent Uptake of Semivolatile Organic Compounds and Metals by Desert Plants

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Soil matrix plays an important role in the fate of organic and inorganic compounds in the environment. As a temporal and final sink as well, soil is the space where intrinsic properties of the abiotic environment interact with biotic components. The real characterization of contaminant effect to terrestrial living beings persists as a challenge both to traditional analytical and toxicology methodologies. In the risk assessment, ecotoxicologic focus is looking for the behavior of toxicants in the natural environment and it include vegetal component. Looking for a closer approach to soil complexity, microcosms essays protocols begin to be used and standardized, allow geographical location in relation to soil units.

The American Society for Testing Materials (ASTM) developed a soil core microcosms protocol (E 1197) which integrate some of these variability factors. The information generated by this bioassay can be focused at different levels. Soil physics properties, biologic and edaphic conditions can be used to test organisms of regional occurrence as plants. The same parameters will be considered to determinate the distribution of the toxic substances in the natural environment. Toxicology and analytical techniques can be used to study directly the effect of concern organic and inorganic compounds and their possible interaction in the bioavailability to plants. At molecular level, these factors determine the bioavailability in a specific unit of soil. Soil survey data provide a valuable source to delimiting and to refer the produced data of this study, in the confidence level correspondent to soil survey intensity and homogeneity of the soil area.

Plant Organic Matter Deposition Alters Sedimentary Organic Matter Composition and PAH Desorption

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PAH desorption behavior from sedimentary organic matter is an important parameter to assess PAH bioavailability. This study assessed the impact of plant organic matter on PAH desorption from labile and refractory sediments fractions at two different sites that are contaminated with petrogenic PAHs. Both sites have naturally re-vegetated with Phragmites australis; one site is a coastal refinery distillate waste pit where Phragmites has been present for several decades. The other site is a fuel-oiled freshwater canal with recent establishment (2-3 years) of Phragmites. Composite sediment samples were collected in distinct zones of barren and Phragmites areas from both sites; sediments were fractionated into bulk sediment and humin fractions prior to desorption studies. Desorption isotherms were conducted by two methods, batch aqueous and Tenax™ beads extractions. Sediment fractions were analyzed for organic matter composition by 13C nuclear magnetic resonance (13C NMR), Δ14C AMS (accelerator mass spectrometry), fourier transformed infrared spectroscopy (FTIR), and elemental analyses. PAH concentrations in sediments, water extracts, and solvent extracts of Tenax™ beads were determined by gas chromatography mass spectrometry select ion mode monitoring (GC/MS SIM). Bulk and humin sediment fractions with recently established Phragmites desorbed fewer PAHs than non-vegetated sediments. Phragmites sediments were also less polar than non-vegetated sediments due to the presence of aliphatic carbon from plant organic matter. Bulk and humin sediment fractions with established Phragmites desorbed more PAHs than non-vegetated sediment fractions. Sediment fractions from established Phragmites sediments were more polar due to the presence carbohydrate and aliphatic carbon from plant organic matter. Thus, at each site, differences in PAH desorption behavior between Phragmites and non-vegetated sediments fractions can be related to changes in sediment polarity due to plant organic matter deposition.

Engineering Non-Food Plants for Phytoremediation of Heavy Metals and Metalloids

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Heavy metals and metalloids contaminated soils, sediments and water supplies are major sources of food chain contamination and thereby endanger human health. We have developed a genetics-based phytoremediation strategy for arsenic (As) by combining the expression of bacterial arsenate reductase (*ArsC*) and γ-glutamylcysteine synthetase *(γ-ECS*) genes into single test plants *Arabidopsis* and demonstrate dramatic increases in As resistance and hyperaccumulation aboveground. When grown on As, these plants accumulated 4- to 17-fold greater fresh shoot weight and accumulated 2- to 3-fold more As than wild-type or plants expressing γ-ECS or ArsC alone (Dhankher et al., 2002, Nature Biotech. 20:1140-45). Additionally, to enhance As movement to aboveground tissues, we examined the endogenous plant activity that affects the electrochemical state and binding of As in roots. Recently, we have identified an endogenous arsenate reductase, AtACR2, from *Arabidopsis* that reduces arsenate (As^V) to arsenite (As^{III}) in plants. We knocked down the ACR2 expression using RNAi approach in *Arabidopsis* and the transgenic lines were more sensitive to As^V. The AtACR2 knockdown plants translocated 10- to 16-fold more As from root to shoot tissues when these plants were exposed to As^V (Dhankher et al., 2006, PNAS 103: 5413-18). For field phytoremediation, we are in the process of creating engineered As hyperaccumulation in a non-food high biomass plant, *Crambe abysinica*- industrial oil rapeseed, by combining the expression of ArsC and γ-ECS with AtACR2 knockdown plants. The synergistic activity of these genes could leads to more than 50-fold levels of As accumulation in aboveground tissues for later harvest.

Furthermore, we have isolated hundreds of genes from *Crambe abysinica* that are differentially regulated by As and chromium (Cr) exposure using PCR-Select Subtractive cDNA Hybridization approach. Currently, we are analyzing these genes for expression analysis and functional characterization using both forward and reverse genetic approaches. The candidate genes will be used to engineer non-food high biomass *C. abyssinica* plants for phytoremediation of As, Cr and other toxic metals contaminated soil and sediments.

Investigation of Fluoride Distribution in Deciduous Trees at a Hazardous Waste Landfill

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Phytoremediation is being considered to reduce landfill leachate volumes and mitigate the migration of groundwater that contains elevated fluoride concentrations at a Landfill in Kentucky. The landfill is a RCRA hazardous waste landfill that was used to dispose spent potliners from a nearby aluminum plant. The purpose of the project is to demonstrate the ability to use phytoremediation to reduce fluoride contamination in groundwater. Fluoride is anticipated to accumulate in plant tissues. Leaves, twigs, and trunk tissue samples were collected seasonally from mature sycamore, ash, tulip poplar, oak and sweet gum trees both in non-impacted areas (as background) and impacted areas, In addition, tulip poplar, ash, and cottonwood bare-root seedlings were planted within the fluoride plume down-gradient of the landfill prior to the leachate being intercepted by a collection trench. The results show that fluoride predominately accumulated in leaf tissues in tulip poplar trees. The ratio of accumulation between spring and full in tulip poplar leaves is approximately 5 times. Therefore, leaf collection in fall may be needed for fluoride phytoremediation using certain species of deciduous trees.

Regulatory

Beyond Horse Trading: Legal Defenses to Natural Resource Damages Claims

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PCBs in Precipitation and Surface Waters in Georgia: Are Water Quality Standards Achievable?

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Urban Polycyclic Aromatic Hydrocarbons (PAHs): A Florida Perspective

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Review of EPA-Approved Risk-Based Cleanups for PCBs under TSCA

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Changes to EPA's Spill Prevention, Control, and Countermeasure (SPCC) Program

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US Environmental Protection Agency Response to the Danversport Explosion Site

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Beyond Horse Trading: Legal Defenses to Natural Resource Damages Claims

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There has been a rapid rise in NRD claims over the past few years. Often the best method of resolving NRD claims is through an exchange of broad brushed estimates of ecological and groundwater damages. However, there are powerful legal defenses to NRD liability that may pose a serious impediment to governmental recovery. This presentation discusses the viability of such defenses under the Oil Pollution Act (OPA) and CERCLA. Defenses under OPA include: the exemption from liability for parties that do not currently own the facet or were not the last parties to own the facility before it was abandoned, the absence of the Trustee's jurisdiction over oil releases that were not into navigable waters, and failure to comply with NOAA's rigorous procedural requirements. Defenses under CERCLA include: the petroleum exclusion, CERCLA's prohibition on recovering NRD for pre-1980 releases, the statute of limitations, failure to comply with DOI's procedural requirements, and failure to select a cost effective remedy. The presentation will also discuss the recent holding in New Mexico v. General Electric, as well as the defenses that the defendant may not have caused the contamination in the first place. Knowing the full range of legal defenses is critical to achieving a fair result in negotiations and litigation.

PCBs in Precipitation and Surface Waters in Georgia: Are Water Quality Standards Achievable?

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PCBs are ubiquitous in natural waters due to their presence in the global atmosphere. Studies have demonstrated that PCB levels in precipitation reflect a regional background signal supplemented by local sources that are evident in the vicinity of urban areas. Background (non-urban) PCB levels in precipitation are on the order of 500 pg/L. The contribution of precipitation to PCB levels in receiving waters is potentially significant in that the background PCB concentrations in precipitation tend to be higher than PCB water quality standards established to be protective of fish consumption. For example, the USEPA water quality criterion for the protection of human health is 64 pg/L, and the Georgia water quality standard is 173 pg/L. PCB concentrations in Georgia surface waters distant from known point sources exceed water quality standards. To evaluate whether precipitation likely accounts for these PCBs, PCB levels were monitored in both precipitation and in surface waters in Georgia. Based on the observed similarities in both total PCB concentration and PCB composition, it was concluded that the primary source of the PCBs to these surface waters is the atmosphere. This has significant implications for the TMDL program, as well as point source discharge permitting. In Georgia, waters with fish tissue levels considered insufficient to warrant fish advisories under risk-based action levels (and therefore not listed for TMDL development) contain PCB levels in the water exceeding water quality standards. Thus, regulatory efforts to establish appropriate water quality standards for protection of human health resulting from fish consumption are confounded by the inconsistency between the various methodologies used to develop risk-based criteria, standards and advisories, as well as the available water quality and fish tissue data. It is critical to consider achievability, necessity and reliability in our efforts to ensure clean water.

Urban Polycyclic Aromatic Hydrocarbons (PAHs): A Florida Perspective

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Over the past decade, polycyclic aromatic hydrocarbons (PAHs) have steadily climbed in importance for the CERCLA list of hazardous substances. Those biennial rankings, comprised of chemicals deemed to pose the greatest potential risk to human health, have seen the PAHs go from 10th in 1997 to 7th in 2005. Though the listing does not necessarily imply that these chemicals exhibit the greatest degree of toxicity, such recognition by ATSDR and USEPA is predicated at least in part on their overwhelming ubiquity in association with many very common sources, coupled with toxicity considerations. Regulatory agencies increasingly are under pressure to define and interpret data describing urban background level, and to appropriately determine the relative importance of waste-producing activities and concentrations resulting from typical natural and/or human activity. Three case studies from Florida sites are presented that confirm the ubiquity of the PAHs at low levels, and that demonstrate the need for more sophisticated and transparent treatment by regulatory agencies. We discuss assessment and risk assessment activities related to two urban redevelopment projects (one in north-central Florida and one in central Florida), as well as one property transaction project in west-central Florida. In each case, considerable sampling of surficial soils and sediment identified total benzo(a)pyrene-equivalent (BaPeq) concentrations in the range of less than one part per million (ppm) to about the 5 ppm. Although those concentrations frequently exceeded the default Florida cleanup target level for both residential and commercial/industrial land use by a wide margin, it was concluded that they are completely consistent with levels reported in a great many urban settings. There is an ongoing need to consider the development of a default urban background level for PAHs in areas characterized by busy roadways or multiple industrial facilities, in much the same way that geological or anthropogenic background levels are established for some inorganics.

Review of EPA-Approved Risk-Based Cleanups for PCBs under TSCA

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The Toxic Substances Control Act and its implementing regulations (40 CFR 761) govern the investigation, remediation, storage and disposal of polychlorinated biphenyls (PCBs). While TSCA was designed to control the distribution of PCBs in commerce, it also governs hazardous waste site cleanups, which can be a painful fit!

Under TSCA, there are three approaches for cleanup and disposal of PCB Waste (761.61): self-implementing, performance-based, and risk-based. The self-implementing approach requires the least amount of EPA involvement, but it has the most stringent requirements, limited disposal options, and only addresses soil. The performance-based approach limits disposal options to incineration or disposal at a TSCA or RCRA Subtitle C Landfill (very costly). The risk-based approach allows the greatest flexibility to design a cost-effective remedial approach for your site. It potentially allows targeted PCB characterization sampling, less expensive treatment technologies, and less stringent cleanup standards. John H. Smith of EPA Headquarters encourages the use of TSCA risk-based approaches, as well as “mixing and matching” elements of risk-based and self-implementing approaches. Many consultants are unfamiliar with how to implement these approaches. What’s involved? How long will it take? What are the benefits?

To answer those questions, we reviewed PCB cleanups conducted with EPA review in EPA Region 1 (New England), conducted under either TSCA or CERCLA. The review was undertaken to find out what approaches were approved by the EPA, including alternative PCB characterization and verification sampling, and alternative treatment technologies. We also identified the methodologies to support the risk-based determinations, including recommended geostatistical analysis software. This review will help consultants to efficiently use the TSCA risk-based approach to design cost-effective, protective solutions for their PCB waste sites.

Changes to EPA's Spill Prevention, Control, and Countermeasure (SPCC) Program

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For more than three decades, EPA's Spill Prevention, Control, and Countermeasure (SPCC) Program has worked at several hundred thousand oil storage facilities throughout the country to prevent the discharge of oil into the waters of the United States. EPA's SPCC Regulation was promulgated under the authority of the Clean Water Act and became effective on January 10, 1974. Oil storage facilities subject to the SPCC Regulation must prepare written SPCC plans detailing the facility's spill prevention and control measures and have the plans certified by a licensed Professional Engineer. Certain facilities may now be eligible to self-certify their own SPCC plans. Facilities must fully implement their written SPCC plans including: constructing secondary containment or diversionary structures to contain spills from tanks, piping, transfer areas, and loading racks; training oil-handling employees; and conducting regular inspections of oil storage, handling, and transfer areas. Substantial revisions to the SPCC Regulation were passed on July 17, 2002, December 12, 2006, and May 10, 2007, in the first instance revising the Regulation with stricter spill control requirements but extending the compliance date for certain facilities to October 31, 2007, in second case providing relief to many qualified facilities within the regulated community, and in the last instance further extending the compliance date for certain facilities to July 1, 2009. This presentation will review the history and scope of the SPCC Regulation, describe the streamlined, alternative methods now available to facilities for compliance with the new requirements, and clarify the eligibility criteria for facilities wishing to take advantage of the July 1, 2009 compliance date extension.

US Environmental Protection Agency Response to the Danversport Explosion Site

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On early Wednesday morning, November 22, 2006, an explosion at the CAI Incorporated facility in Danversport, Massachusetts destroyed the facility and severely damaged many surrounding buildings and homes. The explosion was large enough to register 0.5 on the Richter scale at the Boston College observatory, almost 30 miles away in Weston, and resulted in a 10 alarm fire. Residents of the densely populated area were evacuated to protect them from the fire and exposure to hazardous materials.

The US Coast Guard, Massachusetts Department of Environmental Protection (MA DEP) and US Environmental Protection Agency (US EPA) all responded to assist the local and State emergency response teams. The MADEP and US EPA began ambient air monitoring early on the morning of the explosion to assess the potential exposure of the neighborhood and responders to air-borne contaminants. In addition, water and sediment samples were collected from Waters River to assess releases to the marine environment. The clean up consisted of removal of drums, above ground vats and product from underground storage tanks, and excavation of contaminated soil. This paper will discuss the response and the results of the environmental monitoring and clean up.

Remediation I

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The Effect of Coal Tar on Geomemberane/Geosynthetic Clay Liners in Coal Tar Impacted Soil

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Deep Soil Amendment Alternative for Foundation Construction & Treatment of LNAPL Impacted Soil Deposits

Brandon J. Fagan, Haley & Aldrich, Inc., Boston, MA
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Remediation of Trichloroethene DNAPL and Groundwater Plume Using Enhanced Anaerobic Degradation Technology and Natural Attenuation

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Electrical Resistance Heating of Soils at C-Reactor at the Savannah River Site

Robert Blundy, Washington Savannah River Company
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Habitat Restoration and Challenges Faced in Remediation of Coal Tar in the Connecticut River

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Nanomaterials for Remediation: Applications and Implications

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The Effect of Coal Tar on Geomemberane/Geosynthetic Clay Liners in Coal Tar Impacted Soil

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Vertical containment barriers have often been considered for use at former manufactured gas plant (MGP) sites as an interim measure or as a permanent remedy to contain coal tar dense non-aqueous phase liquid (DNAPL), coal tar impacted soils and/or groundwater. The design and implementation of these vertical containment barriers must be carefully considered to meet site remediation objectives and site conditions. Traditionally sheet pile walls were the standard protocol when it came to installing a vertical barrier. However, the rising cost of steel and associated installation costs have made this option economically undesirable. Recent advances in technology have introduced alternative media such as geomembrane/geosynthetic liners (GM/GSL). Unfortunately, selecting an appropriate GM/GSL is very difficult due to a lack of chemical compatibility data between the commercially available GM/GSL and coal tar DNAPL. This paper presents a compatibility study conducted to evaluate different GM/GSL for their compatibility with coal tar DNAPL.

The study simulated the emplacement of the GS/GSL in the granular unit that is impacted with coal tar DNAPL and determined the effect of coal tar DNAPL interaction with the GS/GSL. The GS/GSL were evaluated based upon both visual observations such as deformation and breakage and laboratory tests such as tensile strength and tear resistance. Nine (9) different commercially available GM/GSL were evaluated in the study. This paper will explain the containment approach, present the design elements of the containment and compatibility testing, and discuss the results of the chemical compatibility studies conducted in the laboratory.

Deep Soil Amendment Alternative for Foundation Construction & Treatment of LNAPL Impacted Soil Deposits

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State building code allowances limited construction of a building addition on filled soils with spread footings. Construction of the structure over a 4-acre LNAPL plume would limit future access to remediation. Site conditions included a 9 foot deep urban fill soil deposit over a conductive glacio-fluvial formation abutting a four story historic building. The site area was underlain by a weathered No. 6 fuel oil LNAPL plume impacting soils at a depths of 13 to 18 feet below ground surface. Existing building foundations constructed with dry field stone foundations supporting the institutional building represented potential building instabilities with excavation.

Selected treatment under the proposed building to establish a permanent solution was evaluated after exhaustive evaluations of alternative locations. Facing limitations on capacity for services in the dining area/facilities, design development was undertaken to institute combined soil strength improvement of the fill, foundation reinforcement and in-situ solidification/immobilization of the LNAPL source utilizing jet grouting techniques. Environmental considerations for soil solidification for performance validation of LNAPL treatment utilized an alternative to TCLP analysis - a modified ANSI 16.1 Static Leaching Procedure to validate t jet grout soil excavation in addition to replacement of the LNAPL soil horizon with a low permeability grout mix ($k<10^{-6}$ cm/s).

Success of the project was measured based on treated soils meeting MA Method 1, S-1 soil standards. The soil treatment was validated based on extractable petroleum hydrocarbon (EPH) procedures and analysis and comparison of the residual saturation of the solidified matrix with field samples. Building underpinning using the same solidification mix met soil strength improvement to excesses of 300 psi unconfined compression strength without building movement. The fill matrix was stabilized from jetting for building construction with spread footings matching existing foundation depths and structural design soil bearing capacity of 0.5 tsf for a 2 story addition.

Remediation of Trichloroethene DNAPL and Groundwater Plume Using Enhanced Anaerobic Degradation Technology and Natural Attenuation

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Enhanced in situ reductive dechlorination of a TCE DNAPL source and 900-foot TCE groundwater plume using a combination of HRC® and HRC-X™ was performed at a former pharmaceutical facility over a 46-month treatment period. The maximum observed initial TCE groundwater concentration in the source area was 390,000 µg/L, despite eight years of prior remediation efforts that included a pump and treatment system. Initially, 39,600 lbs of HRC® were injected into 133 borings in a combination of a grid and barrier applications covering a 40,000 ft^2, treatment area. After 18 months, 31,290 lbs of HRC-X™ were injected into 123 injection borings that expanded the treatment area to cover approximately one third of the total plume area. Groundwater performance monitoring has been performed plume-wide throughout the treatment period. The maximum observed TCE groundwater concentration after the 46-month treatment period has been reduced to 29,000 µg/L and the calculated total mass of TCE (sorbed and dissolved) in the most heavily impacted portion of the plume, approximately 16,000 ft^2, has been reduced by 90%. The reduction in the TCE mass fits a first-order degradation model extremely well, with a R^2 value of 0.92. Complete degradation of TCE within the groundwater plume has been demonstrated based on observed reductions in the total molar concentration of TCE and its daughter compounds and the detection of ethene in post-application groundwater samples. Site-specific BIOCHLOR groundwater modeling and empirical data indicate that intrinsic reductive dechlorination is robust in the downgradient portions of the TCE plume. A natural attenuation remedy based on site-specific source area TCE point decay rate constants and groundwater modeling is planned to meet the state TCE groundwater standard of 2.8 µg/L near the downgradient property boundary and achieve site closure.

Electrical Resistance Heating of Soils at C-Reactor at the Savannah River Site

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Chlorinated solvent contamination of soils and groundwater is a significant problem at the Savannah River Site, and originated as by-products from the nuclear material process. Five nuclear reactors at the Savannah River Site (SRS) produced special nuclear materials for the nation's defense program throughout the cold war era. An important step in the process was thorough degreasing of the fuel and target assemblies prior to irradiation. Discharges from this degreasing process resulted in significant groundwater contamination that would continue well into the future unless a soil remediation action was performed. The largest reactor contamination plume originated from C-Reactor and an interim action was selected in 2004 to remove the residual trichloroethylene (TCE) source material by electrical resistance heating (ERH) technology. This would be followed by monitoring to determine the rate of decrease in concentration in the contaminant plume. Because of the existence of numerous chlorinated solvent sources around SRS, it was elected to generate in-house expertise in the design and operation of ERH, together with construction of a portable ERH system that could be deployed at multiple locations around the site. This paper describes the waste unit characteristics, the ERH system design and operation, together with extensive data accumulated from the first deployment adjacent to the C-Reactor building. The installation heated the vadoze zone down to 62 feet bgs over a 60 day period during summer of 2006 and raised soil temperatures to over 200 oF. A total of 730 lbs of TCE were removed over this period and subsequent soil sampling indicated a removal efficiency of 99.4%.

Habitat Restoration and Challenges Faced in Remediation of Coal Tar in the Connecticut River

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The Holyoke Gas Works operated from 1852 until 1951 and played an important role in the industrial development of the city of Holyoke, Massachusetts. A legacy of its operation included releases of coal tar to the Connecticut River, resulting in the deposition of hardened, asphalt-like tar patches on the river bottom. These coal tar deposits were subsequently identified in an area known to provide habitat for the federally endangered shortnose sturgeon (Acipenser brevirostrum) and two state-protected mussel species. The National Oceanic and Atmospheric Administration and the Massachusetts Department of Environmental Protection (MADEP) made presumptive determination that risk to an endangered species existed and mandated remediation, consequently, a site-specific ecological or human health risk assessment was not conducted. The Remedial Action Plan, involving mechanical excavation methods in both dewatered and submerged conditions, predicted that remediation efforts would be completed within a two year period. Remediation efforts began in 2002 but due to significant logistical and technical challenges, including limited site access, sensitive biological resources and large variations in river flow, velocity, and depth, remediation of the originally identified patches has not been completed. In addition to these technical challenges, a significantly larger quantity of coal tar was uncovered during excavation and during episodic storm events. Further delineation efforts conducted in 2006 within a three mile stretch of the river has resulted in the discovery of significantly more surface exposed coal tar than previously identified. Due to the hardened physical nature and apparent inert characteristics of theses newly identified patches, a proposed risk assessment to prioritize cleanup goals is being reviewed by MADEP. This paper discusses, remediation implementation, lessons learned and regulatory hurtles facing the project as it moves forward to complete its habitat restoration objectives.

Nanomaterials for Remediation: Applications and Implications

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Nanotechnology is a current source of exciting and novel materials with numerous potential applications for remediation of contaminated soils and water. Nanomaterials (NM) include an array of engineered materials that, by definition, are designed and produced to have at least one dimension that is 100 nanometers (nm) or less (1,000 times smaller than the width of a human hair). The variety of NM that have been used or are in development for remediation purposes include nanoscale zerovalent iron, reactive nanoscale iron particles, dendritic NM and carbon nanotubes (CNT) embedded within filtration media; some of their applications include removal of contaminants, such as chlorinated hydrocarbons and arsenic, as well as water filtration, purification and desalination. However, the unique NM properties that contribute to both their beneficial aspects and their potential toxicity are the enhanced reactivity due to the large surface area relative to size and the fact that even common elements like carbon behave differently at the nanoscale level. An important question that emerges regarding application of NM for remediation is whether their use will present new and unanticipated risks for human health and the environment. This presentation will review the types of NM that can be used for remediating soils and water, results of case studies using specific NM, recent information on NM toxicology, and up-to-date positions of federal agencies regarding potential risks for the use of NM. Understanding both the benefits and risks of these new NM can inform good-decision-making regarding the use of these innovative materials to address environmental concerns.

Remediation II

Application of Electrochemical Techniques for the Remediation of Soils Contaminated with Organic Pollutants
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Gianni Andreottola, University of Trento, Trento, Italy

Comparison of Remedial Systems Employed at Drycleaner Sites
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Adjustable Depth Air Sparging Case Study
Michael C. Marley, XDD, LLC, Stratham, NH
Matthew T. Walsh, XDD, LLC, Allentown, PA
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Remediation of Asbestos in Soil under the New Massachusetts Department of Environmental Protection Regulations
James R. Fair, Weston & Sampson Engineers, Inc., Peabody, MA
Prasanta K. Bhunia, Weston & Sampson Engineers, Inc., Peabody, MA

Five-Year Performance Evaluation of a Permeable Reactive Barrier, Needham, Massachusetts
Peter Richards, Massachusetts Department of Environmental Protection, Wilmington, MA

Re-Remediating: Post-Closure Excavation after Source Zone Translocation and MNA Ineffectiveness – A Case Study
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Application of Electrochemical Techniques for the Remediation of Soils Contaminated with Organic Pollutants

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Direct Current Technologies (DCTs) are techniques for contaminated soil remediation, in which an electrical field is created in the polluted medium by applying a low-voltage direct current across electrodes placed in the ground. This study aimed to evaluate the feasibility of using DCTs for the remediation of different organic contaminants from various types of fine grain soils and sediments. For this purpose, a one-dimensional experimental setup for bench scale testing was assembled, and several laboratory tests were performed. The experimental setup included an electrochemical cell, two stainless steel plate electrodes, a stabilized DC generator and tanks for the pore fluid collection.

Two types of soils contaminated by diesel fuel and sediments polluted by polycyclic aromatic hydrocarbons (PAHs) were considered in this investigation. In the experiments the contaminant removal was evaluated under the influence of the electric current generated by a constant potential difference (0.5-6 V/cm) for a fixed period of time (7-28 days). The results showed that a good degree of organic pollutant removal could be achieved via electrochemical methods. About 90% contaminant removal was achieved for PAH-contaminated sediments after a four-week treatment, while the tests with diesel fuel-contaminated soils resulted in about 45-55% TOC removal and 70-85% TPH removal. The main factors influencing the process seem to be the process duration and the soil mineralogy, especially the iron content of the treated medium. On the opposite, the applied voltage seems to have a limited influence on the contaminant removal efficiency, good results being achieved with specific voltages as low as 1 V/cm. The results achieved suggest that DCTs can be effectively used for the mineralization of many organics with low energy expenditure, especially in very fine soils, like clays, which are often more difficult to treat with conventional chemical methods, because of their low permeability and high sorption capacity.

Comparison of Remedial Systems Employed at Drycleaner Sites

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The State Coalition for Remediation of Drycleaners (SCRD) analyzed data from over one hundred site profiles collected from drycleaning site remediation projects across the United States. The comparative analysis evaluates the various remedial technologies and assessment techniques used at chlorinated and petroleum solvent sites. Site data included physical site characteristics, hydrogeology, geology, soil/groundwater contaminant concentrations and distribution, remedial systems employed, site closures, and costs. The paper presents a current snapshot of remedial technologies being employed in most of the states with programs dedicated to remediation of contaminated drycleaning sites. Although conventional remedial technologies have been utilized at many of these sites, chemical oxidation and bioremediation are being employed more frequently. Bioremediation has been employed at over 23% of the sites in this study; while, chemical oxidation was used at 23.3% of the sites.

Site data were analyzed to determine trends regarding remediation successes or failures. Success and/or failure are often difficult to ascertain because of site and program limitations. Some useful observations can however be made regarding certain technologies. Graphical analysis of the data can indicate trends in remediation technology selection. The technology selection process is driven by a variety of technical and programmatic factors, such as: physical site limitations, cost, desired cleanup time, risk-based determinations and expertise of remedial design staff or consultants. Ideally, the audience will be able to use the information in this report to help in the decision-making process when selecting a proven remediation technology for their drycleaning site, or at a site with similar characteristics. When completed, the paper will be available on the SCRD Web Page at www.drycleancoalition.org.

Adjustable Depth Air Sparging Case Study

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Air Sparging is a commonly deployed environmental remediation technology by which pressurized air is injected into a contaminated groundwater zone to remove harmful volatile contaminants. The injected air strips the contaminants from a liquid phase to a vapor phase and transports the volatile compounds via air channels to the unsaturated zone.

The extent of air distribution within the remedial zone of an air sparging site affects the level of contact between the air and the target contaminants and therefore is one of the primary factors leading to a site's successful cleanup. Typically, the greater the uniform air distribution, the greater the contaminant removal rate. Present systems use discrete depth air sparge wells to inject into the subsurface. It has been demonstrated that by varying air injection depth using a composite set of wells, one is able to increase the level of air distribution and therefore significantly improve upon remedial performance.

The Navy has developed a new and innovative technology called Adjustable Depth Air Sparging (ADAS) that is applied within a single air sparge well with infinite adjustability. The technology has the capability to be used with conventional air sparging equipment and methods to help increase overall air distribution and therefore lower project costs and improve cleanup performance.

Results from a site demonstration conducted by XDD at a Superfund Site in NJ of the ADAS system will be presented. Testing of the ADAS system showed that air could be injected at a variety of depth intervals in a single well by simply raising and lowering the technology's packer system. The results confirmed that vertical adjustments to sparging depth clearly influenced and improved the achievable mass removal rate at the demonstration site.

Remediation of Asbestos in Soil under the New Massachusetts Department of Environmental Protection Regulations

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The public involvement, pilot study, and construction processes implemented to remediate asbestos-contaminated soil at a former industrial dumping area in Massachusetts will be presented. Because the asbestos-contaminated site is located within a high profile and densely populated area, innovative approaches to perform the work effectively and safely with public confidence is essential. The project will be conducted in accordance with the recently revised Department of Environmental Protection (DEP) asbestos in soil regulations, and will include conducting an innovative pilot study to help gain public support. In addition to the pilot study, the full-scale remediation process and Best Management Practices (BMP) to be implemented to achieve No Significant Risk (NSR) will be discussed, along with a review of the current asbestos in soil regulations. Asbestos in soil analytical methods and risk-based closure approaches utilizing the Superfund Elutriator method and the DEP activity-based sampling method will also be presented.

Five-Year Performance Evaluation of a Permeable Reactive Barrier, Needham, Massachusetts

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In July 2001 the Massachusetts DEP installed a permeable reactive barrier (PRB) to treat a groundwater plume of chlorinated solvents migrating from an electronics manufacturer in Needham, Massachusetts toward the Town of Wellesley's Rosemary Valley wellfield. The primary contaminant of concern at this site is trichloroethene (TCE), which at the time had a maximum average concentration of approximately 300 micrograms per liter directly upgradient of the PRB. The PRB is composed of a mix of granular zero-valent iron filings and sand with a pure-iron thickness design along its length between 0.6 and 1.7 feet. The PRB was designed to intercept the entire overburden plume; previous study had indicated that the contaminant flux in the bedrock was negligible. Groundwater samples have been collected from monitor wells upgradient and downgradient of the PRB on a quarterly basis since installation. Inorganic parameters such as oxidation/reduction potential, dissolved oxygen and pH are also measured to determine stabilization during the sampling process. Review of the analytical data indicates that the PRB is significantly reducing TCE concentrations along its length. However, in two discrete locations TCE concentrations show little decrease in the downgradient monitor wells, particularly in the deep overburden. Data available for review include the organic and inorganic analytical data, slug test results from nearby bedrock and overburden wells and upgradient and downgradient water level information. These data will aid in refining the conceptual site model for the PRB and in evaluating its performance.

Re-Remediating: Post-Closure Excavation after Source Zone Translocation and MNA Ineffectiveness – A Case Study

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High concentrations of benzene and other petroleum constituents were measured in the groundwater and soils beneath a former filling station in Gallup, New Mexico, fifteen years after leaking underground storage tank closure and removal. The persistence of the constituent concentrations indicated the inability of monitored natural attenuation (MNA) to successfully remediate the site soils and achieve cleanup goals. Subsurface investigation results suggested source zone translocation caused by non-aqueous phase liquid (NAPL) migration in response to pumping well drawdown of the phreatic surface, and subsequent impact to new soils as a smear zone. Mitigation of human exposure, funding availability and the likelihood of upcoming redevelopment led to the decision to excavate the expanded source to a depth of 16 feet below ground surface and an estimated volume of 2500 cubic yards. Simple in concept, the excavation was constrained by limitations on equipment access, slope stability, and the need to protect surrounding utilities, sidewalks and streets. Backfill material was selected to provide low compressibility and high bearing capacity, while being based on local availability. A detailed protocol for monitoring slope movements was implemented and strict limits imposed on personnel access to the excavation areas, to reduce risks from excavation instability while balancing the need for stable, compacted backfill. Air emissions required OSHA Level B protections and impacted nearby businesses, triggering adjustments to the excavation sequence. Off site hauling and the requirements for truck traffic through the surrounding community controlled the project schedule, while insufficient stockpile areas dictated the site layout and operation. Evaluation of this project provides a design template for similar projects of post-closure source excavation in urban areas.

Risk Assessment

Health Effects of Exposure to Soils Contaminated by Hydrocarbon or Heavy Metal Compounds

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Moss Point Community Exposure to Contaminants from a Releasing Facility

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Soil Vapor Intrusion Data – Planning and QA/QC Evaluation for Risk Assessment

Nancy C. Rothman, New Environmental Horizons, Inc., Skillman, NJ
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Application of Geostatistics and Risk Assessment to Property Divestitures

Betsy Ruffle, ENSR, Westford, MA
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Unintended Environmental Risks from Processes and Products Intended to Reduce Environmental Risk

William A. Farone, Applied Power Concepts, Inc., Anaheim, CA

Quite a challenge: Assessment of the Human Health Risks of Asbestos in Soils. A Tiered Approach

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Health Effects of Exposure to Soils Contaminated by Hydrocarbon or Heavy Metal Compounds

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The potential health risk from exposure to chemically contaminated soil is traditionally based on the quantity of chemical that can be removed from soil by vigorous chemical extraction procedures. The approach can overestimate risk since it ignores the complex interactions between chemicals and soil that can result in the reduction in the amount of chemical that desorbs from soil and subsequently absorbs by the body, i.e., bioavailability. The aim of these studies was to determine the dermal bioavailability of soil contaminated chemicals for representatives of hydrocarbon and heavy metal classes of chemicals and examine the relative contribution of soil matrix and chemical sequestration in soil with time ("aging"). In vitro, flow-through diffusion cell studies were performed utilizing dermatomed male pig skin and radioactive chemicals to measure total penetration (sum of each chemical in skin and receptor fluid). While volatilization alone was predominant in reducing the dermal penetration of toluene, immediate contact with soil further reduced skin penetration by 29 fold. Benzo(a)pyrene penetration was reduced >88% following immediate contact with soil, with further reduction occurring after aging for 3 months particularly with soil of high clay content. Similarly, immediate soil contact reduced the dermal penetration of arsenic, mercury and nickel with further reductions occurring after 3 months aging in soil, particularly of high clay content. The results indicate that the potential health risk from dermal exposure to the chemicals studied can be significantly reduced by soil and aging.

Moss Point Community Exposure to Contaminants from a Releasing Facility

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In 2006, a Morton International Inc. facility in Moss Point, Mississippi, was issued the largest-ever civil fine for environmental violations at a single facility by the U.S. Environmental Protection Agency (EPA). The civil settlement was filed by the Justice Department on behalf of the EPA and the Mississippi Department of Environmental Quality (MDEQ). Morton also pleaded guilty to criminal violations of the Clean Water Act and the Resource Conservation and Recovery Act and agreed to pay a $2 million criminal penalty for these violations. The Moss Point Releasing Facility in Jackson County produces plasticizers, synthetic rubber, rocket polymers, and other chemicals and adhesives. Limited tap water sampling was conducted and many homes tested positive for acetamide, ocyclohexanone, and octadecenamide. The extent of the contamination has not been properly characterized or quantified. Many of the chemicals found in the drinking water samples are not regulated and not required to be quantified by the EPA. This paper describes the future uncertainty relating to community exposure to a variety of contaminants from this long term release.

Soil Vapor Intrusion Data – Planning and QA/QC Evaluation for Risk Assessment

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Vapor intrusion, the migration of vapors into a building from the subsurface originating from contaminated groundwater or soil above the water table, has emerged at the forefront of current environmental issues at many sites. Subsurface contamination of volatile organic compounds (VOCs) that exceed regulatory cleanup standards or risk-based concentrations of concern often lead to the requirement to evaluate the risk of an inhalation pathway at the site or off-site, using soil vapor or indoor air sample data. To generate VOC data that will be valid and usable in the risk calculation of exposure point concentrations, the specific sampling and analysis methods must be tailored to improve the representativeness of the sample, decrease VOC losses, and increase overall accuracy and sensitivity of the soil vapor or indoor air sample. VOC results are impacted by field sampling issues such as weather, pressurization of the SUMMA® canister, placement of the sampling train, and interpretation of field quality control samples. Choice of method of analysis (e.g., TO-15), target compound list, and the mode in which the gas chromatography/mass spectrometer (GC/MS) is run for VOC analysis, such as selected ion monitoring (SIM) vs. electron impact (EI), will effect the accuracy and sensitivity of the results. We use real-world examples from CERCLA and state-led sites to explore the impacts of these field and analytical issues on the interpretation and usability of VOC data in air samples. We provide recommendations on how to collect and analyze the samples correctly to obtain usable data for site assessment and risk characterization.

Application of Geostatistics and Risk Assessment to Property Divestitures

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Divestiture of contaminated properties poses environmental and legal challenges for companies. This paper examines an approach that incorporates risk assessment and geostatistics to allow the owner to assess and manage divestiture risks associated with the potential for future liability at the property. This approach applies geostatistics to demonstrate with a desired level of confidence (e.g., 90%) whether significant soil impacts have been identified.

Available soil data are analyzed using standard risk-based approaches to quantify potential risks associated with current and future exposure scenarios. Risk-based target levels (RBTLs) are derived for the risk-driving compounds and applicable exposure scenarios. Soil concentrations below the most restrictive RBTLs will be acceptable for all other potential exposure scenarios.

A geostatistical analysis of available soil data is performed. Two soil intervals (surface and subsurface) are typically considered. For each interval, a map is generated to delineate areas within which there is 90% confidence that concentrations are greater than the RBTL. A second map delineates areas outside of which there is 90% confidence that concentrations are less than the RBTL. Regions between these two areas represent lower confidence in the estimated concentrations. If these regions represent areas of significant impact, more samples are necessary to increase the confidence in the estimates. Significant impact is defined as an area where the concentration within a site-specific target volume of soil is greater than the RBTL.

Based on the initial geostatistical analysis, locations of additional soil samples needed to reduce uncertainty in the regions of lower confidence are identified. The geostatistical analysis is then updated with results of the supplemental samples, and new maps are generated. Typically, one supplemental soil sampling event is sufficient to demonstrate with desired confidence that there are no significant areas of impact that have not been identified.

Case examples of this approach will be presented.

Unintended Environmental Risks from Processes and Products Intended to Reduce Environmental Risk

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For the last 50 years there has been a strong movement to reduce environmental risks from modern society. From the removal of phosphates in detergents in the 1970s through to the wind energy projects of the eighties, the bioremediation and chemical remediation technologies of the 1990s and today, personnel of Applied Power Concepts, Inc. have been involved in this movement. For each of the potentially beneficial products and processes an alternate risk is possible. This presentation provides a historical perspective of these risks from carcinogenicity of potential phosphate alternatives; birds kills, oil leaks and sound pollution from wind turbines; ozone and reduced energy efficiency from ethanol use; increased groundwater and air pollution from gasoline additives; cancer risk from nanoparticles: and many more. The risk to benefit ratio of many of these cases are not in the news when the technologies, products and products are embraced. The result is that the risks come as a surprise when widespread investment in both money and faith has already occurred.

Quite a challenge: Assessment of the Human Health Risks of Asbestos in Soils. A Tiered Approach

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The behavior of asbestos in soil differs from other contaminants. For that reason, neither standard fate and transport processes, nor standard exposure calculations are applicable for assessing human health risks. Therefore, an alternative tiered approach for the assessment of human health risks of soil contamination with asbestos has been developed. When in a specific tier the human health risk can not be rejected the assessment in the following tier has to be performed. The underlying principle is: “simple when possible and complex when necessary”.

In Tier 0 a generic soil quality standard is used. This Intervention Value is 100 mg/kgdw for the sum of the concentration of chrysotile asbestos (or serpentine asbestos or white asbestos) and ten times the concentration of amphibolic asbestos (other asbestos types) for bound (non friable) as well as for friable asbestos. In contravention with the standard procedure prescribed in the Dutch Soil Protection Act this value is derived from measured concentrations of asbestos in soil and air and not using the CSOIL exposure model. Tiers 1 to 3 are site-specific. Tier 1 concerns a simple, qualitative testing procedure, in which the potential or probability of exposure is investigated. In Tier 2 the respirable fraction in the soil, which relates to the potential emission of asbestos fibres and hence to the site-specific exposure to humans through inhalation, is determined and tested. Finally, when the risk can not be excluded, the concentration of asbestos fibres in outdoor and (when applicable) in indoor air has to be measured and tested in Tier 3, according to a standardised protocol.

Recently, this tiered approach was incorporated in the revised “soil quality assessment framework” in The Netherlands.

Sediments

Use of XRF to Characterize Mine Waste Sediment in a Marine Environment

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The Use of Constructed Wetlands for the Treatment of Heavy Metals in Urban Stormwater Runoff

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Electrokinetic Treatment of Marine Sediments Contaminated by Heavy Metals

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Use of XRF to Characterize Mine Waste Sediment in a Marine Environment

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MACTEC utilized XRF for metals analysis of estuarine sediment samples collected to delineate lateral and vertical extent of contamination in support of a remedial investigation/feasibility study (RI/FS) to complete a record of decision (ROD) at a former copper, lead, and zinc sulfide ore mine site on a unique coastal location in Maine. Five hundred and thirty seven samples were collected and analyzed by on-site XRF during a 15 day period. Sufficient sediment volume was collected to fill soil jars. Aliquot was prepped and analyzed in accordance with EPA Method 6200. Remaining original sample was archived. Thirty seven sediment samples (seven percent) were submitted to a contracted commercial laboratory for metals analysis by EPA Method 6010B (ICP)/6020 (ICP-MS). Samples were analyzed for antimony, arsenic, barium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, selenium, silver, thallium, and zinc. Metal concentrations reported by commercial laboratory were compared to on-site XRF concentrations to determine precision, accuracy, and bias of XRF data. Average relative percent differences (RPDs) between XRF and commercial laboratory results ranged from 24 to 68 for copper (24), lead (58), zinc (37), arsenic (68), and manganese (35) indicating good comparability. Barium (192), cadmium (91), and chromium (196) had high average RPDs. General trend of higher concentrations reported by XRF observed indicating possible high bias. Of the 176 calculated RPDs, 70 exceeded 50 (EPA Region I guidelines comparing solid matrices field duplicates). Statistical analysis of variance and comparison of RPDs to grain size analyses were reviewed to determine usability of data and effects on XRF quantitation of metals in sediment. Overall agreement was observed using XRF analysis supported by commercial laboratory confirmation. The XRF demonstrated to be an effective, cost-saving instrument to support contamination assessments of copper, lead and zinc in sediments at the coastal former mine site.

The Use of Constructed Wetlands for the Treatment of Heavy Metals in Urban Stormwater Runoff

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The presence of heavy metals in stormwater runoff is a major concern due to their toxicity, bioavailability, and persistence in the environment. The sources of heavy metals are varied, and their geochemical partitioning in stormwater runoff is significantly influenced by the land-use pattern. Stormwater runoff investigations increasingly focus on evaluating quality and the effectiveness of adopting best management practices (BMPs) to minimize heavy metal inputs to receiving waters. Structural BMPs such as constructed wetlands primarily rely on sedimentation to reduce heavy metal loads associated with particulate matter and improve runoff quality. The continued accumulation of heavy metals in these sediments can lead to their migration and increase the risk for ground and surface water quality deterioration downstream. Additionally, they may also be toxic to benthic invertebrates and aquatic microorganisms downstream of the BMP. These accumulated sediments have to be routinely removed to minimize the risk of contamination and maximize the operational efficiency of these BMPs. However, the frequency of such maintenance practices and the handling of sediments require a full understanding of the quantity and quality of the deposits, especially with reference to their heavy metal content. Chemical speciation studies help in understanding and controlling the behavior of heavy metals, and are recognized as a necessary requirement in designing an effective BMP maintenance protocol. This research is being conducted at U.S. EPA's Urban Watershed Research Facility in Edison, NJ, to evaluate the relative efficiencies of wetlands and retention ponds in attenuating heavy metal loads in urban stormwater runoff. BMP removal efficiencies were assessed for both particulate and soluble heavy metals. The geochemical associations of heavy metals in wetland sediments were investigated by sequential fractionation procedures in order to understand heavy metals behavior in BMP sediments. Additionally, a stormwater wetland BMP in the Staten Island Blue Belt (New York) was monitored to investigate the effects of maintenance and clean up procedures on sediment heavy metal loads and their speciation. Results from different stormwater sampling and sediment monitoring events will be discussed.

Electrokinetic Treatment of Marine Sediments Contaminated by Heavy Metals

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Sediment contamination is a complex technical framework which requires the study of different treatment alternatives. Sediment contamination is problematic also for marine trade routes; in fact, although sediments can be left in place covered by a low permeability capping and innovative in situ treatment technologies are under development, around 500 millions m3 have to be dredged each year for navigational purposes and 1-4% of these requires dewatering and treatment prior to disposal. Despite decades of research, surprisingly little is known about successful treatment of contaminated sediments, which are usually landfilled after dredging. While in soils the contaminated fine fraction is typically less than 50% of the total solid matrix, in sediments usually the opposite occurs, 80-95% are generally very finely grained particles. In these cases many treatment technologies have proved to be ineffective in order to achieve a reduction of the contaminant concentration. Electrokinetics could represent a possible solution in order to achieve dewatering and removal of heavy metals and salts in a single stage. Electrokinetics is reported among the viable treatment alternatives for dredged marine sediments worth to be investigated. In this framework electrokinetics was applied on two types of marine sediments sampled from the Veneto and South-West Sardinian coasts (Italy) in order to achieve at the same time dewatering and removal of heavy metals and salts. The sediments were previously characterised for the contaminant content and the main chemical-physical properties which influence the treatment. Tests were performed either on samples pre-washed with soft water or on samples with the natural content of salts. The efficiency of the process was evaluated on the basis of the achieved cathodic flow and of the residual concentration values of salt and contaminants in the solid sample. The results of the tests proved that the different characteristics of the sediments mirror in the achieved heavy metal removal.

Site Assessment

Laser-Induced Fluorescence for the Delineation & Characterization of Fuel-Contaminated Soils in Subarctic Climates

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Use of a Collaborative Dataset to Enhance Data Representativeness

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Use of Borehole Geophysical Logging, Packer Testing, and Discrete Groundwater Sampling in Assessment and Remediation of a Release of #2 Fuel Oil at a Western Massachusetts Residence

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Sampling Sediment Porewater in the Lower Duwamish Waterway Using a Passive Sampler

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A Study of Tritium in Municipal Solid Waste Leachate

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The Repeated Trespass of Tritium-Contaminated Water into a Surrounding Community from Repeated Waste Spills from a Nuclear Power Plant

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Laser-Induced Fluorescence for the Delineation & Characterization of Fuel-Contaminated Soils in Subarctic Climates

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Fuel-contaminated sites are common projects for environmental professionals. A key factor in successfully designing a remedial approach for these sites is an accurate estimate of the nature, quantity and location of contaminated soil. This is problematic with standard sampling techniques, often leading to large errors, extended field work and cost overruns. These problems are magnified in Alaska and other regions where short work seasons and difficult logistics are common. Using a real-time, in situ laser-induced fluorescence (LIF) technique, the Corps of Engineers has been able to delineate fuel-contaminated soils with great accuracy in and above the saturated zones. The technology can also differentiate between contaminant types such as gasoline, diesel or bunker fuel oil. Subsequent remedial actions can then be more accurately designed and bid, saving time and money. In addition to a discussion of the technology, case studies will be presented of projects in which LIF was used to address soil excavation, in situ treatment, or potentially responsible party issues.

Use of a Collaborative Dataset to Enhance Data Representativeness

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Effective characterization of chlorinated solvent sites in glaciated terrains presents a number of technical challenges. The highly heterogeneous nature of stratified glacial sedimentary deposits results in complex distribution of chlorinated volatile organic compounds (CVOCs-within source zones and associated dissolved-phase plumes. Typically, source zones consist of residual dense non-aqueous phase liquid (DNAPL), diffused CVOCs, and/or sorbed CVOCs located in relatively low permeability zones. In some cases, these relatively low permeability zones are obvious silt or clay layers, but in many other cases they are indiscernibly finer-grained sand lenses that can be difficult to locate. Dissolved-phase CVOC plumes emanating from these source areas typically exhibit the general dimensions of the source area, due to minimal transverse dispersivity, and migrate within relatively high permeability zones.

Cost-effective characterization of CVOC sites in glaciated terrains requires an innovative approach, such as the Triad approach. The Triad approach is characterized by three major components: systematic project planning, dynamic work strategies, and real-time measurement technologies. The ultimate objective of a Triad investigation is to enhance data representativeness and reduce uncertainty. Historically, significant focus has been placed on reducing analytical uncertainty, with significantly less focus placed on reducing sampling uncertainty. One approach for reducing both sample and analytical uncertainty involves the generation of collaborative datasets. Collaborative datasets involve the collection of relatively closely spaced, lower-cost, semi-quantitative to quantitative field data combined with a limited number of strategically located, higher-cost, traditional, quantitative laboratory data (e.g., soil and groundwater samples). The traditional data are used to "calibrate" the field data, resulting in development of detailed three-dimensional characterization datasets.

A Triad investigation was conducted at a complex site in eastern Massachusetts. A collaborative dataset was generated using the membrane interface probe (MIP), modified Waterloo Profiler, and traditional monitoring wells. Collectively, these data were used to define a series of chlorinated solvent source areas and plumes at the site. Relative to historical investigations conducted at the site, development of a collaborative data set significantly reduced uncertainty associated with the site.

Use of Borehole Geophysical Logging, Packer Testing, and Discrete Groundwater Sampling in Assessment and Remediation of a Release of #2 Fuel Oil at a Western Massachusetts Residence

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A release of more than 250 gallons of #2 fuel oil at a Western Massachusetts residence was discovered in April 2006. The release appeared to be attributable to a leaking fuel oil storage tank line that lay under the concrete floor. The released fuel oil entered bedrock fractures beneath the residence and impacted 150- and 250-foot deep bedrock drinking water wells at the subject site and at an adjacent residence. In an attempt to determine the extent of petroleum impacts in bedrock, borehole geophysical logging was performed on the two impacted wells to characterize bedrock fractures in the wells. Equipment utilized in the borehole logging included: a borehole diameter caliper probe; formation resistivity, single point resistance and spontaneous potential electric probes; a natural gamma radiation probe; fluid temperature and resistivity probes; an acoustic televiewer probe; and a heat pulse flow meter probe (under both ambient and stressed conditions). The geophysical results provided data on bedrock fracture size, depth, orientation, and conductivity. Based on the data, packer testing was performed to provide additional information on fracture conductivity and to allow collection of groundwater samples from discrete depths. The geophysical, hydrologic, and chemical data were subsequently utilized to develop a bedrock assessment program including installation, evaluation, and monitoring of five additional bedrock wells located to intercept the more impacted fractures. Data from all bedrock wells were subsequently used to design and implement systems for both groundwater recovery and ex-situ treatment and in-situ soil and groundwater treatment via chemical oxidation (Fenton's Reagent).

Sampling Sediment Porewater in the Lower Duwamish Waterway Using a Passive Sampler

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Collecting porewater samples in freshwater and marine environments is challenging even under ideal sampling conditions. Sampling difficulties may lead to poor data quality, damage to ecologically sensitive areas, and unnecessary expense. To insure data quality and minimize environmental damage, membrane-based passive samplers offer a unique screening method to identify and delineate contaminated porewater and sediment. Subsequent more complex and invasive sampling can then be focused, effective and economical. The Washington State Department of Ecology and the US EPA have been overseeing sediment characterization and cleanup efforts along the Lower Duwamish Waterway, now listed on the Superfund National Priorities List. An embayment was investigated to determine whether groundwater, contaminated by chlorinated compounds from upgradient sources, was entering the river by upwelling through the embayment sediments or through shallow localized seeps. The investigation included deployment of patented, passive samplers, constructed of GORE-TEX® membrane and hydrophobic adsorbents. The samplers proved to be an accurate, sensitive, easy-to-use porewater sampling tool. The passive samplers were driven into the embayment and seep sediment during two phases of investigation. The first phase focused on the embayment area, while the second phase focused on two of the seeps suspected of being the exit points for contaminated groundwater. Sediment samples were also taken and the porewater analyzed. The datasets generated by the passive sampling and the conventional method were closely correlated and confirmed the passive sampler's detection capability in sediment porewater. Seven years later, porewater sampling using piezometers and peepers also confirmed the original passive sampling results. Passive sampling provided an accurate and economical method to characterize the location and extent of contaminated groundwater entering an embayment in the Lower Duwamish Waterway from an upgradient facility, and focused subsequent sampling efforts. The investigation is presented, and includes discussions on the passive sampler and the results of the investigation.

A Study of Tritium in Municipal Solid Waste Leachate

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A study was conducted of tritium levels in leachate from landfills in New York and New Jersey. Recent studies, including this study of landfills in New York and New Jersey, have revealed that leachate from municipal solid waste landfills commonly contains surprisingly high levels of tritium. In this study the mean level of tritium in the leachate from ten different landfills was 33,800 pCi/L, with a high of 192,000 pCi/L. In a similar study of landfills in Pennsylvania, the mean level of tritium was 20,900 pCi/L with values as high as 182,000 pCi/L. In contrast, current levels of tritium in precipitation average 50 to 100 picoCuries per liter (pCi/L) and have been steadily declining since the early 1960's when atmospheric testing of nuclear weapons caused tritium levels over North America to reach levels as high as 15,000 pCi/L. The Maximum Contaminant Level (MCL) set by the USEPA for tritium is 20,000 pCi/L. Tritium also manifests itself in landfill gas and landfill gas system condensates. In a recent study of tritium levels in landfills in California, one landfill gas condensate sample was found to contain 551,000 pCi/L of tritium, a level more than 27 times the USEPA MCL.

The principal source of tritium in municipal solid waste leachate and landfill gas condensates is believed to be gaseous tritium lighting devices. Self-powered exit signs are the most common examples of these devices. Some of these gaseous tritium-containing exit signs contain as much as 25 to 30 Curies of tritium. Although these devices are regulated by the Nuclear Regulatory Commission and require proper handling and disposal methods, they often find their way into municipal solid waste.

This paper discusses levels of tritium observed in this and other recent studies and discusses the implications to landfill worker health and safety, leachate treatment, and leachate monitoring and detection.

The Repeated Trespass of Tritium-Contaminated Water into a Surrounding Community from Repeated Waste Spills from a Nuclear Power Plant

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The Excelon Nuclear Power Plant (ENPP), located in Braceville, Illinois has historically released tritiated water and airborne tritium into the surrounding residential community. ENPP discharges its tritium waste via a “blow down line (BDL),” a pipe that runs through the surrounding community emptying in the Kankakee River. Along the BDL are vacuum breakers (VB-1 to VB-11) which regulate pressure along the line. Since 1996, there have been at least three major spills resulting from failures of the VBs. In November 1996, VB-1 broke, releasing over 300,000 gallons of water containing tritium. In December 1998, VB-3 leaked 2.9 million gallons of contaminated water over a 30-day period; possibly containing tritium concentrations between 624,000 pCi/L and 1,852,000 pCi/L. There was no remediation of the standing water from this release. In November 2000, failure of VB-2 released an estimated 3 million gallons of water containing tritium at concentrations between 167,000 pCi/L and 3,103,000 pCi/L. Ground water sampling from 2005 to 2006 has shown that maximum concentrations of tritium were above the U.S.EPA MCL of 20,000 pCi/L. In addition, sampling was conducted by ENPP and the local environmental agency. As a result, the released tritium has impacted air, ground water, and vegetation of the surrounding community. We conducted a field investigation of the community surrounding the ENPP and have determined that the released tritium continues to impact air, ground water, and vegetation. Litigation against ENPP has been launched due to the repeated trespass of waste products into the surrounding community, diminishing its property value.

Tungsten

Sponsored by ARCADIS and International Tungsten Industry Association (ITIA)

Tungsten Distribution at Camp Edwards Small Arm Ranges

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Analytical Method Development for Tungsten in Groundwater by SW-846 Method 6020 by ICP/MS (Lessons Learned)

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Comparison of XRF to Laboratory Based Methods for Tungsten and Other Metals

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Tungsten Geochemistry: Fate and Transport of Tungsten at Small Arms Ranges

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Tungsten Fate and Transport as a Function of Iron Redox Cycling and Associated Biotic-Abiotic Reactions

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Subchronic (90-Day) Oral Toxicity of Sodium Tungstate in Rats

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Preliminary Assessment of Tungsten Risk-Based Screening Values and Toxicity Benchmarking

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Tungsten Distribution at Camp Edwards Small Arms Ranges

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The US Army has an interest in knowing the distribution and concentration of tungsten present in range soils where tungsten/nylon rounds have been used in training with small arms weapon systems. A study conducted at Camp Edwards, Massachusetts assessed three small arms firing ranges. Surface soil tungsten levels ranged from 82 to 1,534 milligram per kilogram (mg/kg) in the Berm Face, 29 to 932 mg/kg in the Trough, 1.6 to 147 mg/kg at the Firing Point/Range Floor/Target, and 17 to 113 mg/kg behind the berm face. The highest observed tungsten concentrations were observed in surface soil samples (0-5 cm) from the bullet pockets on the berm face. Background surface soil tungsten levels for Camp Edwards are 1.5 mg/kg. Subsurface soil tungsten levels decreased markedly over a 150 centimeter depth interval, although the concentration of tungsten did not reach background levels.

Tension lysimeters were installed at various sampling intervals within the berm face and below the trough to assess pore-water migration of tungsten-laden water. Pore-water tungsten concentrations varied from < 0.05 to 400 mg/L over four sampling events. Five of the lysimeters exhibited an increasing tungsten concentration trend, three a decreasing trend, and the remainder of the 24 total exhibited no trend. Lysimeters installed in background locations indicated ambient tungsten levels of 0.01 to 0.17 mg/L.

A monitoring well completed in the aquifer, approximate depth to water of 36 meters, and tens of meters downgradient of one berm face exhibited fluctuating levels of tungsten. The first two sampling events indicated tungsten at 15 and 22 micrograms per liter (ug/L). Tungsten levels increased to 530 ug/L following a period of heavy precipitation. The fourth and fifth sampling event revealed a groundwater concentration of <5 ug/L. Prior to the fourth sampling event soil from the berm face containing greater than 150 mg/kg tungsten was removed.

Analytical Method Development for Tungsten in Groundwater by SW-846 Method 6020 by ICP/MS (Lessons Learned)

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The Small Arms Ranges at MMR that have been used for training and several ranges have used the tungsten "Green Bullets". The oxidation of the powdered tungsten in these "Green Bullets" forming the leachable species, the tungstate anion, has created a potential treat to tungstate contaminating the sole source aquifer located under the Massachusetts Military Reservation, Camp Edwards, in Falmouth, MA. The NGB USACE and ECC were tasked with sampling and analyzing for tungsten in groundwater monitoring wells in and around several of the SAR target and berm areas where the majority of the tungsten bullets were fired and located.

We readily realized that there were not many of our MMR commercial labs performing tungsten analyses, nor did they have experience with tungsten analysis by Method 6020 ICP/MS. We worked closely with the ERDC, Vicksburg, MS Waterways Experiment Station Chemistry section who had developed their own tungsten methods for soil and groundwater. ERDC also had several years of experience with tungsten analysis by ICP/MS, as well as knowledge of its unique chemical properties and analysis performance issues.

NGB, USACE and ECC headed up an analytical method development team using 4 laboratories (STL-VT, ERDC, MADEP and the University of Northern Arizona) and let them go about their own SW-846 Performance-Based Method Development approach. Since tungsten or the tungstate anion (WO4) is a new emerging contaminant of concern which did not have EPA approved MCL, Risk-based levels/ ground water action levels, sampling/handling, preservation, digestion method, or analysis method approved criteria, there was a great need to develop reliable and robust method specific criteria for tungsten/tungstate analyses at MMR.

The main focus of this presentation will be on the lessoned learned from the different analytical approaches used by the different labs for tungsten analysis by SW-846 Method 6020 ICP/MS. The presentation will cover; analytical performance issues of tungsten/tungstate anions, findings on QA split comparison between labs, discrepancies findings, PE- sample results and matrix effects, speciation of the tungstate anion, and the choices of certified Vender Stock-Calibrations standards. The need for a standardized EPA approved tungsten methodology will be discussed, as well as the need for more toxicity studies and risk assessments; so that we get a better idea of what groundwater concentration levels will be considered toxic to human and ecological species.

Comparison of XRF to Laboratory Based Methods for Tungsten and Other Metals

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As part of a study looking at the mobility of tungsten, the distribution and concentration of tungsten as well as other metals in small arms range soils was evaluated on-site using hand-held X-ray fluorescence (XRF) instruments and in a laboratory by inductively coupled plasma (ICP) analysis. The evaluation consisted of the testing of two different types of XRF units (X-ray tube and radioactive isotopes technologies) along with equipment from the two different manufacturers. In the field, the XRF instruments were used to confirm our conceptual design, rank decision units for quality assurance applications (field sample replicates), and determine the necessity and depth of profile sampling. Comparisons between real-time field measurements and laboratory post-processed samples with the XRF will be presented. Finally, the XRF field results were compared with those obtained utilizing modified versions of the US Environmental Protection Agency (EPA) SW-846 Methods 3050B, 3051, 6010B, and 6020. Replicate XRF analysis of soil samples and soil standards in the field indicates good agreement between the two different types of XRF instruments as well as the two equipment manufacturers. Analysis of the data suggests good reproducibility between XRF measurements in the field (wet soil samples) and laboratory ICP analysis following air-drying and digestion of ground soil samples. The advantage of using a field instrument such as an XRF instrument is the generation of real-time data allowing for decision-making in the field and the maximum utilization of time and resources. In addition, if the quality of the data with the XRF can be demonstrated to be as accurate as the ICP then it may be possible to reduce sampling and analysis costs.

Tungsten Geochemistry: Fate and Transport of Tungsten at Small Arms Ranges

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Between October 1999 and February 2006, tungsten/nylon projectiles were used at small arms ranges at Camp Edwards, Massachusetts. In January 2007 the U.S. Army Corps of Engineers (USACE) released a study of the fate and transport of tungsten at three of the small arms ranges at Camp Edwards. As anticipated, tungsten was found in the surface soils at concentrations consistent with its use as a small arms projectile. Information was also provided regarding subsurface soils, soil pore water, and groundwater concentrations of tungsten. This presentation uses the data presented in the USACE report as a basis for geochemical modeling of tungsten fate and transport in the environment. The presentation provides an overview of the model protocol and outputs with respect to tungsten mobility at Camp Edwards. The model results are then compared with conclusions reached in the USACE report.

Tungsten Fate and Transport as a Function of Iron Redox Cycling and Associated Biotic-Abiotic Reactions

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Tungsten is an emerging contaminant of concern at several U.S. military installations in subsurface systems. This study aimed to identify factors influencing tungsten fate and transport. Tungsten is most often present as tungstate (WO42-) in moderate pH groundwater. Tungstate binds to Fe(III) (oxy)hydroxides as a function of pH; however, it has not been determined what effects iron redox cycling has on tungstate mobility or whether tungstate itself can be reduced chemically or biologically.

Our investigation used bicarbonate buffered suspensions of sodium tungstate amended with poorly crystalline Fe(III) hydroxide in the presence and absence of the electron shuttle anthraquinone-2,6-disulfonate (AQDS). These suspensions were run at pH 7.0 and pH 4.0. The reduced form of AQDS (AH2QDS) is a strong abiotic reductant and can quickly reduce Fe(III) to Fe(II); it is unknown whether it can directly reduce tungstate. Tungstate alone or with the oxidized form of the electron shuttle (AQDS) did not vary over the four day incubation. The reduced form of the shuttle at pH 7.0 did not alter tungstate concentration. However, when the pH was lowered to 4.0 the tungstate immediately dropped from 2.0mM to 0.4mM and was further depleted to 0.2mM over the four day incubation. AH2QDS is a more efficient electron donor at low pH, and EH/pH plots suggest that WO42- can become WO2 at pH 4.0. Tungstate was slowly removed from solution in Fe(III) amended suspensions; from 1.5mM to 0.7mM over four days. Tungstate dropped immediately from 2.0mM to 0.7mM in Fe(III) + AH2QDS suspensions, which dropped to 0.5mM over the remaining three days with concomitant Fe(III) reduction.

These data suggest that iron redox cycling influences tungstate fate by adsorptive and possibly reductive processes. The project will continue investigating these chemical transformations, as well as mixed biological-abiotic reactions with Fe(III)-reducing microorganisms in defined and heterogeneous environmental media.

Subchronic (90-Day) Oral Toxicity of Sodium Tungstate in Rats

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Tungsten metal was used for the manufacture of small caliber ammunition in a tungsten/nylon matrix referred to as the "green bullet". A recent study conducted by the Corps of Engineers at Waterways Experimental Station indicated that soluble forms of tungsten could be formed from the tungsten bullets and enter the ground water. Sodium tungstate dihydrate, a highly soluble form of tungsten, was administered orally to male and female Sprague-Dawley rats by gavage for 90 consecutive days. This induced a number of statistically significant alterations in weights, hematology and clinical chemistry at 200 mg/kg. It was concluded that administration of sodium tungstate at 200 mg/kg to male and female Sprague-Dawley rats via oral gavage for 90 consecutive days resulted in pronounced renal changes, specifically renal tubular necrosis. Based on a careful evaluation of the data, the Lowest Observable Adverse Effect Level (LOAEL) for the subchronic oral toxicity of sodium tungstate in male and female Sprague-Dawley rats is 200 mg/kg. The No Observable Adverse Effect Level (NOAEL) for the subchronic oral toxicity of sodium tungstate in male and female Sprague-Dawley rats is 20 mg/kg. A second study exploring the dosage range between 10 and 200 mg/kg was recently completed. Preliminary information is presented.

Preliminary Assessment of Tungsten Risk-Based Screening Values and Toxicity Benchmarking

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During a recent investigation into a purported childhood leukemia cancer cluster in the western US, the Centers for Disease Control (CDC) identified a data gap associated with basic toxicological information on tungsten, the naturally occurring metal. This concern by CDC, along with the use of W in various industries has stimulated a dramatic increase in the amount of information available on this metal. Investigations into the toxicity of W have been conducted by academic institutions and military research labs. A review of a number of these recent studies, some of them not yet published in the scientific literature, provide an insight into the relative potency of W, especially when compared to other naturally occurring and industrial use metals. Because some of these studies have been conducted using standard protocols, the resulting information can form the basis of a “strawman” toxicity factor which can be used to develop preliminary “safe” environmental concentrations. Using methods employed by EPA to derive risk-based screening values (RBSV), such as the Region 9 Preliminary Remedial Goals, the toxicity factor for W translates into concentrations in soil and drinking water that would be without the risk of causing adverse effects. These RBSV for soil and water are compared to various levels of tungsten reported in the environment.

In order to compare the toxicological database that exists on tungsten to that of other heavy metals, information presented in the Agency for Toxic Substances and Disease Registry’s (ATSDR’s) draft or final toxicological profiles for 8 heavy metals, including arsenic, beryllium, cadmium, chromium, lead, mercury, tungsten, and uranium were reviewed and summarized. Additionally, several recently published (within the last 5 years) review articles concerning these heavy metals (excepting uranium) were reviewed. The purpose of this review was to compile, and subsequently compare, the adverse health effects that have been observed in humans or experimental animals following exposure to these metals as noted by the ATSDR or the authors of the various review articles. Results from this review will be presented.

Vapor Intrusion

Incorporating Engineered Controls into Vapor Intrusion Evaluations
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Assessing the Public Health Significance of Subsurface-Contaminant Vapors Intruding into Indoor Air
Henry J. Schuver, U.S. EPA – OSW, Washington, DC

Issues Related to Residual Subsurface Petroleum Odors at a Railroad Yard in Central Pennsylvania
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Incorporating Engineered Controls into Vapor Intrusion Evaluations

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Currently, some of California brownfields are being considered for residential redevelopment. Based on economic changes within California, commercial redevelopment is often not a viable financial option. These brownfields include former fuel transfer stations, chemical manufacturing facilities, land fills, and manufactured gas plants. Site specific redevelopment exposure assessments pose an interesting challenge. Most property redevelopments can be designed to eliminate direct contact to soil and groundwater. However, the vapor intrusion pathway could potentially still be complete. To assess potential human health risk associated with residential redevelopment, evaluations were performed to estimate indoor air concentrations inside hypothetical buildings. The results of the evaluations were used as a risk management tool to assess whether vapor controls would be a necessary part of the property redevelopments. LFR uses soil gas or groundwater data as the source concentration for the Johnson & Ettinger vapor transport model. Each identified volatile organic compounds detected in the subsurface is considered. If the results of the modeling indicated that the estimated cancer risk would be above the California regulatory target of 10-6, then the model would be modified considering the influence of engineered controls. Engineering controls include vapor barriers, open podium garages, and subterranean garages. Various modeling parameters were adjusted to replicate the influence of the chosen engineered control on vapor intrusion. Where necessary, the result of the modeling evaluations has been incorporated into the building design as a risk mitigation measure.

Assessing the Public Health Significance of Subsurface-Contaminant Vapors Intruding into Indoor Air

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While an increasing number of individual contaminated sites are being investigated for 'vapor intrusion' (VI), the overall frequency and magnitude of subsurface contaminant vapors intruding into indoor air and their significance to public health remains largely unevaluated. The objective of this risk assessment is to assess VI at a sufficient number of contaminated sites to gain insight into its public health significance. Specifically, this risk assessment is intended to predict the number of health outcomes that may be observable in an epidemiologic study of VI over a large geographic area. Central-tendency probabilistic estimates of exposure-point concentrations are made using groundwater samples from 2,381 contaminated sites, involving 11,210 wells and 55,132 samples of the indicator VOC tricholoroethylene (TCE). The estimated extent of groundwater contamination from sites with the highest potential for volatilization into the indoor air of residential properties is mapped using ESRI GIS IDW software and data from a state's Hazsite database. The attenuation of vapors generated from the upper-most groundwater is estimated for 884 hypothetical overlying residential structures using the USEPA's empirical database of attenuation. Receptor characteristics based on county-level statistics are used to estimate individual and age-specific exposures. These are combined with central-tendency probabilistic estimates of toxicity to estimate central-tendency risks for the outcomes under study (Central Nervous System effects and Non-Hodgkin's Lymphoma). Few individuals are estimated to be subject to significant risks. However, uncertainty in the groundwater concentration underlying each building dominates the calculated risks. This data limitation, the lack of site-specific extrapolations of upper-most water concentrations away from monitoring well observation points and under buildings, prevents more accurate risk estimates. Three policy recommendations could address this data gap: Iso-concentration e-maps for VI; Bldg-specific point estimates; and Site-specific outlines of VI study areas. These data could be used to inform and allow pre-construction savings for new buildings.

Issues Related to Residual Subsurface Petroleum Odors at a Railroad Yard in Central Pennsylvania

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The subjective nature of subsurface odors can be a negative factor when considering development of industrial properties. An example is a property located in Central Pennsylvania that was used as a railroad yard between the 1840s and the 1970s. At this site, which is centrally located in a small town, weathered petroleum hydrocarbons and a petroleum odor, were encountered in shallow soils. A detailed site characterization was subsequently completed following a through review of rail yard history and identification of possible source areas. Soil, soil vapor, and ground water samples were collected using conventional methods and analyzed for an extended suite of organic and inorganic parameters. Laboratory testing showed that concentrations met the State cleanup levels and closure of the site was obtained from the State regulatory agency. A caveat to avoid, or manage, those areas where petroleum odors may be encountered was included in the final report. In spite of laboratory results at acceptable concentrations and obtaining closure from the regulatory agency, the issue of residual subsurface odor was sufficient to impede development of the property. At the time of the site characterization, measurements for odor were not easily obtained and field-testing for odor was not conducted. As a result, it was difficult to dispel the perception that odors might have a negative impact on future development, even if properly controlled. Although evaluation of odors is typically subjective, methodologies to measure odors in the field are developing and some States have published regulatory compliance values. As this technology continues to develop, field measurements for odor may be an option to minimize subjective interpretations and allow for a more objective comparison of alternatives.

Tuesday, October 16, 2007

Poster Session- Arsenic

Experimental and Biogeochemical Modeling Studies on Arsenic Release in Soil under Anaerobic Condition

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Arsenic Contamination in Groundwater of Vietnam

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Arsenic Contamination of Ground Water in some parts of Eastern India and its Remedial Measures

Gopal Pathak, Birla Institute of Technology, Mesra, Ranchi, India

Applicability of Biological Techniques for the Remediation of Arsenic Contaminated Soils

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Experimental and Biogeochemical Modeling Studies on Arsenic Release in Soil under Anaerobic Condition

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Arsenic is now a major concern on a global scale due to its severe toxicity effect for the human body. The identification of release mechanisms may assist in designing safe and effective remediation strategies. In this regards, experiments were carried out to observe the release of As from soil to water under anaerobic condition. The concentrations of total As and arsenate (As(V)) measured in soil was same and it was 9.4 mg kg^{-1} that indicated As remained primarily as As(V) in soil. The concentrations of As, Fe, Mn, Mg, Ca and NO^{3-} were measured by the inductively coupled plasma and mass spectrometry (ICP-MS) and ion chromatography (IC), respectively in effluents of soil column, and also physical properties were measured during the experiment to find out their interrelationships. It was observed that As concentration increased with decreasing oxidation reduction potential (ORP). Arsenic concentrations demonstrated negative covariation with the concentrations of NO^{3-} but strongly correlated with Fe and dissolve organic carbon (DOC) concentrations. These relationships suggest that As may mobilized from soil to water by reductive dissolution of Fe oxyhydroxide with microbial reduction of organic matter under anaerobic environment. A numerical simulation of arsenic transport model, coupled with bacteria mediated biogeochemical processes was also applied to verify this hypothesis.

Arsenic Contamination in Groundwater of Vietnam

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The groundwater of Vietnam was characterized and the potential risks from groundwater were investigated in Vietnam. Arsenic contamination in groundwater was found in Ha Nam province in the northern part of Vietnam. Since groundwater has been used as one of the main drinking water sources in this region, groundwater (n=40) and hair (n=54) samples were collected in four districts in Ha Nam province. As(III) and As(V) species in groundwater were separated with disposable arsenic speciation cartridge at site. The concentrations of arsenic in groundwater ranged from less than 1 to 582 μg/L. According to the results of arsenic speciation, approximately 90% of arsenic in groundwater existed as As(III) species. Average concentrations of iron and manganese were 18 and 0.7 mg/L, respectively. Most samples exceeded the Vietnamese drinking water standard of 10 μg/L for arsenic. However, a real intake of arsenic to human is less than analyzed arsenic concentration because sand filtration units is used to remove iron and arsenic in groundwater in this region. After treatment, arsenic concentrations decreased from <1 to 82 μg/L. The concentrations of arsenic in hair samples and treated groundwater were compared. Arsenic concentrations in hair sample and treated groundwater had significantly positive correlation.

Arsenic Contamination of Ground Water in some parts of Eastern India and its Remedial Measures

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Arsenic contamination of ground water has led to a massive epidemic of arsenic poisoning in many districts of eastern India. The same type of problem has been observed in neighboring country like Bangladesh. The arsenic in the ground water is of natural origin & is released from the sediments into the ground water due to anoxic conditions of the subsurface. Arsenic has a tendency to get accumulated in body tissues to cause arsenicosis. It affects liver & heart and is carcinogenic .Its permissible limit in potable water supply is 0.05 mg/lit.

The present paper deals with the arsenic contamination situation in some parts of eastern India. Health impacts on humans residing in these areas have been discussed. Special emphasis has been given on the remedial measures.

Applicability of Biological Techniques for the Remediation of Arsenic Contaminated Soils

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Arsenic is a common and highly toxic pollutant of soils, emanating from several industrial activities. It occurs mainly in the form of anions which are strongly bound on the Fe(III)-oxides of soil. The biological reduction of Fe(III)-oxides has been often reported as the most important mechanism contributing in the release of associated As and the subsequent contamination of aquifers. Present study investigates whether this natural biogeochemical process can be used for remediation purposes, i.e. for obtaining the removal of As from contaminated soils.
The effectiveness of this treatment was evaluated on two soil samples with different characteristics. The first sample, originating from Lavrion, Greece, is a calcareous soil very poor in organic matter, i.e. 0.76% and contaminated with As up to 1000 mg As/kg, due to past mining activities. The second soil originates from Auzon, France, it has high organic carbon content, i.e. 8%, and it is contaminated with As up to 4500 mg As/kg due to wood preservation activities. The biological treatment of the soils was conducted under anaerobic conditions using the Fe(III)-reducing microorganism Desulfuromonas palmitatis. To enhance the reductive dissolution of Fe(III)-oxides and avoid the reprecipitation of As(V) with biogenic Fe(II) in the form of ferrous arsenates, some of the experiments were carried out in the presence of EDTA.
Simple biological treatment with D. palmitatis was not able to enhance the mobilization of As neither from Lavrion, nor from Auzon soil. Addition of EDTA in the aqueous solution has greatly stimulated the Fe(III) reducing activity of D. palmitatis and resulted in removing up to 90% of As from Lavrion soil and 70% from Auzon soil. Moreover, in the case of Auzon soil it was found that it is possible to obtain the removal of As by simply stimulating the biological activity of endogenous bacteria. Control experiments that were carried out on Auzon soil, using nutrients and EDTA but without addition of D. palmitatis, resulted in removing the same percentage of As, i.e. 70%, though with a much slower kinetics, i.e. after 60 days of treatment compared to 10 days with D. palmitatis. No endogenous bacterial activity was observed with Lavrion soil, probably due to the very low content of organic matter.

Poster Session- Environmental Fate

Risk Assessment and Remediation Criteria of Oil Leaking from Fluid-filled Underground Power Cables

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Behaviour of Phenanthrene in Water-Polymerin-Alumina Three-Phase System

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Dendrochemical Application to Evaluate the Absorption of Diesel and Hydrocarbon Contaminants in Tree Rings for Recent Contamination Event

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Risk Assessment and Remediation Criteria of Oil Leaking from Fluid-filled Underground Power Cables

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Linear alkylbenzene (LAB) cable oils are used for the electrical insulation of high-voltage underground power cables. At present, the electricity transmission system in the city of Buenos Aires consists in 400 Km of power lines running 2 meters deep. Due to thermal movement of the cables or third-party damage, leaks can occur, resulting in oil leaking into the surrounding environment. The present literature indicates that relatively little is known about the fate of LAB as a bulk pollutant in soil. A model of an underground cable was constructed to provide data on the conditions developed following a leak or damage, the dispersal properties of the fluid into the terrestrial subsoil and its potential ecological impact. At a first instance, a simulation experiment was designed (soil in graduated flasks and oil columns) to study the permeability of the fluid and the migration rates. It was observed that the vertical migration velocity in soil is 2.2 meters / year average, considering the physicochemical properties of the matrix assayed. In addition, risk assessment protocols were applied to evaluate the potential toxicity of LAB. Alkylbenzene has a low order of fish, mammalian and human toxicity and may be degraded naturally under aerobic conditions. As a result, environmental damage resulting from accidentally fluid release is likely to be small. Besides biodegradation, it was studied the chemical remediation as an alternative for immediate intervention and periodic monitoring.

Behaviour of Phenanthrene in Water-Polymerin-Alumina Three-Phase System

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Polymerin, the polymeric organic fraction from olive mill wastewaters, possesses humic acid-like properties and could represent a suitable biosorbent of potential economic interest. However, its interaction with phenanthrene is not known, especially in the presence of oxide particles. The aim of this study was to investigate the behaviour of phenanthrene in water in the presence of polymerin and in a polymerin-oxide-water system. Using a dialysis method, the interaction between polymerin and phenanthrene was studied as well as the interaction between phenanthrene and oxides (micro and nanoparticles). In addition, adsorption of polymerin on these oxides was examined and, during this experiment, the chemical properties of the polymerin left in solution after adsorption were analyzed by ultraviolet-visible spectroscopy and FTIR. Moreover, sorption of phenanthrene in a ternary system was evaluated at a fixed phenanthrene concentration with increasing polymerin concentration on both micro and nanoparticles. The results showed that phenanthrene sorption is linear for both micro and nanoparticles with the sorption of microparticles being one order of magnitude lower than the nanoparticles. Sorption by polymerin is nonlinear, and its sorption capacity is two orders of magnitude higher than that of nanoparticles. Sorption of polymerin on the two types of particles follows a Langmuir type, with a Sm of 204000 and 2970 mgOC/kg for nano and microparticles, respectively. Chemical property analysis showed that the nanoparticles are able to adsorb polymerin indistinctly, but the microparticles caused fractionation, adsorbing preferentially the aromatic fraction. Sorption studies in a ternary system demonstrated that the amount of phenanthrene sorbed on particles is related with the amount of organic carbon complexed, until a saturation point beyond which polymerin predominates the phenanthrene sorption on the Al-polymerin complex.

Dendrochemical Application to Evaluate the Absorption of Diesel and Hydrocarbon Contaminants in Tree Rings for Recent Contamination Event

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In June 2006, CN freight cars derailed near Charette, a municipality located on the north shore of the St. Lawrence River about 140 kilometres northeast of Montréal. According to CN officials, two tank cars containing gasoline, oil and diesel derailed, one spilling an undetermined quantity of oil, with three others dripping oil. Some of the derailed cars leaked petroleum substances into the Wolf River. One of the cars reportedly emptied the 200,000 litres of gasoline or diesel fuel it was carrying. Federal and provincial environment officials and workers have created a dam on the river to contain the spill. All of the spillage is on the east side of the tracks, with a body of water on the western side of the tracks not at risk of being impacted. The train accident contaminated the surface soil and probably the grounwater. The contamination event appears to be an opportunity for researchers who use dendrochemical analysis to measure the absorption rate of hydrocarbon contaminants in tree rings. The first objective of this study is to determine the response of trees located near the contamination site and use dendrochronological and dendrochemical methods. Field work began in November 2006, five months after the contamination event, and will continue over the next years (2006-2009). Red ash (Fraxinus pennsylvanica Marsh.) was used for the dendrochemical analyses. This species is the same as the trees that were used for the study on the Saint-François and Massawippi rivers, and all the results will be used for a comparative analysis. At present, the results obtained for the soil surface samples (0-5 cm depth) surrounding the contamination site show very high levels of contaminants (BTEX) ranging from 4,900 to 21,000 mg/kg (ppm), and the initial results of the dendrochemical analyses also indicate high concentrations of contaminants on the tree rings.

Poster Session- Environmental Forensics

Use Dendrochronological and Dendrochemical Methods for Dating Hydrocarbon Contamination of the Saint-François and Massawippi Riverbanks

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Julien St-Laurent and Patricia Duplessis, Sciences de l'Environnement, UQTR, QC Diane Saint-Laurent, Département de Géographie, UQTR, QC. Joëlle Marion, INTS-ETE, QC. Sediments contaminated with hydrocarbons (C10-C50) were recently discovered in the banks of the Saint-François and Massawippi rivers (Saint-Laurent and St-Laurent, 2004). The aim of this study is twofold: to determine the spatial distribution of the contamination along the banks of these rivers and to date the contamination period using dendrochronological and dendrochemical methods. Sampling for the two types of analyses was done on the banks of the Saint-François River in Windsor and Richmond stations, and Massawippi River station, where the level of hydrocarbon contamination in the sediments is among the highest. Five core samples were taken from a red ash (Fraxinus pennsylvanica Marsh.) at Windsor Station and twelve core samples were selected at Richmond station. Also dendrochemical analyses were done on the tree rings. Dendrochemistry was successfully used to determine that there were heavy metals in the rings. Also, soil materials were used for evaluate the heavy metals concentration (e.g. As, Cd, Cu, Pb and Zn) and ratio-isotope analyses (204Pb/206Pb, 207Pb/206Pb and 208Pb/206Pb). The total lead concentration in the tree rings increased drastically around 1958 due to the absorption of lead from the sediments that may have been contaminated by hydrocarbons possibly in 1955 or around this date. The total lead concentration in Richmond trees (F. pennsylvanica Marsh.) are very high to compare at the Windsor station.

Poster Session- Pesticides

Enhanced Atrazine Natural Attenuation in Agricultural Soil Exposed to a Major Spill

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Enhanced Atrazine Natural Attenuation in Agricultural Soil Exposed to a Major Spill

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Conventional soil tests, culture-based microbial methods, and the novel method of 15N-DNA stable isotope probing (SIP) were employed to illustrate atrazine biodegradation as related to the physiochemical properties of a Cisne soil from a major atrazine spill site. This soil appeared to exhibit enhanced atrazine degradation when compared to five reference soils in our laboratory and previous reports in the literature, and therefore was a good candidate for natural attenuation. Mineralization kinetics in the Cisne soil underestimated the rate of atrazine dissipation demonstrated by the accumulation of several metabolites. The soil showed high ambient concentrations of NO^{3-}, either from excess fertilization or mineralization of atrazine N; however the presence of NO^{3-} did not suppress atrazine degradation. Instead, natural attenuation of atrazine appeared to be primarily limited by incomplete distribution of the compound through the unsaturated soil matrix. Direct plating experiments from the Cisne soil isolated an atrazine-degrading microorganism, ES-1. Analysis of the 16S rRNA gene sequences from the isolate confirmed that ES-1 is closely related (99%) to Arthrobacter sp, a genus containing other known atrazine-degrading isolates. In pure culture, the isolate rapidly converted atrazine to cyanuric acid. Accumulation of this product was consistent with metabolites accumulated in the Cisne soil, suggesting that isolate ES-1 was a critical element in the microbial community influencing in-situ remediation of atrazine. To verify this theory, 15N- SIP experiments were conducted using 15N-ethylamino-atrazine. The results of these experiments failed to establish a causal relationship between in-situ atrazine-degradation and ES-1 enrichment; however these inconclusive results are likely due to isotopic dilution. Further experiments using 13C-ethyl/isoproylamino-atrazine (to increase the sensitivity of the SIP technique) may yet verify a link between ES-1 and the enhanced natural attenuation exhibited in the Cisne soil.

Poster Session- Phytoremediation

A Novel Non-tissue Culture Approach for Developing Transgenic Plants of a Potential Phytoremediator, *Brassica juncea* with *Agrobacterium tumefaciens*

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Plant Spacing for Optimal Arsenic Phytoremediation using *Pteris cretica*

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Analysis of Arsenic-Induced Transciptome of *Crambe abyssinica* to Isolate Genes for Phytoremediation of Arsenic

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Asma Zulfiqar, University of Massachusetts, Amherst, MA
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Isolating Chromium-Induced Genes from *Crambe abyssinica* for Phytoremediation of Chromium Contamination

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A Novel Non-tissue Culture Approach for Developing Transgenic Plants of a Potential Phytoremediator, *Brassica juncea* with *Agrobacterium tumefaciens*

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Indian mustard is a high biomass producing crop that accumulates heavy metals (Pb, Cd, Ni) in large amounts. The development of transgenic Brassica juncea will able to efficiently remediate heavy metal polluted soils of different origin and in a wide range of environments. In present study, a simple and efficient non-tissue culture approach for the generation of transgenic Indian mustard (Brassica juncea) plants using Agrobacterium tumefaciens has been developed for the first time. This procedure involves infiltration of inflorescence with flower buds in a suspension of Agrobacterium tumefaciens strain EHA105 carrying a binary vector pCAMBIA2301 that contained β-glucuronidase (GUS) gene (uidA) as a reporter gene and neomycin phosphotransferase (nptII) gene for resistance to the antibiotic kanamycin as a selectable marker. The seeds of agro-infiltrated plants (T0) were germinated on 130 mgl-1 kanamycin containing medium and the seedlings which remained green produced T1 transgenic plants. The presence, integration and expression of transgenes in T1 plants were confirmed by PCR, genomic Southern and histochemical GUS assay. Southern analysis revealed independent stable transformants carrying single or two copies of transgenes. An overall transformation frequency of 0.8 % from 250 seeds was obtained. The analysis of T2 generation indicates that transgenes inherited in Mendalian fashion. This method may facilitate large-scale insertional mutagenesis for functional genomics of Brassica and the development of transgenic mustard with improved phytoremediation ability for toxic metals and other agronomic traits.

Plant Spacing for Optimal Arsenic Phytoremediation using *Pteris cretica*

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The brake ferns *Pteris vittata* and *Pteris cretica* have been suggested for phytoremediation of arsenic contaminated soil. Edenspace Systems Corporation has demonstrated the practical application in an ongoing remediation project in the Spring Valley area of Washington DC. where Pteris species were grown on one foot centers. In that Pteris are tropical to subtropical (USDA plant hardiness zone 7-10), use in colder climates will be problematic. The plants inability to over winter will require annual replanting, and the radius of single-season root spread will determine minimum planting density to ensure root coverage of the remediation area. Researchers at Rochester Institute of Technology's Environmental Management department determined the single season radial root spread of *P. cretica* in a lab study using four soil types. Three replicates of four soil types were prepared in cubic 1 ft^3 planting containers. Seedlings of 4-6 fronds in 40 cm^3 seed starting media were planted centrally and grown under light with abundant water. Plants were misted and fertilized and grown for seven months to simulate one growing season. Soil was then sectioned and excavated to determine root density Vs. depth and distance from the plant crown. Root density was determined using the standard measurement of dry root mass/soil volume and using a novel GIS pixel-based measurement of root length/soil volume. Preliminary results indicate significant root growth beyond the original starting media, but exponential decline in density with distance from the planting center. This indicates that most soil beyond 0.3 foot from the plant crown will not be within a root rhisosphere and will remain unremediated. An arsenic contaminated site planted with *P. cretica* on 1 ft centers likely contains nodes of remediated soil surrounded by unremediated soil after one growing season.

Analysis of Arsenic-Induced Transciptome of *Crambe abyssinica* to Isolate Genes for Phytoremediation of Arsenic

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Arsenic (As) has been known as a carcinogen as well as an acute poison for centuries. Well-known high As groundwater areas have been found all over the world, particularly in South and southeast Asia and central and south America. Further, due to the repetitive use of As-contaminated water for irrigation, very high levels of As build up in the agricultural soils around the world. Millions of humans, livestock and vegetation face the increasing threat of As toxicity. Phytoremediation renders an eco-friendly and sustainable method to remediate the As polluted sites. Crambe (*Crambe abyssinica*)- a non-food high biomass crop, is reported to be able to tolerate and accumulate unusually high amount of As. Understanding the molecular mechanism of high As tolerance is essential to improve the efficiency of uptake thereby exploiting the plant for commercial phytoremediation.

The objective of the present study is to isolate and characterize the As responsive genes in Crambe. A PCR-Select Subtractive cDNA Hybridization approach was employed to isolate As-induced genes from Crambe seedlings. After differential screening, 105 positive cDNA clones from the subtracted library were sequenced. The sequences were categorized based on their similarity with reported sequences in the databases. Many novel sequences were present in the library, which were hitherto uncharacterized or not reported. A variety of reductases viz. peptide methionine sulfoxide reductase, oxophytodienoate reductase, dioxygenases, aldo-keto reductase and sulfite reductase, were found to be differentially expressed implying that the As alters the redox potential at cellular level. Glutathione transferases, both the *Tau* and *Phi* subfamily that are involved in cellular detoxification were also represented in the library. Other important sequences included ATPases, drug transporter/antiporter, phosphosulfate kinases, adenylyl transferase, methionine synthetase and proteins involved in ubiquitin proteolytic pathway along with transcription factors and RNA binding proteins. Expression analysis and functional characterization is being carried out and expected to reveal the mechanism of plant arsenic tolerance. The candidate genes will be used to engineer non-food high biomass *C. abyssinica* plants for phytoremediation of As-contaminated soil and sediments.

Isolating Chromium-Induced Genes from *Crambe abyssinica* for Phytoremediation of Chromium Contamination

STUDENT PRESENTER

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Chromium (Cr) is a serious environmental pollutant due to its widespread use in industries such as tanning, corrosion, plating, pigment manufacturing and nuclear weapons production. Cr (VI) is generally considered to pose the greatest human health risk because of it being toxic, mutagenic and carcinogenic. There is no cost-effective environmental-friendly Cr remediation strategy available so far. Plants can be used to cleanup the Cr pollution by accumulating, stabilizing or transforming into less toxic form Cr(III). Previously, we have analyzed the uptake of Cr and other toxic metals in *Crambe abyssinica* and other Brassica species. Crambe accumulated high levels of Cr and As in the shoot tissues and thus has potential to be utilized as an ideal non-food crop for phytoremediation of heavy metals and metalloids. The present study was undertaken with an aim to isolate and characterize the genes induced in response to Cr stress in Crambe using a PCR-Select Subtractive cDNA Hybridization approach. After subtraction and differential screening, 71 positive cDNA clones from the subtracted library were sequenced. The sequences were categorized based on their similarity with reported sequences in the databases. Forty-five different types of genes were found to respond to Cr stress. Among these were Transcription factors, Chitinases, Thi-J like protein, Peroxidases, Glutathionases-S-Transferases , Aquaporins, oxidoreductases, harpins, zinc and iron binding proteins and many novel sequences with some unknown functions. Currently, we are analyzing these genes for expression analysis and functional characterization using both forward and reverse genetic approaches. The candidate genes will be used to engineer non-food high biomass *C. abyssinica* plants for phytoremediation of Cr contaminated soil and sediments.

Poster Session- Remediation

Organoclays Trap Recalcitrant Organic Compounds and Metals in Sediments Simultaneously
George R. Alther, Biomin, Inc., Ferndale, MI
Eric C. Hince, Geovation Engineering, Rochester, NY
Eric L. Zimmer, Geovation Engineering, Rochester, NY

Case Study of the Design and Operation of a Deep Air Sparging System to Remediate Petroleum Impacted Groundwater
James F. Cuthbertson, Delta Environmental Consultants, Inc., Novi, MI
Jason Phillips, Delta Environmental Consultants, Inc., Novi, MI

Performance-Based ERH Remediation of DNAPL in a Tight Soil Matrix
Robert F. Davis, Jr., Tetra Tech NUS, Inc., Pittsburgh, PA
Christopher Pike, Tetra Tech NUS, Inc., Pittsburgh, PA
Anthony B. Robinson, Naval Facilities Engineering Command, North Charleston, SC
Dan W. Waddill, Naval Facilities Engineering Command, Norfolk, VA
Howard Hickey, NAVFAC Midwest, Great Lakes, IL

Pilot Testing Pneumatic Fracturing to Enhance Petroleum Hydrocarbon Recovery
Chester A. Hitchens, Delta Environmental Consultants, Inc., Loveland, CO

Economic Optimization of Existing Pump and Treat Groundwater Remediation Systems
Brad Johnson, CH2M HILL, Otis ANG Base, MA
Rose Forbes, Air Force Center for Environmental Excellence, Otis ANG Base, MA
Ken Martins, CH2M HILL, Santa Ana, CA

Evaluation of Pneumatically Induced Fractures for Enhanced Delivery of Substrates within Low Permeable Soils
Michael Liskowitz, ARS Technologies, Inc., New Brunswick, NJ
Charlotte Riis, NIRAS, Allerod, Denmark
Anders Christensen, NIRAS, Allerod, Denmark

EDC Remediation with Microbubble Ozone Diffusion
Dennis L. Mast, Shine Holdings, Inc., Apex, NC

Pilot Experiment of Immobilization of Contaminants In-situ
Jiří Mužák, DIAMO, Straz pod Ralskem, Czech Republic
Ludvík Kašpar, DIAMO, Straz pod Ralskem, Czech Republic

Design and Implementation of a Comprehensive Thermal Remedy at a Former Drum Disposal Site

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Robin R. Swift, Geosyntec Consultants, Inc., Acton, MA
Peter J. Zeeb, Geosyntec Consultants, Inc., Acton, MA

Case Study - The Excavation of MGP Residuals in Soil Adjacent to an Active Rail Line and within a Residential Community

Mikel Pype, Jacques Whitford Company, Inc., Plymouth Meeting, PA
Barry Raus, Jacques Whitford Company, Inc., Plymouth Meeting, PA
Lindsay Guiliano, Jacques Whitford Company, Inc., Plymouth Meeting, PA
Joseph Foglio, GZA GeoEnvironmental, Inc., Fort Washington, PA

Low Permeability Barrier Wall for Control of Groundwater Contamination: Performance Verification and Case Histories

David Smyth, Golder Associates, Mississauga, ON, Canada
Robbie Laird, C3 Environmental Limited, Breslau, ON, Canada
Robin Jowett, Waterloo Barrier Inc., Rockwood, ON, Canada

Design vs. Reality: An Analysis of the Design and Performance of a Dual Phase Extraction System

Paul Uzgiris, Weston & Sampson Engineers, Inc., Peabody, MA
Frank Ricciardi, Weston & Sampson Engineers, Inc., Peabody, MA

Kinetic Study of Nitrate Reduction with Nanoparticle Bimetallic Fe-Ni

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Organoclays Trap Recalcitrant Organic Compounds and Metals in Sediments Simultaneously

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Extensive research at a university, which was conducted over the last few years, has revealed that certain organically modified clays are well suited to fixate organic hydrocarbons of polar and non-polar nature, anionic organic compounds and metals, and cationic heavy metals, in sediments.

Organoclays are blended with sediments in permeable barriers, landfill liners, slurry walls, and sediment caps.

Organoclays have been used in permeable walls to block the movement in groundwater of DNAPL plumes from abandoned wood treating sites, and for sediment stabilization at an old MGP site (from a power and light company).

Laboratory column and batch tests with various types of organoclays have revealed that a standard, non-polar organoclay fixates all heavy metals, including lead, zinc, nickel, chromium and cadmium, but also inorganic aqueous mercury. In terms of organic hydrocarbons, such diverse compounds as dioxin and nitro-benzenes, potassium sorbate, as well as PCB, PCP, PNAH, BTEX and oil are effectively trapped.
Polar organoclays will fixate arsenate, selenite, phosphate, nitrate, fluoride, silicate, perchlorate and the like.

This article presents the capabilities of organoclays based on lab tests, and recommendations as to how to use them.

Case Study of the Design and Operation of a Deep Air Sparging System to Remediate Petroleum Impacted Groundwater

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Air sparging is a very well known technique for the remediation of petroleum impacted groundwater near the upper portion of the groundwater table. However, the application of this technique at a depth significantly below the groundwater table is not a common approach and the design considerations are not well documented in the literature. Review of available literature indicated a scarcity of information and widely varying pressure requirements needed to initiate air flow. Case study results of the pilot study, system design, installation and effectiveness for a site in Michigan where the sparge points are installed approximately 50 to 60 feet below the groundwater table will be presented.

Performance-Based ERH Remediation of DNAPL in a Tight Soil Matrix

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Remediation of tetrachloroethene (PCE) in a tight soil matrix was completed at a former dry cleaner located at Naval Station Great Lakes in Illinois. The site lithology consists of low permeability silt and clay (mean hydraulic conductivity of 0.19 feet per day). The maximum PCE concentration in soil observed at the site was 1,500 mg/kg, indicating the presence of DNAPL; the maximum depth of contamination observed was 20 feet. Electric Resistance Heating (ERH) was utilized to address the DNAPL and other areas of high concentration PCE-contaminated soil.

The remedial goal for the site was to reduce average PCE concentrations in the soil matrix from 445 milligrams per kilogram (mg/kg) to less than 20 mg/kg (95.5 percent reduction). Pore water concentrations, though expected to decrease as part of the remediation, were not utilized in determining the performance-based goals. The success in meeting the goal was based on the analytical results of soil samples collected from 15 locations at various depths prior to and following treatment.

The ERH system contained 16 electrodes designed to treat a total area of 2,400 square feet. The treatment area was divided in to three smaller regions to treat various depth intervals; Area 1 extended from the surface to a depth of 25 feet; Area 2 extended from the surface to a depth of 18 feet, and Area 3 extended from the surface to a depth of 8 feet. The total soil volume treated was 1,400 cubic yards. Start-up of the system occurred on May 23, 2006 and the system operated for approximately 4 months. During operation, the ERH system removed 1200 pounds of VOCs from the subsurface. The final average VOC concentration in the soil was 4 mg/kg; this equates to a reduction of greater than 99 percent, surpassing the project goals.

Pilot Testing Pneumatic Fracturing to Enhance Petroleum Hydrocarbon Recovery

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A number of service stations that operated in Glendo, Wyoming since the early 1930s had leaked and caused wide spread ground water contamination. Results of a field investigation indicated that both free- and dissolved-phase hydrocarbon plumes were extensive. Two large plumes were identified, and the areal extent of the free product plume was approximately 5.7 acres and the dissolved phase plume was approximately 100 acres in size. Over the project area, the free product thicknesses range from a trace to over seven feet. The results of the subsurface investigation indicated that approximately 12 to 20 feet of unconsolidated silt and minor amounts of sand overly the buff-colored siltstone and claystone (Miocene). The soil contamination was not extensive, and the majority of the soil contamination outside of the free product plume appeared to be caused by contaminated water adsorbing onto the soil matrix.

The pilot test involved drilling nine borings for fracture wells, and then conducting pneumatic fracturing in both the saturated and unsaturated zone. ARS Technologies Inc. was selected to perform the pneumatic fracturing. The pneumatic fracturing was conducted in a ten-foot zone that straddled the water table. Nitrogen injection was conducted for about 15 seconds, at 150 to 380 psi, with a flow rate of about 800 to 3,000 scfm. After the pneumatic fracturing was completed, the pre-fracturing aquifer testing was repeated. Results of the post-fracturing aquifer testing showed that water production rates essentially doubled, with the same drawdown. During the post-fracturing SVE testing, the operating vacuum could be reduced to 68 inches of water, and vacuum influence was measured in all nearby site monitoring wells. A graph of vacuum verses distance test suggested an SVE effective radius of influence of approximately 60 feet. A full scale remediation system is scheduled to be installed in the summer of 2007.

Economic Optimization of Existing Pump and Treat Groundwater Remediation Systems

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Treatment plant operating conditions at groundwater remediation sites typically change with time. For example, contaminant concentrations may vary, the contaminant mix may change, and operating flow rates may be adjusted. Equipment installed to operate at original conditions may perform inefficiently at revised conditions. Reductions in operating costs can be achieved in many cases by including engineering reviews of equipment as a part of any changes to operating conditions.

As sites at the Massachusetts Military Reservation have been remediated, the flow rate of water entering some of the treatment plants has been reduced. The pumps in the plants were designed for higher flow rates and were throttled back or flow was recirculated in order to operate at lower flow rates. Variable Frequency Drives (VFDs) were installed to allow pumps to operate at lower speeds, reducing the electricity demand to pump the required amount of water. The resulting annual reduction in electricity costs totaled $125,000. For smaller systems, it may be more economically attractive to resize a pump. For instance, if the flow rate to a remediation system is reduced, installing a pump that operates more efficiently at the new flow rate without the need for throttling or recirculation can reduce operating costs. Depending on the cost of electricity, reducing power requirements by one horsepower can reduce annual operating costs by $500-$1000.

Another potential area for optimization is treatment plant lighting systems. Plants may be designed and built with incandescent or metal vapor lighting systems that require large amounts of electricity to produce adequate lighting. Additionally, some lighting systems require a warm-up period before full output is reached. This may result in personnel leaving lights on at all times. Replacement of metal vapor lighting systems with high efficiency fluorescent lighting at MMR plants is estimated to reduce annual electricity costs by $55,000.

Evaluation of Pneumatically Induced Fractures for Enhanced Delivery of Substrates within Low Permeable Soils

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This study presents the results of a pilot scale investigation performed in December 2005 at a site in Hedehusene, Denmark. The purpose of the study was to assess the effectiveness of pneumatic fracturing technology as a permeability/hydraulic conductivity enhancer and delivery mechanism to augment reagent and/or substrate distribution within low-permeable formations. Contaminated sites are frequently located in areas with low permeable soil types requiring permeability enhancement methods to provide direct access to these contaminants resulting in accelerated cleanup times. The results generated from the study were used to ascertain the fracturing characteristics and/or mechanism through evaluation of achievable radius of influence, uniformity and apparent density of the induced fracture network within a clayey till. Fracture mapping was accomplished using different tracers which were injected with the nitrogen gas used during the fracturing process. The tracers provided visual identification of the fractures at various distances and depths from the fracturing well thereby allowing documentation of the actual radius of influence, mass balance and fracture density obtained through pneumatic fracturing. The results identified a number of induced fractures in core samples taken at distances of up to 3 meters from the fracturing well. The use of digital imaging under UV-light proved to be a very efficient way to locate the fractures in the core samples. A preliminary mass balance indicated that 90% of the tracer mass was distributed within 1-2 meters from the fracturing well. Distinct fractures with high concentrations of tracers were observed over the entire fracturing interval (3-8 meters bgs) at distances up to 6.8 meters from the fracturing well.

EDC Remediation with Microbubble Ozone Diffusion

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The Problem:
Endocrine Disrupting Compounds (EDCs), and other chemicals of concern are now practically omnipresent in wastewater wherever modern human habitation is encountered. Contemporary wastewater treatment systems, (WWTPs) were never intended or designed to accommodate such materials.

Goals and Objectives:
Numerous published studies have reached a consensus view that identifies the enhanced oxidative properties of ozone as a most potent removal mechanism for most EDCs and the many compounds of emerging concern. The principal goal of this study was to perform construction of an individual ozone diffusion technology.

Approach:
The analog for such a system presently exists. Using a proprietary high-efficiency aeration technology for wastewater, an oxygenation system was designed in 2001 that initiates upstream wastewater treatment. These O_2 systems are presently in nationwide operation. It is now for EDC removal applications downstream of WWTPs that a new ozone prototype device has been constructed, albeit with changes in materials.

The existing oxygen system consists of a reduced pressure Mass Transfer Contactor (MTC) where production of microbubbles of 5 microns in diameter and bubble rise rates of 0.2 to 0.8 cm/sec yield Standard Oxygen Transfer Efficiencies (SOTE) exceeding 60%, with Standard Aeration Efficiencies (SAE) of 3.17-kg/KW hour have been measured. A high transfer efficiency of oxygen or ozone into the effluent occurs due to the exponentially increased surface area provided by the small micron-sized bubbles and the long duration of bubble persistence. The ozone diffuser data is expected to produce similar efficiencies as those described for the oxygen diffusion technology. The SOTE data points for the oxygen diffuser were actually 60.9%. Corresponding efficiencies are expected in the ozone-based system with field trials now to be completed by Fall 2007.

Pilot Experiment of Immobilization of Contaminants In-situ

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At the end of 2006 the project of pilot experiment of immobilization of contaminants in-situ was in DIAMO, s. p., o. z. TUU prepared. Realisation of the experiment is planned for years 2007 and 2008.

The principle of immobilization of contaminants in-situ is to develop special conditions in water bearing sandstone sediments when transformation of contaminants from mobile form to immobile form can happen. Under the conditions of remediation after chemical mining (using sulphuric acid) of uranium on the deposit Straz it means injecting suitable alkaline medium and it's spreading in contaminated sandstone aquifer. It will lead to decreasing of acidity of contaminated groundwater and precipitating of contaminants (SO42-, Al, Fe) in pores. This process leading to decreasing of concentration of dissolved contaminants in groundwater is followed by co precipitation and sorption of other toxic contaminants as As and Be.

The numerical model of groundwater flow and contaminant transport for evaluation of pilot experiment results was developed. The model mesh covers the all influenced area of the aquifer. It is sufficiently fine in the area of planned pilot experiment. It follows from the testing preliminary calculations that for example effect of gravity separation of solutions cannot be omitted. During the preliminary phase of pilot experiment another tests of calculation accuracy will be performed. These calculations will allow us to determine rates of change of follow-up parameters and consequently the necessary frequencies of piezometric head measuring, groundwater sampling and analysing.

The results of the pilot experiment will be used for design of application of method of immobilization in-situ in the frame of remediation after chemical mining of uranium on the deposit Straz with the aim to decrease time and costs of the whole remediation process.

Design and Implementation of a Comprehensive Thermal Remedy at a Former Drum Disposal Site

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Drum disposal sites face many challenges to effective remediation and eventual site closure. The large variety of contaminants often present at these sites makes many remedial technologies inefficient or prohibitively expensive. In the 1930s, a portion of a residential property in southeastern Massachusetts was excavated for fill for an off-site construction project. Between 1950 and 1965, the resulting borrow pit was gradually filled with an estimated 2200 drums containing a variety of volatile and semi-volatile organic wastes. Client and regulatory concerns drove the selection of In Situ Thermal Desorption (ISTD) as the principal remedial technology employed at the Site. ISTD heats the subsurface to volatilize and steam strip contaminants. At this Site, a target temperature of 150 °C was to be achieved through 70 heater wells installed over a 420-m^2 area. Volatilized contaminants were removed via vapor collection trenches, treated by thermal oxidation, and discharged to the atmosphere. This remedy was augmented with a dual-phase recovery and treatment system, which removed dissolved constituents in groundwater outside of the thermal treatment zone and extracted nonaqueous phase liquid (NAPL). NAPL in the extracted liquid was removed by phase separation via gravity. Contaminated groundwater was then treated to remove volatile and semivolatile organic compounds, trace heavy metals, and iron and manganese. Extracted NAPL was disposed off-site. Preliminary data indicate that over 15,000 kg of mass have been removed from the subsurface to date. This presentation describes the selection, design, and implementation of the combined remedy at this site. The aggressive nature of this remedy presented many technical challenges, and innovative approaches to these challenges will be highlighted. Additionally, preliminary data on the efficacy of the implemented remedy will be discussed.

Case Study - The Excavation of MGP Residuals in Soil Adjacent to an Active Rail Line and within a Residential Community

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A remedial action was completed at a former MGP in New Jersey involving the installation of sheeting, active de-watering, and the deep excavation of 20,717 tons of soil. The former MGP encompassed a 0.2-acre property in a residential setting adjacent to an active rail line. Impacted soil was delineated at the site and two adjoining properties during remedial investigation activities requiring the excavation of soil to depths ranging from 2.5 to 34.5 feet below ground surface (bgs) to provide for future unrestricted use. Due to the small size of the work area, proximity to an active rail line and the presence of an active roadway that bisected the proposed excavation, the project posed several logistical challenges related to work zones, traffic controls, and the approach to sheeting installation in close proximity to residential dwellings.

Technical challenges included, but were not limited to, the excavation of soils to the top of a competent clay unit (approx. 34.5' bgs) which required the depressurization of two highly permeable silt layers that exist within the top 20' of the extensive clay unit. Excavation was completed adjacent to the right-of-way of an active rail line at depths ranging from 2.5' to 25.5' bgs which required the earth-support design to comply with requirements set forth by the rail road. Construction of an on-site groundwater treatment facility with the capability of addressing MGP related impacts prior to discharge was one of many physical challenges overcome during the project.

Design and implementation challenges and outcomes regarding remediation of contaminated soils will be presented in detail. Post excavation, groundwater data is being evaluated as part of a proposed monitored natural attenuation remedy.

Low Permeability Barrier Wall for Control of Groundwater Contamination: Performance Verification and Case Histories

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The control and remediation of contamination in the subsurface can benefit from the application of low permeability barrier systems. In combination with natural geologic features, barriers can be used to entomb zones of contamination in the subsurface, either for long-term isolation or to facilitate active in situ remediation. Barrier systems can also be used for partial isolation or to enhance groundwater control in the vicinity of subsurface contaminant sources.

Waterloo Barrier® (sealable-joint steel sheet piling) has provided excellent hydraulic and contaminant containment in subsurface applications over the past fifteen years where geological and geotechnical conditions are appropriate for sheet-piling use. Recent large-scale laboratory testing has generated hydraulic conductivity values of an individual sealed joint consistent with bulk hydraulic conductivity values (<10-8 cm/sec) determined for field-scale systems in the past. Site driving trials have confirmed that installation of the piles to depths of more than 30 m can be achieved using conventional equipment. In combination, the availability of sealants compatible with a wide range of contaminants, the documented low permeability characteristics of the sheet piling and sealed-joint system, and a demonstrated ability to install the system to depth, Waterloo Barrier® systems are suitable for contaminant control and isolation at many commercial, industrial and waste management sites.

A full enclosure Waterloo Barrier® was installed at a former MGP site to facilitate dewatering during excavation of coal-tar contaminated soils and prevent further lateral migration of contaminant into the adjacent waterway. At a refinery, a riverbank Barrier wall was keyed to bedrock at depths of 3 to 12 m with a pressure-grouted contact. In addition to contaminant control, the Barrier also acts as a structural shoring system. At an abandoned chemical manufacturing plant where Brownfields redevelopment has occurred, a Waterloo Barrier® wall was installed to enhance contaminant control for an up-gradient pump and treat system.

Design vs. Reality: An Analysis of the Design and Performance of a Dual Phase Extraction System

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A high-vacuum dual phase extraction (DPE) system was designed to recover LNAPL at an active maintenance facility that has had historical releases of petroleum from underground storage tanks and measured LNAPL thicknesses of up to 2.5-feet atop the groundwater table. The DPE system encompasses a strategy to maximize recovery of LNAPL through groundwater table depression and an applied wellhead vacuum. Extracted groundwater is processed through the treatment system to remove contaminants and a wellhead vacuum provides airflow through the subsurface and oxygen to indigenous bacteria resulting in aerobic in-situ degradation of the hydrocarbons in the soil capillary fringe. The DPE system was constructed between February and October 2006 and has been running 24-hour-per-day since October 12, 2006.

System construction involved the installation of thirteen extraction wells and a DPE treatment system housed in a prefabricated building. Components of the DPE treatment system include: an aboveground storage tank for recovered LNAPL; groundwater treatment components such as an oil/water separator, air stripper, particulate filters, inorganic sequestering, and carbon canisters; and vapor phase treatment components such as an air/water separator, vapor-phase carbon canisters, and a catalytic oxidation unit.

Due to inconsistent field conditions, unique subsurface stratigraphy, and unpredictable aquifer responses to engineering controls, the actual performance of the constructed DPE system inevitably varied from the original design parameters. This presentation will compare design parameters (i.e. flow rates, expected removal efficiencies, etc.) to actual field conditions and contaminant recovery from data collected during the start-up and the first nine months of operation and maintenance of the constructed DPE system. In addition, this presentation will detail unforeseen field conditions and challenges, and describe equipment optimization efforts to meet the design parameters, including:

- Adjustments to vapor-phase treatment equipment to increase removal efficiencies
- Adjustments to transfer pumps and sequestering agent dosing rates to improve flow through liquid-phase carbon vessels
- Groundwater and vapor-phase treatment efficiencies during initial start-up and after equipment optimization
- Mass balance calculations to determine contaminant removal via granulated carbon vessels and catalytic oxidizer unit
- Field measurements showing groundwater, LNAPL, and vapor capture zones

Kinetic Study of Nitrate Reduction with Nanoparticle Bimetallic Fe-Ni

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Bimetallic iron-nickel nanoparticles with high surface area were prepared with two different procedures. One is synchronous chemical synthesis method, the other is mixture of Fe and Ni nanoparticles with different weight ratios. The BET surface area of Fe/ Ni(1:1) nanoparticles is 49.31 m2/g. They were used as a reagent to evaluate the nitrate reduction efficiency in aqueous solution. The aim of this study is to realize the nitrates reduction efficiency and reaction kinetics treated with Fe/Ni nanoparticles in aqueous solution. Several factors, including pH, Fe/Ni weight ratio, nitrate concentration were discussed with batch experiment and the observed rate constants (Kobs) and half-life for nitrate reduction was calculated. Results show that the removal efficiencies of nitrate are all significant at the low pH (2 and 3) no matter what addition of Fe, Ni or Fe/ Ni ratio of nanoparticles. The reduction efficiency of 50 mg/L nitrate which was mixed with 2 g/L nanoparticles excellently fitted pseudo-first-order reaction model with coefficient of determination (r2) among 0.91~0.99. The values of observed rate constants (Kobs) were 0.1748 for (Fe/ Ni(5:1)), 0.0686 for (Fe/ Ni(1:5)), 0.0227 for Ni nanoparticle, and 0.0159 min-1 for Fe nanoparticle at pH 2 for 50 mg/L nitrate. The half-life for nitrate reduction was 4, 10, 31, and 44 minutes for Fe/ Ni(5:1), Fe/ Ni(1:5), Ni, and Fe, respectively. The value of Kobs decreased and the half-life increased with the increase of pH from 2 to 3. The higher Fe/ Ni ratio (9:1) had higher Kobs value (0.1185 min-1) than the Kobs value (0.0105 min-1) of Fe/ Ni ratio (1:9) at uncontrolled pH. The removal efficiency of nitrate by addition of bimetallic Fe/ Ni was better than only Fe or Ni nanoparticles. Meanwhile, the higher Fe weight percentage in Fe/Ni nanoparticle can improve the better reduction efficiency of nitrate. The influences of bimetallic Fe/ Ni on nitrate reduction with different manufacture methods also discussed. The different weight ratio of bimetallic Fe/ Ni nanoparticles synthesized from Fe and Ni ion solution have larger nitrate reduction efficiency than mixture of Fe and Ni nanoparticles power synthesized separately. The synchronous synthesis of bimetallic Fe/ Ni(5:1) nanoparticles could have 0.0379 min-1 of Kobs. However, the mixture (5:1) of Fe and Ni nanoparticles, which have synthesized before only had 0.0131 min-1 of Kobs. The higher ratio of Fe/ Ni nanoparticles will make better reduction efficiency of nitrate.

Poster Session- Sediments

PAH Bioavailability and Toxicity in Freshwater Sediments

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Phosphorus Fractionation in Marine Sediments, Singapore using a Fractionation Extraction Procedure

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Up-to-date Technology for Treatment Dredged Sediments and its Beneficial Applications in Ago Bay, Japan

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Funnel and Gate Design for the Capping of Impacted Sediments

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Joanna Moreno, Adventus Group, Conifer, CO
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Enclosing Dioxins Contaminated Sediment by Geotextile Tubes

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Assessment of Risk of the Release of Combustible Vapors during Solidification/Stabilization Treatment of Highly Contaminated Sediment

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Remediating Sediment with Hydraulic Dredging and Geotubes®

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PAH Bioavailability and Toxicity in Freshwater Sediments

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Recent data have shown that PAHs in sediments from urban and industrial sites are often much less toxic than is generally assumed by generic screening values and toxicity is often not related to the concentration of total extractable PAHs using EPA standard methods. To increase the scientific understanding of what governs chemical exposure in sediments and how to measure it, the Sediment Contaminant Bioavailability Alliance (SCBA) initiated a program to develop a comprehensive database evaluating the bioavailability of hydrophobic organic compounds in aquatic sediments. To date, the SCBA has completed more than 12 case studies, with measurements of PAH bioavailability on 147 freshwater sediment samples. One hundred of the 147 (68%) sediment samples analyzed exceeded the PEC value for total PAHs (22.8 mg/kg); however, only 31 (21%) reduced survival of the aquatic amphipod *Hyalella azteca*. The SCBA has supported the development of a new analytical technique, measurement of dissolved PAHs using Solid-Phase Micro-Extraction (SPME). This chemical test is an excellent predictor of toxicity to the aquatic freshwater amphipod Hyalella azteca. Statistical analysis of the dose-response relationship using SPME PAH concentrations demonstrates the high precision of this analytical tool to predict amphipod toxicity. The application of this new analytical method is being demonstrated through a series of North American case studies that are being conducted in collaboration with various regulatory agencies. The goal of this effort is to develop technical guidance on the use of site-specific measures of contaminant bioavailability that can be used for establishing remedial goals and management strategies for impacted sediments.

Phosphorus Fractionation in Marine Sediments, Singapore using a Fractionation Extraction Procedure

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Phosphorous in benthic sediments is one of the main factors that control the trophic status of aquatic systems. To determine the role of sediments as a source of phosphorus to the overlying water column, total phosphorus content and the fractionation of phosphorus in sediment phases was investigated in benthic sediments collected from Singapore's marine environment. Fractionation measurements were conducted using the European Programme, Standards, Measurements and Testing (SMT) protocol. Phosphorous fractionation in benthic sediments subjected to agitation and exposure to water of varying salinities was determined, as well as phosphorous migration into in water. Data are used to evaluate transfer rates of phosphorus from benthic sediments into the water column.

Key words: Sediments, phosphorus fractionation, eutrophication, STM protocol

Up-to-date Technology for Treatment Dredged Sediments and its Beneficial Applications in Ago Bay, Japan

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Ago Bay is a typical enclosed-coastal sea, which is connected with the Pacific Ocean with very narrow and shallow entrance of the bay and is well known to be the most world-famous area as the starting bay on the culture of pearl. The bay is contaminated in the continuation of pearl culture for the span of 110 years. In recent years, the dredging of the organic contaminated sea bottom sediments has been developed in order to restore the sea environment condition and prevent from deteriorating the serious damage of pearl industry in Mie pref., Japan. However, the aspects of technical feasibility, economy, environmental and possibilities of product reuse could not be resolved. On 2005, up-to-date technology for a new in-situ prototype treatment system, exactly named the Hi-Biah-System (HBS), was developed and demonstrated in our project. Furthermore, the coagulant developed from the Paper Sludge Ash (PSA) could progress the solidification/stabilization processes such as the hydration reaction and ettringite formation with the pozzolanic reaction after adding the dredged sediment. With the HBS using PSA, the dredged material (>90 wt% is water) was reduced to 60 wt% placed in the confined disposal facilities (CDFs), which was replaced the technical turning point in muddy sediment belongs to the high watery, organically-enriched and much finely fraction (<75 μm) with beneficial applications for creating the new coastal environments. This paper describes the following points. (1) Constructing the biologically productive/environmentally friendly artificial tidal flat. (2) Making the bio-activated micro-habitat pellets for microorganism in order to promote the remediation of contaminated seawater and sediments. (3) Creating the stable surface area for culturing seaweeds and seagrasses since their plants provide shelter and feeding grounds for a diverse assemblage of organism. The present work is supported by “Environmental Restoration Project on enclosed Coastal Seas in Ago Bay” under the CREATE program of Japan Science and Technology Agency (JST).

Funnel and Gate Design for the Capping of Impacted Sediments

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Sub-aqueous sediments may be capped to protect the overlying water and biota from continuing contamination or the effects of sediment removal. Permeable caps may not be protective for the required lifetime and low-permeability caps may alter the natural flow system and in some cases need to be vented to address gaseous disruption. A new technology, combining two well-established technologies: zero-valent iron (ZVI) (O'Hannesin, 2003) and low-permeability capping (Battelle, 2005, 2006) proposes to provide treatment for a wider range of applications than impermeable or permeable caps alone. The technology is analogous to funnel and gate systems that have been implemented at multiple sites for groundwater plume remediation. This paper presents a modeling analysis of funnel and gate designs for a range of typical, full-scale subsurface sediment capping conditions. Basic model conditions are derived from field data and observations at existing sites and model assumptions are based on field data funnel and gate systems using either ZVI or granular activated carbon for the treatment medium. Flow and reactive transport modeling was used to evaluate the migration of naphthalene, arsenic, copper, and trichloroethylene to justify cap gate design parameters (areal extent, residence time, and hydraulic conductivity). The expected lifetime of the reactive gate materials is discussed. The results of the modeling analysis are being used to design a pilot application.

Enclosing Dioxins Contaminated Sediment by Geotextile Tubes

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In 2002, Japan enacted environmental standards for dioxins contaminated sediment. A nationwide sediment dioxins survey of public waters found sediment exceeding environmental standards in some rivers: a problem requiring countermeasures. The Eco-tube is a permeable geotextile container with soft and high water content sediment deposited in rivers, lakes, and marshes. It promotes dewatering of the sediment, and the filtering function of the tubes can purify the drain and enclose toxic substances such as dioxins. After dewatering, they are used to build embankments by taking advantage of their tensile strength. This report describes a trial execution of Eco-tubes that enclose dioxins contaminated sediment. The trial followed preliminary testing: measuring the quantity and turbidity of the drain by pressurized filtering test to examine the geotextile's filtering performance and select the coagulant. Next, 0.2m^3 tubes of the selected material were filled with sediment and used for laboratory experiments based on the actual execution, confirming the dewatering speed and filtering effectiveness of the method. The trial applied 2 patterns (5 cases) based on the test results. (1) Filling high density tubes with sediment already containing coagulant. (2 cases) (2) Filling tubes with sediment and adding coagulant into drain. (3 cases) Results: (1) Drain of 130pg-TEQ/g dioxins contaminated sediment becomes 2.4 pg-TEQ/l. (2) Drain including the 960pg-TEQ/l dioxins went down 0.42pg-TEQ/l by adding coagulant. Pattern (2) was much easier to execute, and more effectively reduced turbidity of the water. The tube height fell to 1/2 to 1/7 of maximum height in about 5 months. These findings confirmed that Eco-tube enclose dioxins contaminated sediment and reduce the volume of sediment by dewatering.

Assessment of Risk of the Release of Combustible Vapors during Solidification/Stabilization Treatment of Highly Contaminated Sediment

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Solidification/stabilization is a widely used method of decreasing the toxicity of sediments contaminated with metals and PCBs to allow them to be left in place or disposed of safely. For sediments that are also highly contaminated with volatile organic compounds, however, it is possible that the physical act of mixing or the reaction between the sediments and the solidification agent may release toxic material into the air. A treatability study was performed to assess this risk for a sediment contaminated with metals and volatile hydrocarbons and to determine whether solidification/stabilization was a viable option for sediment with the potential to release combustible vapors.

Sediment from a lagoon that is to be excavated at a facility in Louisiana was expected to require solidification. Very high levels of hexane and heptane were present in the sediment and there was a concern that treatment could vaporize combustible levels of the hydrocarbons from the sediment.

Solidification tests were set up using different concentrations of solidification agents. In order to determine whether solidification of the sediment would result in the production of potentially combustible heat or vapors, the temperature of the sample and the air above the sample were monitored during the mixing tests. Calcium oxide (quicklime) was the preferred solidification agent, but was expected to produce heat on contact with the wet sediment, and was therefore associated with the highest risk of combustion. Analysis of the vapor above the sample showed that the heat generated by the reaction of typical treatment dose did not appear to increase volatilization of hydrocarbons from the sediment. However, significant volatilization occurred if a larger amount of quicklime was mixed with the sediment.

This bench scale treatability study allowed the optimum solidification and dose to be selected and the potential for the release of combustible vapors to be assessed in a safe, timely and cost effective manner.

Remediating Sediment with Hydraulic Dredging and Geotubes®

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At a Massachusetts Contingency Plan site more that a century of backfilling and erosion of metals impacted soils into a near shore marina basin resulted in deposition of metals impacted sediments to significant depths across a third of the marina area. Planned maintenance dredging of the marina would resuspend and expose the sediments to ecological receptors. This project was undertaken to achieve sufficient depths to accommodate marina operations and to remove identified impacted sediments from a portion of the marina in accordance with the MCP. The remedial alternatives evaluation concluded that the least intrusive alternative that would provide a permanent remedy was hydraulic dredging of the unimpacted and impacted sediments from the marina, treatment of dredge effluent, dewatering of dredged sediments in Geotubes®, consolidation of these sediments with impacted soils from other upland areas of the site and subsequent capping. Federal, state and local permits restricted dredge operations to occur only between November and February. The sediment dredging was accomplished utilizing a hydraulic dredge positioned on a barge platform. The marina was dredged to target depths using a GPS positioned rotary cutter head and a suction pump. The resulting sediment/sea water slurry was pumped through a slurry pipeline and an on shore booster pump to a Smartfeed® effluent processing facility. The Smartfeed system conditioned the dredge effluent with polymer and distributed the treated effluent to designated Geotubes based on predetermined sediment segregation requirements. Dewatering run-off was clean and free of suspended solids and was routed through two temporary infiltration basins. Any overflow was pumped back to the dredge area and discharged inside the silt curtain. This presentation will include project photographs, figures and narrative illustrating the project benefits, roadblocks and modifications required to successfully complete the remediation within the permit required seasonal window.

Poster Session- Tungsten

International Tungsten Industry Association (ITIA) Global Stewardship Program
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Carmen Venezia, CIH, OSRAM, Towanda, PA
Zan Persichetti, Kennametal Inc., Latrobe, PA
Michael J. Pardus, ARCADIS Inc., Pittsburgh, PA

Sustainable Manufacturing: A Case Study from the Tungsten Hardmetal Industry
Michael J. Pardus, ARCADIS Inc., Pittsburgh, PA

Hardmetal Safety: An Industry Perspective
Zan Persichetti, Kennametal Inc., Latrobe, PA
Michael J. Pardus, ARCADIS Inc., Pittsburgh, PA
Dianne Green, ARCADIS Inc., Hamilton, OH

Tungsten Carbide/Cobalt Hardmetal Powder: Are they Carcinogenic?
John D. Schell, ARCADIS Inc., Houston, TX
Salvatore Giolando, ARCADIS Inc., Hamilton, OH
Michael J. Pardus, ARCADIS Inc., Pittsburgh, PA

International Tungsten Industry Association (ITIA) Global Stewardship Program

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In the United States and European Union there has been an increased pace of scientific research, regulatory initiatives, and media and NGO activity concerning the overall safety of tungsten, tungsten compounds, and processing facilities. Thus with the strong support of it's membership the ITIA Health Safety and Environment Committee initiated in 2004 a Global Stewardship Program which is expected to evolve along with the emerging science and the global regulatory environment. The ITIA member companies have had on-going regulatory compliance and employee safety and stewardship programs for years, however through this global stewardship program ITIA seeks to provide a unified voice for the tungsten industry and to develop credible science to support stewardship and growth of the industry. This presentation will describe the overall program, including assembly of an international scientific advisory group and industry sponsored scientific research programs. Key elements of this Global Stewardship Program include:

Establishing ITIA as a pre-eminent representative of the industry to regulators and all global stakeholders by establishing positive proactive relationships with key agencies and stakeholders.

Develop a comprehensive Environmental Health and Safety database, including full tungsten product life cycle characterization, to support definitive human health and ecological risk assessment along the tungsten supply chain, and support compliance with emerging regulations including the European Union's New Chemicals Policy -REACH.

Sustainable Manufacturing: A Case Study from the Tungsten Hardmetal Industry

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Sustainable practices and maximizing resource efficiency has long been a hallmark of the hardmetal industry. For purposes of this paper, hardmetal refers to products prepared from tungsten carbide and a suitable metal binder (typically cobalt or nickel). This paper presents information on sustainable practices within the hardmetal that form a part of a global tungsten supply chain. With a price that is equivalent to or higher than silver, maintaining high levels of resource efficiency is critical to the vitality of the hardmetal industry. Recovery and reclamation rates in the manufacturing operations are frequently in excess of 98%.

Sustainable practices within the industry that will be the focus of this presentation include:

- Use of technological advances to improve the working life of hardmetal tools and wear resistant parts;
- Advanced design techniques to reduce the amount of hardmetal required in tooling and metalworking applications;
- Minimizing product losses (and employee exposures) throughout the production cycle;
- Reclamation and recovery of non-product outputs; and
- End of life management activities for hardmetal products.

Hardmetal Safety: An Industry Perspective

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Hardmetal powder (tungsten carbide with a cobalt or nickel binder) is used to manufacture high value wear-resistant products that are critical to the aerospace, automotive, mining, construction, and energy industries, to name a few. In the United States and European Union there has been an increased pace of scientific research, regulatory initiatives, and media and Non Governmental Organization (NGO) activity concerning the overall safety of hardmetal. This presentation consists of four major themes:

1. A very small number of employees work in the hardmetal manufacturing industry in such a capacity where they are exposed to hardmetal.

2. Occupational exposures are controlled to very low levels across the hardmetal manufacturing industry.

3. The high intrinsic value of hardmetal results in an extremely high degree of hardmetal recovery, recycling, and reclamation throughout the life cycle of hardmetal products. The high recovery rates for this valuable product also lead to a high degree of control that limits occupational exposures, and minimizes environmental emissions of hardmetal.

There is virtually no hardmetal exposure to end users of hardmetal products, who are primarily engaged in industrial and manufacturing activities. The extreme wear resistance of hardmetal products means that very small amounts of hardmetal are needed to provide maximum benefit in product applications. This wear resistance results in no significant exposure to hardmetal dusts or fumes by end users. Additionally, few hardmetal products are designed for use by consumers (i.e., non-industrial applications).

Tungsten Carbide/Cobalt Hardmetal Powder: Are They Carcinogenic?

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Occupational exposure to hardmetal is associated with different types of lung disease including asthma, alveolitis, and interstitial fibrosis. In addition, limited epidemiological investigations have purported a link between occupational exposure to cobalt tungsten carbide (hardmetal) and lung cancer. These recent reports lead the International Agency for Research on Cancer (IARC) to classification hardmetal compounds as “probably carcinogenic to humans (Group 2A) on the basis of limited evidence for increased risk of lung cancer” (IARC, 2003). In July, 2004, the Senate Commission of the Deutsche Forschungsgemeinschaft (DFG) published its evaluation of the scientific substantiation for the categorization of “hardmetal”, the binary mixture of tungsten carbide and cobalt. The DFG rated hardmetal dusts as “category 1 carcinogens since they cause lung cancer in humans.”

The epidemiological studies cited by the IARC and DFG were reviewed, analyzed and subjected to causation analysis, a broadly accepted and scientifically objective methodology that utilizes a number of criteria in order to establish the existence of a cause and effect relationship between chemical exposure and an adverse health outcome, such as cancer. The specific criteria examined in this causation analysis included: 1) consistency of the association; 2) strength of the association; 3) dose (or exposure)-response relationships; 4) temporality; 5) biological plausibility; 6) confounder analysis; and 7) coherence of the evidence.

Application of these criteria to the four epidemiological studies cited by DFG in support of their categorization of hardmetal dust reveal that all four studies were plagued by study design weaknesses (e.g., low number of deaths), uncertainties, particularly in estimating exposure, and an inability to address important confounding variables, e.g., cigarette smoking and co-exposure to other IARC carcinogens. These study design weaknesses are amplified by the fact that three of the studies – Lasfargues et al. (1994), Moulin et al. (1998), and Wild et al. (2000) – are interrelated in that they study the same workforce, although not in its entirety in all studies, and hence are not independent investigations. Thus, the weak associations reported by these investigators should not be used to classify hardmetal dust as “category 1 carcinogens since they cause lung cancer in humans.”

Poster Session- Vapor Intrusion

Comparison of Naphthalene Measurements between Laboratory Methods and an Ultra-Fast Field Gas Chromatograph

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A Vapor Intrusion Study Using Multiple Lines of Evidence

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Vapor Intrusion Investigations Utilizing Passive Soil Gas Sampling

James Whetzel, W. L. Gore and Associates, Inc., Elkton, MD
Harry Anderson, W. L. Gore and Associates, Inc., Elkton, MD
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Comparison of Naphthalene Measurements between Laboratory Methods and an Ultra-Fast Field Gas Chromatograph

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Naphthalene is becoming an increasing concern in regards to vapor intrusion investigations. A number of states (Massachusetts, New York, New Hampshire) have the compound listed as a target analyte in vapor intrusion guidance documents, and that TO-15 is the preferred methodology for detecting this compound, although naphthalene is not considered a "VOC" as defined in this method. This paper presents the results of a side-by-side comparison of field and conventional laboratory analysis techniques for measuring naphthalene from a flux chamber. The zNose® Model 4200 Ultra-Fast Gas Chromatograph has been used for several years to monitor airborne naphthalene concentrations in real-time during remedial activities. Results from the zNose® are compared with results for samples collected with evacuated fused-silica lined canisters that were analyzed by using US EPA TO-15, and samples collected on an PUF/XAD resin cartridge and analyzed by US EPA TO-13.

A Vapor Intrusion Study Using Multiple Lines of Evidence

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Over the past 4 years we have evaluated 58 buildings located over six groundwater plumes at the Former Raritan Arsenal in Edison, NJ to determine if VOC-contaminated groundwater is affecting indoor air quality. Initially USACE developed its own methodology for evaluating risks under CERCLA, including site-specific risk-based non-residential criteria, in the absence of state regulatory guidance. The vapor intrusion pathway was subsequently assessed in accordance with the New Jersey Department of Environmental Protection (NJDEP) vapor intrusion guidance (VIG) beginning in 2004. Initial screening criteria (e.g. presence of buildings within 100 feet of the delineated groundwater plume boundary) were used to determine what buildings required investigation. Subsequent investigations included sampling subslab soil gas, soil, indoor air and ambient air concentrations of VOCs. A weight of evidence approach was used to determine whether further action was required, based on:

- Exceedances of residential VIG benchmarks in subslab soil gas and subsequently, indoor air;
- Evaluation of individual constituents as potential DOD-related contaminants;
- Comparison of indoor air concentrations with background ambient air concentrations;
- Comparison of concentrations of VOCs in groundwater, subslab soil gas and indoor air;
- Replicability of sampling results and consistency of ratios of VOC concentrations in groundwater, subslab soil gas and indoor air;

The NJDEP has concurred that over 40 buildings require no further action. Twenty buildings require ongoing monitoring and investigations, of which 10 have had remedial systems installed to address vapor intrusion. Where systems have been installed, USACE has followed its own risk-based criteria, consistent with CERCLA.

Vapor Intrusion Investigations Utilizing Passive Soil Gas Sampling.

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Investigating the vapor intrusion (VI) pathway is a critical part of the overall investigation of a site where the potential exists for human exposure to chemicals of concern. Determining whether or not an exposure pathway exists can be a complex and expensive endeavor. Recent state and advisory group guidance documents provide good overviews of the investigative process and of the techniques available; one of these techniques is passive soil gas sampling. Passive soil gas (PSG) sampling is a versatile tool that can be used to screen sites for the presence of potential chemicals of concern, to map subsurface soil gas plumes, and to focus subsequent sampling by more complex and costly methods. Advantages of PSG include simple and quick installation and retrieval, the ability to collect soil gas in low permeability high-moisture soils, time integrated sampling, and the ability to detect a broad range of chemicals at low concentrations. Although PSG data is often reported in units of relative mass levels, recent laboratory and field studies have been performed to examine the technique as a tool to estimate soil gas concentrations. Providing soil gas concentrations improves the ability of the technique to focus subsequent sampling and to screen sites for potential vapor intrusion risk. This presentation will include a description of a PSG sampling tool, the GORE™ Module, will describe the calculations used to determine concentrations, will include a summary of laboratory study results, and will present examples of field studies and investigations that incorporate estimated concentration values. The presentation will also discuss how PSG sampling data are being used as a part of VI investigations.

Wednesday, October 17, 2007

Poster Session- Acid Mine Drainage

Bioremediation of Acid Mine Drainage in a Uranium Deposit by Means of a Multibarrier

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Bioremediation of Acid Mine Drainage in a Uranium Deposit by Means of a Multibarrier

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Acid drainage waters generated in the uranium deposit Curilo, Bulgaria, since the summer of 2004 are efficiently treated by means of a multibarrier consisting of an alkalizing limestone drain and a section intended for microbial dissimilatory sulphate reduction, biosorption and additional chemical production of alkalinity. This section was filled by a mixture of solid biodegradable organic substrates (cow manure, plant compost, straw) and crushed limestone and was inhibited by a microbial community consisting mainly of sulphate-reducing bacteria and other metabolically interdependent microorganisms. The waters had a pH in the range of about 2.5 – 4.2 and contained radionuclides (uranium, radium), toxic heavy metals (copper, zinc, cadmium, lead, cobalt, nickel, iron, manganese), arsenic and sulphates in concentrations usually much higher than the relevant permissible levels for water intended for use in the agriculture and/or industry. The water flow rate through the multibarrier usually varied in the range of about 5 – 15 m3/24 h, reflecting water residence times of about 70 to 23 hours. An efficient removal of pollutants was achieved by the multibarrier during the different climatic seasons, even during the cold winter days (in December - February) at water and ambient temperatures close to 0 oC. The removal was due to different processes but the microbial dissimilatory sulphate reduction and the sorption of pollutants by the living and dead plant biomass played the main role during the warmer months of the year. During the cold winter periods, when the plant and microbial growth and activity were markedly or even completely inhibited, the sorption by the dead plant biomass and the chemical neutralization by the limestone were the prevalent mechanisms in the pollutants removal. The effluents from the multibarrier usually were enriched in dissolved organic compounds and sometimes contained manganese and iron in concentrations higher than the relevant permissible levels. However, these residual pollutants were removed by means of natural and/or constructed wetlands located near the multibarrier.

Poster Session- Analysis

Analysis of Sulfur in the Copper Basin and Muddy River Sites Using Portable XRF Instrumentation

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Laura Stupi, Thermo Fisher Scientific, Billerica, MA
Robert Schleicher, Thermo Fisher Scientific, Billerica, MA

Analysis Method for Congener Isomer by Series of Polar and Non-polar Column GC Combination

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Congener Specific Analysis of PCBs by High Resolution GC with Low Resolution MS – The Need For a Standardized Method

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1,4-Dioxane: The Impact of Analytical Method – A Case Study

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Determination of Acidic Pharmaceutically Active Compounds in Seawater by on Field Solid Phase Extraction and Liquid Chromatography — Tandem Mass Spectrometry

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Jie Zhang, National University of Singapore, Singapore
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Analysis of Sulfur in the Copper Basin and Muddy River Sites Using Portable XRF Instrumentation

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Copper Basin, located near the junction of Tennessee, Georgia, and North Carolina and the Muddy River in Boston, Massachusetts both present elevated levels of sulfur (S) in soils and sediments. The Copper Basin was once an active mining site and the elevated sulfur presence there is a result of pollution from the mining activities. One of the first steps is the identification and removal of S rich soils (greater than 2%) which are thought to have the greatest potential for acid mine drainage. The Muddy River is the backbone of the Emerald Necklace and the historic landscape surrounding Boston which has accumulated sediments with high levels of metals, petroleum hydrocarbons and decaying vegetation. The selection of a remediation strategy that minimizes sulfur volatile emissions during sediment dredging operations could be aided by a sulfur analysis of Muddy River sediments.

Previously, sulfur (S) has been considered too light an element to be detected with portable X-ray Fluorescence (XRF). However, with recent technological advances it is now a possibility to detect and sometimes quantify sulfur. The detection limit of sulfur had previously been established at approximately 1%, but new He-purge capabilities are pushing that number down to one-third of that value. Data will be presented from investigations of Copper Basin soils and Muddy River sediments to demonstrate the capabilities and effectiveness of the analyzer for site characterization and remediation activities. Analytical results obtained with XRF are compared to traditional Sulfur analytical methods.

Analysis Method for Congener Isomer by Series of Polar and Non-polar Column GC Combination

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In the environment, there are so many substances related with human health that should be known whether present or not and how much. Current analysis methods for complicate environment samples such as dioxin, PCB, VOC etc, have had some problem. In case of dioxin analysis methods, the problem is that not all of 17 toxic isomers could separate with single column. Therefore, 7 of dioxins and 10 of furans should be separated and quantified with polar and non-polar column one by one exactly. To resolve these problem pre-treated samples should be analyzed with more than 2 columns, which needs much more time and causes increasing cost due to readjustment of sensitivity and calibration curve. This study was to find out the method that can separate toxic 2,3,7,8-chlorinated dioxin with one time analysis quickly by combination with 2 different columns without the problem of existing single column method, which is difficult to separate isomers exactly. Polar SP-2331 column and non-polar DB-5MS column were connected in-line using 2 units of GC, maintaining the optimum temperature for each polar and non-polar column, 350℃ and 275℃ respectively. With one shot of sample, after first GC with relatively higher temperature separated substances from low chloride to high chloride using 60m non-polar DB-5MS column, second GC with relatively lower temperature separated substances using polar SP-2331 column, which had various length of 1m, 2m, 3m, 4m, 5m, 6m and 10m to see the change of resolution degree. The resolution degree of specific isomer from 2, 3, 7, 8-chlorinated dioxin could be improved by changing the elution characteristics.

Congener Specific Analysis of PCBs By High Resolution GC with Low Resolution MS – The Need For a Standardized Method

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PCB manufacture and distribution was banned in the USA in 1977, but to this day they remain a ubiquitous contaminate. PCBs are the focus of remediation efforts and are intensely monitored in natural resources such as groundwater, surface water, sediments, soils, fish, wildlife, and air.

PCBs were manufactured as Aroclor® formulations in the United States. The Aroclors® were produced to contain a fixed weight percent of chlorinated biphenyl to yield fluids that were useful in applications such as transformers, capacitors, heat transfer systems, hydraulic systems, and sealants. The PCB congener patterns exhibited by the original Aroclors® can be accurately and routinely measured by traditional analytical techniques (GC/ECD), with pattern matching the key tool in all routine methods of analysis.

As PCB entered the environment changes occurred to the original PCB patterns that make routine determinative methods ineffective in accurately identifying and quantifying PCB concentrations. Changes to the original PCB congener patterns have been mediated by; (1) physical changes such as mixing and evaporation, (2) extensive biotransformation by bacteria, and (3) alteration in the food web by bioaccumulation and enzymatic metabolism. Also, in many situations, PCBs exist with other environmental contaminates such as pesticides, Chlordane, Toxaphene, PCTs, and PCNs that will interfere with measurement by routine techniques.

This presentation will describe and present information on development of a gas chromatographic low resolution mass spectrometry method. Data will be presented on samples that have proven to be difficult to analyze by traditional GC/ECD techniques. Information will also be provided on certified standard reference materials (SRMs) and the accuracy of this method in quantifying PCB congeners. Lastly, we will demonstrate the sensitivity of the method by employing large volume injection (LVI) techniques to analyze low concentration samples.

1,4-Dioxane: The Impact of Analytical Method – A Case Study

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1,4-Dioxane (C4H8O2, CAS No. 123-91-1) often has been used with chlorinated solvents, particularly 1,1,1-trichloroethane (TCA), as a stabilizer and corrosion inhibitor. In recent years, evaluation of the presence of this compound where chlorinated solvent contamination exists has become of increasing concern because of the low regulatory concentration, resistance to biodegradation, and water solubility that limits treatment effectiveness by methods normally employed for volatile organic compounds.

Commercial laboratories commonly analyze for 1,4-dioxane in groundwater by either EPA Method 8260 or 8270, though the latter method does not list 1,4-dioxane. Method 8260 does not generally achieve reporting limits that meet regulatory concentrations. Determination of 1,4-dioxane in water at low detection levels may also be accomplished using a modified approach to Method 8270 with isotope dilution. Because of time and sample volume concerns, many laboratories have begun analyzing for 1,4-dioxane using a modified Method 8260 with Specific Ion Monitoring (SIM) GC-MS to improve the detection limits.

During a recent characterization sampling at a central Florida site with groundwater impacted by chlorinated volatile organic compounds and 1,4-dioxane, split samples of groundwater were collected and analyzed by both Method 8270 and 8260 SIM. The difference in reported concentrations of 1,4-dioxane by the two methods was significant, sometimes by orders of magnitude, creating a potentially severe regulatory impact. A study was initiated to evaluate the effect of the different analytical methods on reported concentrations.

This paper presents an evaluation of the comparison of Method 8260 SIM, Method 8270, and Method 8270 with isotope dilution using native samples, multiple-level spike addition, and multiple-concentration laboratory control sample analysis to evaluate the overall accuracy and precision of the three methods. Potential interference by other compounds that may effect the reported concentration by Method 8260 SIM was also evaluated.

Determination of Acidic Pharmaceutically Active Compounds in Seawater by on Field Solid Phase Extraction and Liquid Chromatography — Tandem Mass Spectrometry

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An in-field, solid phase extraction (SPE) procedure for the determination of pharmaceutically active compounds in large volume of seawater has been developed. In this study, ≥1L of seawater sample was collected using an on-vessel pump. An HLB polymeric SPE catridge (1g) was used directly for extraction of the sample. In the laboratory, SPE extract is analyzed by using Liquid Chromatography- Electrospray Ionization tandem mass spectrometry (LC-ESI-MS-MS). . The API 4000 tandem mass equipped with an atmospheric pressure chemical ionization source and operated in multiple reaction monitoring (MRM) mode. An Agilent 1100 equipped with a phenyl-hexyl column is used to introduce the sample to the MS. A 2 mM ammonium acetate buffer solution (pH 5.5) in a methanol gradient was used. The method has been used to determine several pharmaceutically active compounds in seawater samples from Singapore with good recoveries (greater than 80% in most cases). Among these target analytes, ketoprofen, naproxen and clofibric acid have been detected in the lower ng/l range. Data are presented for Singapore coastal seawaters and compared to available international data sets.

Poster Session- Bioremediation

Results of Detailed Field Pilot Study Applications of Magnesium Sulfate Solution to Remediate Petroleum Impacted Groundwater

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Characterising and Testing a Novel Biological Reduction Cell to Remediate Heavy Metal and Acid-Containing Mineral Processing Leachates, Heybridge, Tasmania

Alison L. Dann, University of Tasmania, Hobart, Tasmania
John P. Bowman, University of Tasmania, Hobart, Tasmania
Rodney Cooper, Echo Remediation PL, Wynyard, Tasmania

Spill Cleanup of Fuel Contaminated Soils after Roadway Accidents Using In Situ Bioremediation

Satya Ganti, Sarva Bio Remed, LLC, Trenton, NJ
Bob Frye, GEC Environmental Contracting Corp., Lovettsville, VA

^{13}C Bio-Traps™ Prove DBB Effectiveness Despite Pilot-Scale Treatment Downgradient of an Unmitigated Source Area

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Sheila McGroddy, Geovation Engineering, P.C., Florida, NY
Robert Zimmer, Geovation Engineering, P.C., Florida, NY
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Bioremediation of TOCs present in Fuel-contaminated Desert Mining Soil and Sawdust in the Atacama Region (Chile)

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Bioluminescence Bioassays by Testing Whole Solid and Their Solid-aqueous Extracts from Various Sites in Korea

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Comparison of In-Situ Groundwater Bioremediation Technologies at a Dry Cleaner Release Site

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Feather Wastes as Petroleum Sorbents: Study of its Structural Biodegradation

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Jaime García-Mena, CINVESTAV, Mexico City, Mexico

Enhanced Bioremediation Pilot Study of a Cr (VI)-Impacted Overburden Groundwater System in Kanpur, Uttar Pradesh, India

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Rajiv Kumar Singh, Govt. of India, Gomtinagar, Uttar Pradesh, India
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Use of Denitrifying Bioretention Systems to Control Non-Point Sources of Nitrogen

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Aerobic Degradation of 3-Nitrophenol by Pseudomonas aeruginosa Strain 3-NP-1 Isolated From Sewage Treatment Plant

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Results of Detailed Field Pilot Study Applications of Magnesium Sulfate Solution to Remediate Petroleum Impacted Groundwater

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Anaerobic degradation is the dominant driving force in natural attenuation of petroleum contamination in the subsurface. The contribution to natural attenuation by electron acceptors other than oxygen, such as nitrate, iron III, manganese IV, sulfate, and even carbon dioxide, has been the subject of considerable research in recent years. The addition of these alternative electron acceptors has been shown to have many potential advantages over the traditional approach of attempting to add dissolved oxygen to the plume. Kolhatkar et al. (2000), Wiedemeier et al. (1999), and Wilson et al. (2002) have shown that of these natural anaerobic processes, sulfate reduction accounts for most of the degradation. Cuthbertson et al. (2006) presented case studies that demonstrated the benefits of using Magnesium Sulfate solution to stimulate the biodegradation of petroleum contaminants in groundwater under field conditions at various sites. Results of detailed pilot studies performed at two sites in Michigan including changes in petroleum constituent concentrations, effects of application rates, determination of radius of influence, potential for aquifer clogging, influence of application solution concentrations and evaluation of potential adverse changes in soil gas composition will be presented. The results of these pilot studies demonstrate the technical feasibility of utilizing sulfate solution to stimulate biodegradation to safely and expeditiously remediate petroleum impacted groundwater. Updated results from case study sites presented in 2006 will also be discussed.

Characterising and Testing a Novel Biological Reduction Cell to Remediate Heavy Metal and Acid-Containing Mineral Processing Leachates, Heybridge, Tasmania

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At Heybridge a titanium processing plant operated between 1948 and 1996. The process used hydrochloric acid to extract the titanium from the ilmenite ore resulted in acidic metal-rich waste water being pumped into holding dams and left after the plant closed down. These dams leaked into the Blythe River catchment and ultimately Bass Strait. The leachates (pH 3.5 – 4.8) contained 620 – 1200ppm iron and other significant metals present included aluminium (93 – 320ppm), manganese (15 – 44ppm) and lead (18 – 160ppb) with low levels of cadmium, chromium, copper and zinc. These metals concentrations are 2 to 3 times higher than any acid mine drainage leachates in the published literature. The bioremediation system that was set up in 2001 utilises locally sourced agricultural waste products such as potatoes, mushroom compost and straw in enclosed bioreactors which promote the growth of sulfate- and metal-reducing bacteria. At present the system is running at 20 – 60% efficiency, hence an improved bioremediation system was required. To monitor the microbial diversity in the bioreactors a TRFLP (Terminal Restriction Fragment Length Polymorphism) method was used. TRFLP data correlated with 16S rRNA clone libraries constructed from the existing bioreactors. The clones sequenced were similar to iron- and sulfate-reducing and iron-oxidising *Proteobacteria* and *Acidobacteria* as well as *Bacteroidetes* and *Firmicutes*. Nearly half of the clones sequenced fell into lineages that are poorly represented by cultured organisms or have thus far been represented by only a few environmental sequences from contaminated aquifers. Laboratory-scale microcosms were set up to trial different amendments such as the addition of bicarbonate, ethanol, and molasses as well as heating and retention time to promote the growth of the metal-reducing and sulfate-reducing bacteria identified. This work will be followed by pilot-scale trials in small bioreactors on site leading to improvements to the full scale bioreactors.

Spill Cleanup of Fuel Contaminated Soils after Roadway Accidents Using In Situ Bioremediation

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Release of fuel oils during transportation or during roadside accidents is very common. According to the figures available, number of incidents involving hazmat accidents has increased from 7,297 in 1990 to 14,443 in 1999. In most cases the standard cleanup protocol is followed but in some cases it is not possible to follow the protocol because of the accident locations. It is particularly difficult to excavate surface soil where utility lines are very near to the surface. In such situations, it is considered safe to use effective bioremediation solution for on-site cleanup. In these situations, AgroRemed has been employed with successful results. Two case studies are presented in this paper, one study demonstrating revitalization of roadside vegetation through bioremediation after a spill of motor oil and in another case application of AgroRemed to sites affected by diesel spill with underlying utility cables. The TPH of the soil after bioremediation was reduced by more than 95% from 65,000 ppm in the first case while in the second case, the TPH was found to be below the detectable values from the initial value of 47,000 ppm. Both AgroRemed and VaporRemed are available in a ready to use liquid form and have been known to effectively bioremediate the contaminated soils and fumes in a very short period of time. They de-toxify the contaminated soils and facilitate growth of vegetation.

Virginia Department of Transportation (VDOT) was actively involved in the cleanup operations and although Virginia DEQ (VDEQ) was not directly involved, the department reviewed the data to confirm that the values of TPH were below the accepted levels.

^{13}C Bio-Traps™ Prove DBB Effectiveness Despite Pilot-Scale Treatment Downgradient of an Unmitigated Source Area

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An in-situ denitrification-based bioremediation ("DBB") pilot study was initiated in the fall of 2004 downgradient of a DoD-owned gasoline service station in Maine. The suggested remedial action plan for the site (developed by others) included targeted excavation to remove petroleum-impacted saturated-zone soils upgradient of the pilot-study area. However, the targeted-excavation remedy was not implemented, and consequently a continuing source of gasoline contamination remained immediately upgradient of the pilot treatment area throughout the pilot study. Limited batch-scale introductions of DBB nutrients in a few mini wells located within the source area induced significant changes in microbial monitoring parameters indicative of greatly enhanced gasoline biodegradation; however, these efforts were generally insufficient to make a measurable impact on the overall contaminant mass present in the source area as evidenced by apparent contaminant rebound downgradient of the source area, particularly in the upgradient-most sample locations in the pilot area. As a result of the contaminant rebound (or false positive "contamination" associated with biogenic compounds co-eluting in the GRO – TPH analytical ranges), the use of molecular biological tools ("MBTs") became critical to the overall evaluation of the DBB pilot study.

A Bio-trap™ study was conducted from November to December 2005 to evaluate the ability of denitrification-based bioremediation to degrade the aromatic hydrocarbons present in the aquifer. Bio-traps™ containing Bio-sep™ beads loaded with ^{13}C-labeled benzene were installed in two key wells: DP-13 located in the source area of the historical gasoline release and DB-04 located mid-plume and in the main DBB treatment area. The Bio-trapsTM were incubated for approximately one month and then retrieved and shipped to Microbial Insights, Inc. (MII) for molecular microbiological assays and determination of the mass of remaining ^{13}C-labeled benzene. MII also sequenced the eubacterial 16s rDNA separated via DGGE and analyzed the stable carbon isotope profiles (^{13}C/^{12}C) of the phospholipid fatty acid (PLFA) biomarkers recovered from the microbial biomass in the Bio-trapsTM. The isotopic abundance of fatty acids comprising greater than 1-2% of the total PLFAs were determined by gas chromatography-isotope ratio monitoring mass spectrometry (GC-IRMS).

The analytical results are among the most conclusive observed to date for the anaerobic oxidation and assimilation of benzene using ^{13}C-labeled benzene in Bio-traps™. Approximately 78% and 43%, respectively, of the ^{13}C-labeled benzene was degraded in the Bio-traps™ installed in DP-13 and DB-04 over a one-month period corresponding to first-order degradation rates of 0.050 day^{-1} and 0.019 day^{-1}, respectively. The majority of PLFA mass was associated with biomarkers indicative of the Proteobacteria. Partial 16S DNA sequences obtained via DGGE were dominated by Pseudomonas-related Gammaproteobacteria and Betaproteobacteria affiliated with the family Comamonadaceae. Whereas the DGGE profiles were dominated mostly by 16s rDNA sequences of Pseudomonas-related bacteria, quantitative fluorescence in-situ hybridization ("FISH") assays indicated that bacterial affiliated with the Class Betaproteobacteria were usually more abundant in response to DBB treatment.

Evaluating the "progress" of pilot-scale in-situ remediation methods is complicated by the fact that remediation is carried out in the subsurface where it is not possible to directly observe and control the treatment process to the extent desired. In-situ bioremediation under field conditions is not a controlled "black box" -- such as in a treatment tank or microcosm scenario – such that it is often impractical to collect a sufficient time series of "influent" and "effluent" data. This inherent problem with in-situ pilot programs is magnified when pilot-scale treatment activities are restricted to locations downgradient of a known or suspected source of continuing contaminant migration. However, even under these conditions, we were able to employ multiple MBTs in order to understand (a) whether or not the desired subsurface remediation process was occurring; and (b) to measure, describe and document the rates and mechanisms of in-situ bioremediation. At this site, the GRO and TPH levels measured in pilot area soils initially declined, significantly, then subsequently increased ("rebounded"). Hence, it was difficult to directly evaluate the pilot program using (only) these gross measures of "contaminants" (GRO, TPH). Despite this problem, the Bio-traps™ and other MBTs provided irrefutable evidence that the DBB process stimulated rapid and effective biodegradation and proved that DBB was a feasible and potentially cost-effective option for larger-scale site remediation.

Bioremediation of TOCs present in Fuel-contaminated Desert Mining Soil and Sawdust in the Atacama Region (Chile)

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Continuous fuel spills in the Atacama region due to Chilean mining industry, and consecutive pollution abatement using sawdust as a low-cost locally available adsorbent material, have resulted in large amounts of fuel-contaminated material. The Chilean legislation treats this fuel-contaminated material as hazardous waste and therefore, it should be contained or treated. This research sought to investigate the application of in-vessel composting of a fuel-contaminated desert-mining soil and sawdust in the Atacama region (Chile) as a bioremediation treatment technology. The composting reactors were operated using five soil to sawdust ratios (S:SD, 1:0, 3:1, 1:1, 1:3, 0:1, on a dry weight basis) under mesophilic temperature (30-40°C), humidity (50% MC) and ventilation (16 L/min) over 56 days using laboratory-scale in-vessel composting reactors. Total organic carbon (TOC) concentration in the composting reactors was monitored according to the Standard Methods (USEPA SW 846). The highest (50%) and the lowest (35%) TOC removals were observed in the sawdust and soil reactors after 56 days of treatment, respectively. The proportion of sawdust, time of treatment and interaction between both parameters had a significant effect ($p<0.050$) on the TOC removal. Additionally, correlations between TOC removal, pH, TOC/N ratio and total N were encountered in the different treatments. In the abiotic controls, no TOC removal was observed, suggesting that TOC removal in the treated reactors was due to biodegradation mechanisms. Higher levels of sawdust corresponded with an incremental number of O.T.U. (T-RFLP) at the microbial communities. The results of this research indicate that bioremediation of an aged fuel-contaminated mixture of soil/sawdust is feasible in desert mining soils in the Atacama region. Nevertheless, this research also suggests the necessity of providing a correct balance of nutrients in order to optimize the bioremediation treatment towards a maximum TOC removal.

Bioluminescence Bioassays by Testing Whole Solid and Their Solid-aqueous Extracts from Various Sites in Korea

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Ecosystems are mostly exposed to complex mixtures made up of various pollutants, different chemical forms (chemical species), metabolites, or pollutants in complexes with non chemical stressors. Release of some chemicals into the ecosystem causes concern because of their toxic effects at very low concentration. Chemical data alone, therefore, are not sufficient to evaluate the toxic effects of the contaminants and characterize contaminated environment, because they are not able to provide information on the effects of the chemical compounds and do not take into consideration the interactions between contaminants, matrix and biota. And only a limited number of compounds can be analyzed by chemical analysis. One major advantage of biological toxicity tests, over chemical analysis, is direct assessment of the potential hazard to the soil ecosystem caused by the mixture contaminants. The aim of this present study was to demonstrate a rapid bioluminescence bioassay to determine toxicity of complex mixtures in various solid samples collected from Korea.

Developed method was applied on whole and extracted solid samples. Test results with extracted samples showed lower toxicity and more variation than those with direct test. No significant correlation was observed between two test results. Such results may be due to the effects of complexity of the interactions of various contaminants with solid components, according to soil characteristics, such as pH, organic contents, redox potential, and contaminants properties. Though the solid-direct ecotoxicity tests indicated more harmful effect of the contaminated soil than the tests using soil extracts, the high variable toxicity by the soil extracts may be well related with the extractable portion of pollutant concentration in samples. According to these results it is highly recommended to complement the direct toxicity testing with soil extract toxicity testing to characterize the risks of contaminated soil. Future aim is to develop a practical interpretation for the relationship between contaminants by chemical analyses and both toxicity results.

Comparison of In-Situ Groundwater Bioremediation Technologies at a Dry Cleaner Release Site

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Two pilot-scale in-situ engineered bioremediation technology and monitoring programs were conducted at a project site located in north-central Pennsylvania to compare the potential effectiveness of patented groundwater treatment technologies to address dissolved-phase volatile organic compounds (VOCs) in groundwater. Groundwater and soil at the site are impacted with chlorinated ethenes resulting from an historic dry cleaner release.

Initially, after formula injection of the first substrate, groundwater monitoring results were favorable and indicated that chlorinated VOC degradation was beginning to occur. As time progressed, however, data clearly indicated that the in-situ microbial VOC breakdown that had been initiated was no longer occurring.

Evaluation of the groundwater monitoring results from the first groundwater treatment technology led to the conclusion that its failure was the result of a combination of the following factors:

Groundwater pH was severely affected by the production of acids post-injection and the acids inherently part of the substrate causing aquifer microbes to negatively respond through reduced reductive dechlorination activity.
The relatively high viscosity of the substrate at the time of injection contributed to an uneven distribution of the injection material into the aquifer.
The dehalococcoides bacterial population present in the aquifer was somewhat low relative to what could be described as an “optimal” population count.

Based on the results of the first program, a modified in-situ treatment and monitoring program that included a focused application of a second commercially available substrate into the subsurface was initiated. The second substrate injection program also included the introduction of sodium bicarbonate as a buffering agent to better manage the reduced groundwater pH levels.

Evaluation of analytical results and field-measured bioremediation parameters from the second, modified treatment suggested that a site-wide groundwater remediation strategy utilizing the alternative substrate is more appropriate at this particular site.

Feather Wastes as Petroleum Sorbents: Study of its Structural Biodegradation

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In México, it is common to find hydrocarbon-contaminated sites in areas of difficult access such as marshes and mangles. This problem has encouraged the use of sorbents for hydrocarbon spills, being the most used synthetic sorbents of low cost and high effectiveness. However the disposal of these materials is complicated due to the cost related to their confinement and incineration which cause even more contamination and promotes climate changes. The use of biodegradable sorbents for hydrocarbon removal is an “earth-friendly” attractive alternative. Chicken feathers (CF) are a suitable option because in addition to its high affinity for petroleum, the waste resulting can be degraded by keratinolytic microorganisms. The present report evaluates by scanning electron microscopy (SEM), the biodegradation of CF occurring when they were used in combination with a defined-mixed culture with abilities to remove hydrocarbons and produce keratinases in liquid culture (unpublished results). Treatments were carried out in Erlenmeyer flasks, containing 25 ml of mineral media, 6% w/v of CF and petroleum hydrocarbons (64,800 mg/l). Flasks were inoculated with the keratinolytic-mixed culture and incubated at 28ºC, 180 rpm during 21 days. Every 7th day, samples were analyzed by SEM and the residual hydrocarbons were extracted and quantified by gas chromatography. Controls without inoculum were processing at the same conditions. The micrographs show the different stages of CF biodegradation; at initial time, CF are complete and the microorganisms from the mixed culture only are in the supernatants. After 7 day of treatment, the biodegradation of CF begins as well as the colonization of feathers. Since the day 14 was very considerable the biodegradation and the adhesion of the microorganisms on the CF. We conclude that feathers are excellent support for hydrocarbon contamination removal due to their dual function as support, sorbent and their concerted biodegradation by the same microorganisms.

Enhanced Bioremediation Pilot Study of a Cr (VI)-Impacted Overburden Groundwater System in Kanpur, Uttar Pradesh, India

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Pilot-scale electron donor injection enhances hexavalent chromium Cr (VI) biochemical reduction to Cr (III) in an overburden groundwater system impacted by Cr (VI) disposal in Kanpur, Uttar Pradesh, India. The Study Area is located in the Indo-Gangetic alluvial plain, and is characterized by overburden stratigraphy consisting of up to about 50 meters of generally fine to medium sand interbedded with silty clay, which is underlain by about 100 meters of laterally continuous clay. The clay is underlain by interbedded fine to medium sand and clay to a depth of about 500 meters, which overlies granitic bedrock. Cr(VI) has been detected for about 20 years at concentration up to 16 milligrams per liter in groundwater samples collected from the shallower fine to medium sand unit. The source is believed to be indiscriminate dumping of wastes resulting from production of Basic Chrome Sulfate [$Cr(OH)_2SO_4$] and other reagents used by local leather tanneries. Approximately 540 kilograms of a carbohydrate-based remedial additive were injected into two wells screened in the fine to medium sand unit using about 40,000 liters of groundwater. Treatment solution make-up water was obtained from a downgradient extraction well located within the Cr (VI) plume, amended with remedial additive, and then injected into the upgradient wells to establish hydraulic control on the injection and to minimize dilution. Performance monitoring included five rounds of groundwater sampling for Cr (VI), total chromium, and certain indicator parameters, including total organic carbon (TOC) as an electron donor surrogate. Pilot study results suggest that remedial additive amendment resulted in an up to 99.9% reduction in Cr (VI) concentration; an up to 97% reduction in total Cr; and up to an order of magnitude increase in TOC concentration over the four month study.

Use of Denitrifying Bioretention Systems to Control Non-Point Sources of Nitrogen

STUDENT PRESENTER

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Non-point sources of ammonia, organic N, nitrate and nitrite cause eutrophication in freshwater and marine ecosystems. Eutrophication degrades water quality due to algae growth and depletion of aquatic life. Public health is another concern with high nitrate or nitrite levels in drinking water, since these compounds are known to cause methaemoglobinaemia in infants. Control of point sources of nitrogen, such as discharges from municipal wastewater treatment plants, has been a focus of environmental agencies over the last few decades. However, control of non-point nitrogen sources, such as atmospheric deposition, leaking septic systems and runoff from fertilizer use and animal wastes has been inadequate. This research focuses on the use of bioretention systems to control non-point sources of nitrogen. Two pilot-scale bioretention systems were designed and constructed with an aerobic nitrification layer and an anoxic denitrification layer. The anoxic denitrification layer differed in the two systems in that one was composed of a wood chip media to support the growth of heterotrophic denitrifiers and the other was composed of an elemental sulfur/oyster shell media and supported the growth of autotrophic sulfur oxidizing denitrifiers. The units were tested in the laboratory under varying total nitrogen (organic N, ammonia and nitrate) and co-contaminant (e.g. suspended solids, phosphorus, metals) loading rates and transient conditions typical of stormwater treatment units. Once the units are optimized they will be field tested at an agricultural site in Connecticut. The results of this study will be presented at the meeting.

Aerobic Degradation of 3-Nitrophenol by *Pseudomonas aeruginosa* Strain 3-NP-1 Isolated From Sewage Treatment Plant

STUDENT PRESENTER

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Nitrophenols are widely used in the manufacture of explosives, pharmaceuticals, pesticides, pigments, dyes and wood preservatives. Thus they will be present in the industrial effluents and have the potential to contaminate surface/ground water. Due to their high solubility and xenobiotic character, removal of nitrophenols requires specialized bacterial strains. Reports on the degradation of 3-nitrophenol (3-NP) are scarce. The present study reports the isolation and characterization of a bacterial strain degrading 3-NP.

3-NP degrading strain was isolated by serial enrichment from the sludge of a sewage treatment plant situated at Jajmau, Kanpur city. The strain was identified to be Pseudomonas aeruginosa by using biochemical tests as well as 16S rDNA sequence analysis. This strain was able to utilize 50mg/L 3-NP in the minimal medium devoid of any other carbon and nitrogen source. With ammonium chloride and 10mg/L yeast extract, degradation was observed up to 100mg/L 3-NP .However when succinate (1 mM) was used, the strain could tolerate and degrade even 200 mg/L 3-NP efficiently. No intermediate could be detected during growth phase. Release of ammonia (56%) and absence of nitrite in the culture broth during degradation indicate that 3-NP degradation was proceeding through reductive pathway. Total organic carbon (TOC) analysis of culture filtrate at the end of exponential growth phase indicated the extensive mineralization of 3-NP.Resting cell preparations could degrade repeated additions of 3-nitrophenol (100mg/L) even up to six cycles. Further studies are underway.

Poster Session- Brownfields

Remediating Asbestos at a Brownfields Site Under the New MCP Regulations

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Remediating Asbestos at a Brownfields Site Under the New MCP Regulations

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New Massachusetts Contingency Plan (MCP) regulations governing the management of asbestos containing material are being promulgated in 2007. This presentation will provide an overview of the new regulations and the practical implications. On a specific project basis, the presentation will examine those activities that will be required at the Former Oxford Paper Mill Site in Lawrence Massachusetts in order to comply with the new regulations. Details are provided regarding the design and project changes that were required to address the new regulations. In general, some of the potential impacts to Brownfields construction are discussed.

Poster Session- Chemical Oxidation

Chemical Oxidation Treatment at the Former Nitchequon Meteorological Station
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Mathieu Barbeau, Golder Associés Innovations Appliquées (GAIA) Inc., Montreal, Quebec, Canada
Kateri Normandeau, Golder Associés Innovations Appliquées (GAIA) Inc., Montreal, Quebec, Canada
Adriana Peisajovich, Transport Canada, Dorval, Quebec Canada
Ginette Lajoie, Cree Regional Authority, Montréal, Quebec, Canada

Evaluation of In Situ Chemical Oxidation of Soils at a Mixed Waste Site and Assessment of Effects on Ground Water Quality
Richard C. Bost, Environmental Resources Management, Houston, TX
Robert G. Perry, Environmental Resources Management, Houston, TX

The Application of Sodium Persulfate to Achieve Drinking Water Standards
James R. Fair, Weston & Sampson Engineers, Inc., Peabody, MA
George D. Naslas, Weston & Sampson Engineers, Inc., Peabody, MA

In-situ Chemical Oxidation of Residual Chlorinated Solvents - A Case History
Philip J. Knotts, URS Corporation, Salem, NH

A Pilot Study Using The iSOC® System To Remediate Diesel Range Petroleum Hydrocarbons
Daniel Servetas, Shaw Environmental, Inc., Latham, NY
Cecelia Campbell, Shaw Environmental, Inc., Monroeville, PA
Heather Fariello, Shaw Environmental, Inc., Latham, NY
Paul J. Kurzanski, CSX Transportation, Inc., Jacksonville, FL

Chemical Oxidation Treatment at the Former Nitchequon Meteorological Station

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The Nitchequon project involves the dismantling of petroleum tanks and the chemical treatment of diesel impacted soil to eliminate the risks for wildlife, fauna and flora, and allow the Cree community to develop the land as an outfitting operation.

The complexity of the project resides greatly in the logistical aspects, due to site location, accessible only by helicopter or hydroplane, with no access route, landing field, electricity or services, and where the short summer period reduces the treatment period

The remediation technique selected consists in a soil chemical oxidation treatment with potassium permanganate combining in situ and ex situ treatment. The process developed is innovative because permanganate is not usually used for hydrocarbon treatment.

The ex situ step of the soil mixing in the reactors allows a 50% reduction of hydrocarbons. This first phase of treatment required the design of efficient mixers, a perfect oxidant dosage and more importantly the optimization of the reactive agents' addition sequence. The in situ process allows increasing of the percentage of hydrocarbon reduction of about 10 to 30%. The oxidant used has a kinetics that allows the retention of a residual concentration of permanganate in soils that oxidizes the most refractory hydrocarbons in the long run.

Sustainable development was a priority throughout the entire project, in order to maximise the economic, social and environmental repercussions. The site remediation, the minimal use of fuel, the recycling of dismantled metal, the fixing of various installations on site, the maximal implication of Cree labour (direct source of revenue and development of their competence) and finally the possibility of an economic activity in the region constitute a heritage for future generations. The Canadian government has invested over 5 M$ for the realization of this project. The management of the project was done in collaboration with TC and CRA.

Evaluation of In Situ Chemical Oxidation of Soils at a Mixed Waste Site and Assessment of Effects on Ground Water Quality

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In Situ Chemical Oxidation (ISCO) entails the application or introduction of chemical oxidant into the subsurface for the oxidation and thereby the destruction/mineralization of organic constituents of concern (COCs) as a remedial technology. The purpose of this paper is to present a case study that involved research and both bench-scale testing and field demonstration of ISCO for a mixture of chemicals, many of which have been identified as recalcitrant. The paper also presents an assessment of ISCO's effects on the underlying aquifer. This paper illustrates an improved strategy that entailed the use of ISCO with mechanical mixing of clayey and silty soils to a depth of 25 feet in an affected area overlying a deeper aquifer. This paper provides evidence of the successful application of ISCO at a site that resulted in over 95% removal of the principal COCs. Based on the apparent effectiveness of persulfate as demonstrated in bench-scale tests, ISCO utilizing persulfate and a source of alkalinity was then applied to an affected area at the site. The site is a 1970s era waste disposal area where a multitude of different types of wastes were disposed. Six chemical constituents comprised the most abundant COCs at the subject site. These compounds are: 1,1-dichloroethane, vinyl chloride, acetone, 1,2-dichloroethane, benzene, and tertiary butyl alcohol. It was found that sodium persulfate can oxidize these compounds; however, the optimal reaction conditions vary for the different compounds. Solutions of 20% sodium persulfate and 2% of different alkaline sources were found to be most effective in bench scale tests. After the successful field demonstration, it was noted about a year later that dissolved oxygen and in situ natural attenuation degradation rates appear to have increased. The ground water data as well as the confirmatory field test and bench-scale test data are presented in the paper.

The Application of Sodium Persulfate to Achieve Drinking Water Standards

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The rapid remediation of petroleum-contaminated groundwater using sodium persulfate at a site located in a potential drinking water source area in Weymouth, Massachusetts will be presented. The groundwater at the site was contaminated with diesel and gasoline originating from leaking underground storage tanks (USTs). When initial attempts to remediate the groundwater to meet the stringent drinking water standards using accelerated natural attenuation failed, an activated sodium persulfate compound was used because of its oxidation potential and its ability to be safely applied. The results of groundwater monitoring illustrating the rapid oxidation of petroleum constituents, along with other key oxidation parameters, will be presented. Because of the effectiveness of sodium persulfate, site closure was achieved quickly, resulting in significant savings. The pitfalls and byproducts of sodium persulfate will also be reviewed. In addition, the successful use of sodium persulfate to remediate volatile organic compound (VOC) contaminated groundwater will be discussed.

In-situ Chemical Oxidation of Residual Chlorinated Solvents - A Case History

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At a manufacturing facility in New England, tetrachloroethylene, a dense non-aqueous phase liquid (DNAPL), leaked from an underground tank system. The solvent percolated down through saturated silty sand, encountered an underlying saturated low-permeable clay, and migrated down-slope on the surface of the clay until adsorbed and immobilized by the soil. As ground water flows through and around the impacted soil, the residual DNAPL gradually dissolves into and is transported with the ground water, resulting in a quasi-steady-state dissolved-phase plume that extends downgradient from the source area.

In-situ chemical oxidation was selected as the initial step of the remedial action plan, with significant reduction of the residual mass of DNAPL in the soil as the primary goal, which will ultimately reduce the time required to achieve ground water quality standards at the site. In-situ chemical oxidation bench and pilot-scale tests were performed, and a ten percent solution of RegenOxTM was injected into the soil at the site, as recommended by the vendor (Regenesis).

Prior to the initial injection event, an injection and soil sampling grid was established, and pre-injection soil samples were obtained and analyzed to provide a baseline for performance evaluation. The ground water quality baseline was established from the results of several years of monitoring conducted at the site. Injections were performed in November 2005 and May and August 2006. Post-injection soil and ground water samples were obtained and analyzed following each injection event.

This presentation includes descriptions and photos of the procedures and equipment used to mix and inject the oxidizing solution, observation of the chemical reactions and problems encountered, and an evaluation of the impacts of the injections on soil and ground water quality at the site to date.

A Pilot Study Using The iSOC® System To Remediate Diesel Range Petroleum Hydrocarbons

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A pilot test was designed and conducted to evaluate the effectiveness of the in-situ Submerged Oxygen Curtain (iSOC®) technology on the treatment of diesel range petroleum hydrocarbons and fuel oil at a site located in northern New York State. The pilot study was based upon results of previous investigations and eight years of routine groundwater monitoring conducted at the site. iSOC® is an oxygen delivery technology that infuses high levels of oxygen into the groundwater (without sparging), thus promoting natural attenuation. Results from previous investigations at the site indicated that there was residual hydrocarbon impacts (both dissolved and non-aqueous phase) in an area of the site where historical releases occurred. A Corrective Action Plan was developed and implemented to address the residual light non-aqueous phase liquid (LNAPL) contamination. Upon completion of the LNAPL removal from the site, a round of groundwater and soil sampling delineated the extent of residual dissolved and non-aqueous phase hydrocarbons located within the saturated zone of the site. Down gradient groundwater and soil investigations and monitoring show that the extent of the hydrocarbons in the groundwater and soil has remained limited to the confines of the site. Due to the shallow depth to groundwater (approximately 3 feet), the limited extent of residual hydrocarbons, tight soils, poor groundwater recharge, extreme weather conditions and the presence of structures on site which further reduce direct access to the subsurface, iSOC® technology was identified as a potential means to further remediate the site. Data gathered during the pilot study indicates that both volatile organic carbon (VOC) and semi-volatile organic carbon (SVOC) concentrations have been significantly decreased in two of the three monitoring wells located within the pilot test area. An evaluation of this pilot test will be presented, including the results of performance monitoring.

Poster Session- Emerging Issues with Energy in the Environment

Production of Electricity from Low Cost Oxy-hydrogen Bio-fuel Cell Using Hydrogen from Blue Green Algae

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Municipal Solid Waste Used as Bioethanol Sources and its Related Environmental Impacts

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Sustainable Geothermal Energy Systems - Lessons Learned and Future Designs

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Production of Electricity from Low Cost Oxy-hydrogen Bio-fuel Cell Using Hydrogen from Blue Green Algae

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Bio-fuel cell has several advantages over existing fuel cell technologies. In conventional fuel cells typically use platinum as a catalyst, and which is not widely accessible for its high cost. An oxy-hydrogen bio-fuel cell, based on a carbon-carbon electrode has been fabricated. The electrode pellets were made by mixing activated carbon powder with suitable binder. Polyvinyl alcohol was proven to be a better binder than other alcohol taken in trials. The anode carbon plate was charged with Co-Al spinel mixed oxide at high temperature. The electrolyte used was 30% KOH. As cynobacteria can split water into hydrogen, various blue green algae like Anabaena spp., Nostoc spp. and Spirulina spp. were taken to split water into hydrogen. Various nutrient enrichment techniques were employed to increase the water splitting capacity of these algae in order to increase the efficiency for hydrogen production. One liter algal bioreactor was attached to the fuel cell, at the anode end for hydrogen gas input. About 350 to 400 mV of voltage and a 150 mA of current were generated. This finding may be helpful as an impressive model for commercializing this technology.

Municipal Solid Waste Used as Bioethanol Sources and its Related Environmental Impacts

STUDENT PRESENTER

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Using municipal solid waste (MSW) as biomass sources to produce bioethanol production has been investigated in the laboratory. The Experimental results showed that highest conversion rate can be reached more than 90%, which is relatively high compared with other conventional biomass. By taking into account the existing waste collection system and the cost for disposing waste, makes this waste-to-ethanol system economically valuable. This paper identifies the possible application of this technology on both energy production and waste management by providing valuable product to meet energy demand and protecting environment from pollution. The potential impacts on related environmental issues, such as biodegradability, sustainable waste management, climate change, waste issues, land use and biodiversity, are discussed. Sustainable waste management solutions are also discussed under different economic, environmental, social scenarios.

Sustainable Geothermal Energy Systems - Lessons Learned and Future Designs

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Alternative energies are receiving increased attention from developers and the public, in response to concerns of climate change, reduction of carbon footprint, and a renewed interest in reducing our oil dependency. Consistent with this trend, the number of ground-source heat pump systems (geothermal systems) has increased dramatically in New England in the past few years, and many new systems are in the planning stages.

Case studies will be described to illustrate recent successes and failures in the development of geothermal energy systems, and to describe lessons learned. In general, the state-of-the-practice in geothermal design suffers from a lack of understanding of well design, aqueous geochemistry and changes that occur under pumping conditions (such as air entrainment and the resultant precipitation of metal oxides). The paper describes recurrent problems related to drilling methods that result in a failure to reach design depth due to high inflows from bedrock fracture zones. When wells fall short of the design depth, groundwater must be pumped to waste in order to maintain thermal efficiency. Also discussed will be thermal testing to verify geothermal performance and optimize configuration, and assessments of water quality with respect to maintenance issues for geothermal systems.

Problems in the design of geothermal energy systems can be avoided through design using a multi-disciplinary approach that employs the skills, knowledge and experience of drillers, scientists and engineers with backgrounds in well design and hydrogeology.

Poster Session- Heavy Metals

Effects of P Amendments on Lead, Zinc and Cadmium Uptake by Triticale from Industrially Polluted Soils

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Stabilization and Removal of Arsenic and Other Metals from Groundwater Using EHC-M

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Recent Record of Mercury in Precipitation in Central Virginia

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George Mushrush, George Mason University, Fairfax, VA
Douglas Mose, George Mason University, Fairfax, VA

Remediation of Mercury Impacts to a Public Water Supply System

George D. Naslas, Weston & Sampson Engineers, Inc., Peabody, MA
Paul Uzgiris, Weston & Sampson Engineers, Inc., Peabody, MA
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Cadmium: A Sufficient or Holistic Approach towards Risk Assessment and Regulation within the Danish Landscape!

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Demonstration Project: Immobilization of Lead in Soil and Groundwater using Apatite II™

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In Situ Stabilization of Zinc in Soil and Groundwater

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Kinetics and Isotherm Equilibrium Adsorption of Copper(II) Ions onto Chemically Modified Barley Waste

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Application of Calcium Oxyphosphate and Ferrous Sulphate for Pb and As Stabilization

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Effects of P Amendments on Lead, Zinc and Cadmium Uptake by Triticale from Industrially Polluted Soils

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Chemical immobilization is a promising technique for decrease of the mobility of the contaminants in ecosystems, in case of which chemical substances are added to the contaminated soils, for the purpose of reduction of the solubility and phytoaccessibility of metals, by means of absorption and/or sedimentation. The soil additives, used in phytostabilization, have to deactivate the metals quickly, to have a prolonged action, to be cheap and to be easily added to the soil. In a significant degree, some of the phosphorus-containing substances meet these conditions, among which are a certain part of the phosphate fertilizers, widely used in practice. The examinations in this respect are, however, episodical, while the results are often contradictory and they do not give a definite answer to the raised questions. This directed us to the conduction of a systematic examination having several basic tasks: (i) to determine the impact of some phosphate fertilizers on the quantity of the phytoaccessible forms of Pb, Zn and Cd, (ii) to compare the relative effectiveness of the selected additives on the accumulation of heavy metals in plants and (iii) to estimate the effect of the introduction of additives on the phytostabilization of contaminated soils. The obtained results show that the materials, containing P, examined by us, are effective in respect of the immobilization of heavy metals and they may be used in the growing of Triticale on moderately contaminated soils. One should have in mind that in the cases of soil contamination with Pb only, the superphosphate is more effective, while in case of combined contamination, it should be applied very carefully, because it leads to increase of Zn and Cd content in the epigeal parts of plants. In this case the application of KH_2PO_4 is more appropriate, because it is effective in respect to the three elements. The effect of the application of phosphorous-containing additives on the phytostabilization of soils, contaminated by heavy metals is compared to the effect of some organic fertilizers and sapropel (sediments on sea bed).

Stabilization and Removal of Arsenic and Other Metals from Groundwater Using EHC-M

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EHC-M™ is a specially formulated version of controlled-release, integrated carbon and zero valent iron (ZVI) technology for in situ chemical reduction. EHC-M encourages the precipitation and adsorption of dissolved metals such as chromium, lead, arsenic, zinc and mercury, to limit their movement downstream of a treatment zone. Arsenic in ground water is largely the result of minerals dissolving from weathered rocks and soils. Arsenic is naturally occurring in the environment and is present in groundwater at concentrations ranging from 1 to >50 micrograms per liter (ug/L).

The primary mechanism of removal entails physical precipitation with iron and other inorganic compounds. For arsenic, this involves primarily the reduction of sulfate to form arsenopyrite. Given that the removal mechanisms are precipitation and adsorption, the metals are transferred from the aqueous phase to a solid phase.

EHC-M has been shown to rapidly reduce the concentration of dissolved arsenic in groundwater from >1,000 to <10 ug/L. Under continuous-flow laboratory conditions, removal efficiencies exceeding 98% were achieved. After a period of loading the column with arsenic, a series of influent groundwater conditions were introduced into the column to demonstrate the ability of EHC-M to retain the arsenic despite conditions that could in theory reverse the process. Arsenic removal using EHC-M technology has been shown to be non-reversible by change in Eh or pH. The total length of the study is 950 days, or 2.6 years, and counting. Data from these tests will be presented along with field application data and field implementation methods.

Data from tests to remove and stabilize chromium will also be presented.

Recent Record of Mercury in Precipitation in Central Virginia

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Since 2002, weekly measurements of mercury in rain and snow have been gathered in central Virginia, as part of the National Atmospheric Deposition Program (http://nadp.sws.uiuc.edu/mdn/). The major sources of mercury in the atmosphere are coal-fired electrical power plants. The collaboration between our central Virginia deposition site and the other mercury deposition sites across North America documents weekly deposition patterns. These can be used to determine situations in which the mercury in precititation is excessive. Such information can be used to modify power plant emission regulations. The average mercury depositions in central Virginia were about 7.5 ng/L, with higher concentrations occurring mainly in the spring and summer. The weekly mercury concentrations were greater in rainstorms following weeks without rain (and less during weeks of frequent rain). Unusually high concentrations occurred just prior to the passage of Hurricane Isabel in September of 2003, and unusually low concentrations just after the passage. Taken together with deposition patterns of other stations in the national network, the patterns of mercury concentrations do not serve to identify any of the power station sites known to emit mercury. Instead, the source of mercury in rain and snow in central Virginia is a global "mercury pool" that is mixed and transported over long distances for weeks or months before it is deposited.

Remediation of Mercury Impacts to a Public Water Supply System

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A release of mercury at a municipal water well pump station building resulted in measurable concentrations of mercury in the water supply system, as well as in the concrete floor of the pump station building, in surrounding soil and mercury vapor in air in the building workspace. The well, one of only two water supply wells for the community was immediately shut down. Following an initial response to the spill, an approach to remediate all media including was developed, which not only provided technical challenges but also required the coordination between four departments of the Massachusetts Department of Environmental Protection (DEP).

Initial response actions included the disconnection of the well from the system and excavation of impacted soil. The problem was to rapidly evaluate if the mercury was present further down the distribution system and to evaluate all impacted media, including how deep mercury was released in soil, whether groundwater was impacted and how much of the concrete floor had absorbed mercury, which subsequently was de-gassing into the workspace. To further complicate matters portions of the water main were asbestos pipe, requiring additional regulatory oversight.

Response activities performed include: physical recovery of spilled mercury, removal of impacted piping and equipment, decontamination of mercury-impacted surfaces in the building, basement ventilation, excavation and off-Site disposal of mercury-impacted soil, installation of three soil borings/shallow groundwater monitoring wells, and collection of air, soil, and groundwater samples for laboratory analysis. The pipe was sampled at selected locations and no mercury was detected after a junction T-box located approximately 150-feet from the well. The pump station was washed down using HG-X to remove potential off-gas sources of mercury. The response actions resulted in regulatory closure and reconnection of this important water supply.

Cadmium: A Sufficient or Holistic Approach towards Risk Assessment and Regulation within the Danish Landscape!

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Cadmium, belonging to the group of heavy metals, is an environmental toxicant which is non essential to humans and living organisms but however implicated in many manufacturing processes. Over the course of the past years, there have been considerable efforts through established regulatory and risk reduction mechanisms in Denmark, to curb the spread, exposure and consequently toxic effects of this contaminant onto man and the entire ecosystem. However, some environmental exposure effects still abound. The soil remains to be the final recipient of all deposition pathways from anthropogenic parameters. Deposition on agricultural land(soil) in Denmark remains to be the most indirect pathway by which the general population becomes exposed as it is easily being absorbed by food crops largely via the use of phosphate fertilizers. This project aimed at identifying the various channels and parameters by which cadmium gets onto the Danish farmland as well as suggesting further risk reduction measures beyond what is actually in place. The application of phosphate fertilizers, sewage sludge and atmospheric deposition, were all identified as the most likely pathways by which cadmium additionally accumulates into farmland. In order to reduce further soil deposition, the project sought to recommend a general overhaul, of cadmium life cycle from the extraction to waste disposal phases, through the adoption environmentally friendlier innovative processes. This must demand firm commitment from all different relevant stakeholders both nationally and regionally whereby existing regulations be rigorously enforced as well as the establishment of new ones. All these would guarantee us a precautionary approach in a bid to keep levels and hence the resulting adverse effects, as low as possible.

Demonstration Project: Immobilization of Lead in Soil and Groundwater using Apatite II™

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The main purpose of this project is to reduce dissolved lead concentrations in groundwater at an airport site to a level below the standard for drinking water (10 µg/L) by the application of a new phosphate medium called Apatite II™.

Laboratory testing was conducted on soil and groundwater collected from inside the impacted area on the site. Column tests confirmed that Apatite II has good potential for binding lead (Pb). After water comes in contact with the Apatite II, slightly elevated concentrations of phosphorus (1.4 to 4.0 mg/L) seem to quickly resorb downstream of the reactive zone probably as a result of Pb and phosphate heterogeneous nucleation and precipitation as pyromorphite.

During the environmental characterization, lead concentrations in the groundwater reached 120 µg/L. At that time, the impacted area extended 350 m^2 in the surface aquifer and approximately 275 m^2 in the bedrock aquifer.

MODFLOW and MT3D models were used to simulate groundwater behaviour and lead transport beneath the site before and after the emplacement of the reactive barrier in the fall of 2004. Work included excavation of the soil to be treated, mixing of the soil with Apatite II, backfilling and paving of the excavated area.

Groundwater monitoring shows that the reactive barrier has stabilized and reduced the lead contamination by one order of magnitude and to below the drinking water standard (10 µg/L) in some monitoring wells. The reaction time was longer than expected, probably because of the low groundwater temperature and absence of surface infiltration. Monitoring is still ongoing. The use of Apatite II is a promising technology because the material is easy to apply and requires no treatment or maintenance infrastructure that limits the use of a site.

In Situ Stabilization of Zinc in Soil and Groundwater

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A 21-acre parcel in the Mid-Atlantic United States hosted several industrial operations from 1907 to 1982. Groundwater is present at 5 feet bgs in heterogeneous alluvium and saprolite. Flow rates are on the order of 100 feet per year. Groundwater at a pH of 5 SU and containing as much as 30 mg/L of zinc discharges to a small stream on one edge of the facility. The site surface was remediated and redeveloped into an apartment complex. Groundwater remediation to a goal of 2.0 mg/L zinc was deferred until after the apartment complex was built. In situ stabilization technologies that could be applied with minimal interference with site use were evaluated in bench-scale and in-field pilot tests. A slurry reagent that could be injected below the developed site was identified. The bench scale testing using site soil and groundwater samples found a 4 weight percent (wt. %) slurry dose increased pH to 10 SU and reduced zinc concentrations from 14.7 to 0.013 mg/L. The proposed remedial design took the form of a reactive zone at the edge of the facility, which required an evaluation of the long-term stability of an injected reactive zone. Multiple extractions found an extractant pH of 8.5 SU and zinc concentration of 0.088 mg/L of zinc following about 1,200 aquifer pore volumes of leaching, equivalent to 400 years at the site groundwater flow rate. Pilot testing was completed with direct-push injection methods. Approximately 7.3 tons of reagent slurried in 4,205 gallons of water was injected at six points. Temporary well samples within the injection zone had post-injection zinc concentrations of <0.020 mg/L. A monitoring well downgradient of the injection zone yielded 21 mg/L of zinc prior to the injection. Three months later the zinc concentration at the downgradient well was 5.4 mg/L. Approval for full-scale implementation was received and performed in August 2007.

Kinetics and Isotherm Equilibrium Adsorption of Copper(II) Ions onto Chemically Modified Barley Waste

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Barley waste of 30-40 mesh size was chemically modified by combinations of treatments, consisting of either 1% thiourea or no thiourea cross-linkage treatment followed by modification with acidified formaldehyde, 0.6 M citric acid, or sodium thiosulfate to improve the physical and chemical adsorption capacity of copper(II) ions. Adsorption capacity of copper(II) ions from aqueous solution onto chemically modified barley waste adsorbents have been carried out with the variation of pH, temperature, and copper(II) ions concentrations at batch experiment. Maximum adsorption capacities of copper(II) ions for all of the adsorbents had found at around pH 4.5□6.5. The Langmuir, Freundlich and Dubinin-Radushkevich(D-R) adsorption isotherm equilibrium models were used to describe the adsorption behavior. The maximum adsorption capacity (Qmax) of copper(II) ions predicted with Langmuir equation were 0.36 mM/g for citric acid modified barley adsorbent, 0.35 mM/g for thiourea modified barley adsorbent, 0.34 mM/g for barley adsorbents modified with thiourea and sodium thiosulfate and 0.33 mM/g for sodium thiosulfate modified barley adsorbent, when 0.25g adsorbent mix with an initial 100mL 28.5mg/L copper(II) ions at 30 ^{o}C and pH 5.5. Three adsorption kinetic models including pseudo-first-order rate, pseudo-second-order rate, and intraparticle diffusion equations were used to discuss the adsorption mechanism of copper(II) ions and barley adsorbents. The experimental data of copper(II) ions which adsorbed onto modified barley adsorbents fitted excellently the pseudo-second-order rate model and gave the best correlation coefficients (r2□0.94□1.0). It showed that chemical adsorption was the basic mechanism for this process.

The positive enthalpy change ($\Delta H0 > 0$) for the isotherm adsorption process from 15 to 70 15 to 70 ^{o}C was found, indicating that the adsorption of copper(II) ion was endothermic process and the adsorption capacity increase with increasing temperature. The negative Gibbs free energy change ($\Delta G0<0$) showed that the adsorption process was spontaneous. The positive entropy change ($\Delta S0>0$) suggested that the adsorption of copper(II) ion onto chemically modified barley waste increased randomness between adsorbent solid surface and copper(II) ion in the solution. Those results showed that low economical barley waste could be chemically modified into adsorbents for the removal of heavy metals from aqueous solutions.

Application of Calcium Oxyphosphate and Ferrous Sulphate for Pb and As Stabilization

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The potential for chemical immobilization of Pb and As in heavily contaminated soil from Lavrion, Greece was investigated. Calcium oxyphosphate dehydrate ($Ca_2(H_2PO_4)\cdot 2H_2O$) and/or ferrous sulphate ($FeSO_4$) solution were used as stabilizing agents. Calcium oxyphosphate was added to contaminated soil at PO_4 to Pb molar ratios equal to 0, 0.5, 1, 1.5 and 2.5, whereas ferrous sulphate was added at Fe to As molar ratios equal to 0, 2.5, 5, 10 and 20. Stabilization was evaluated by applying both chemical extraction tests and vegetation tests using dwarf beans as inicators. In agreement with previous studies, it was indicated that calcium oxyphosphate addition to contaminated soil significantly decreased Pb leachability, whereas it leads to a significant mobilization of As. In order to address this adverse effect iron was added in the form of ferrous iron sulphate solution. It was found that the addition of both calcium oxyphosphate and ferrous sulphate proved to be an effective method for immobilizing both contaminants in soil. The addition of at least 1.5 M/M phosphates and 10 M/M iron sulphate to the soil sample tested significantly reduced the dissolved levels of Pb and As in the water extracts to values in compliance with the EU drinking water standards. Biological tests using *Phaseolus Vulgaris Starazagorski* indicated that the treatment did not result in any significant change on plants growth and metals uptake.

Poster Session- MECs

Passive Reactive Berm (PRBerm) to Provide Low Maintenance Lead Containment at Active Small Arms Firing Ranges

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Munitions and Explosives of Concern (MEC) Investigation of an Open Burn/Open Demolition (OB/OD) Area

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Passive Reactive Berm (PRBerm) to Provide Low Maintenance Lead Containment at Active Small Arms Firing Ranges

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Live fire training results in the deposition of metals, such as lead and copper, into berm soils ranging in size from whole projectiles to microscopic dust. Surface water runoff and leachate water are two mechanisms with the potential to transport metals off-site. The Passive Reactive Berm (PRBerm) technology incorporates berm amendments that provide the capability to buffer a sand berm and react with metals (i.e. lead) as they are produced during the inevitable metals corrosion. Amendments will allow the pH in the berm to be adjusted near neutral conditions, promoting chemical immobilization of the lead. Treatability studies were conducted using meso-scale lysimeter cells where the runoff and leachate water were evaluated for their metals concentrations (Pb, Cu), Total Suspended Solids (TSS), pH, and Dissolved Organic Carbon (DOC) using 5,000 ppm lead SAFR berm sand. During lysimeter studies, soluble Pb and Cu concentrations were observed at significantly less than the demonstration sites permit discharge limit of 150 and 500 ppb (µg/L) for Pb and Cu respectively. A neutral pH range between 6.5 and 8.5 was maintained, minimal TSS and DOC concentrations were also observed in the lysimeter study leachate waters. The information gathered from the treatability study was used in the design and construction specifications of the PRBerms located at the demonstration site. Small scale Live Fire Lysimeters were built and used to test various amendments prior to application in a field demonstration. The benefits of the PRBerm when compared to traditional earthen berms include a reduction in migration of lead either as dissolved lead, colloidal lead, or lead sorbed to soil material suspended in the surface water. In addition, recycling the lead from the PRBerm can be accomplished with a commercially available rotary screen bucket mounted on a loader.

Munitions and Explosives of Concern (MEC) Investigation of an Open Burn/Open Demolition (OB/OD) Area

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This is a case study of a Formerly Used Defense Site (FUDS), 8-acre property that is currently within the boundaries of a Massachusetts State Park. As would be common to most FUDS Military Munitions Range Program (MMRP) investigations, site remediation is being conducted in accordance with the state regulations (Massachusetts Contingency Plan), FUDS Cleanup standards (based on CERCLA remedial investigation/risk assessment/feasibility studies), and the US Army Corps of Engineers MEC cleanup standards outlined in the Data Item Descriptions (DIDs). The issues associated with this site are common to many of the FUDS that contain known munitions OB/OD areas or landfills at former facility/base sites where munitions were historically present.

Given the past use of the site, the probability of MEC being present was considered very low. However, because it was an OB/OD area, the possibility of MEC needed to be further investigated and resolved at an acceptable risk level. The challenge is to accomplish this goal in a technically robust, cost-effective manner, hopefully without excavating the entire site. A multi-tiered site investigation approach was developed to focus the investigation, based on the assumptions that the actual disposal area was very small, and that there was likely no MEC outside the disposal pit. Several lines of evidence were used to identify the disposal area, including review and analysis of anecdotal history, aerial photographs, soil and ground water chemical data, contaminant fate and transport, magnetometer screening data, and subsurface boring records. Based on this analysis, the actual OB/OD area was estimated at 0.2 acre. Geophysics is the standard initial approach to investigating MEC sites and identifying potential MEC items. However, the OB/OD pit is problematic, since the amount of scrap shows a saturated geophysical response, and must be investigated through subsurface excavation. The first phase of geophysics work was mag and flag, done with the objective of screening the entire site, and identifying some portion of the 8 acres for further investigation. However, the mag and flag resulted in over 1,400 points being flagged as potential MEC targets throughout the entire site, excluding the suspected disposal pit. The following phase involved an electromagnetic (EM) survey of the site, excluding the disposal pit, to provide improved geophysical data. Saturated geophysical results from the EM survey indicated that the disposal area may be more than 7 times larger than anticipated. The final phase of the investigation included excavation to ground truth the geophysical data.

Poster Session- Miscellaneous

Microbial Toxicity of Manufactured Nanomaterials
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Teaching Green – Upper Cape Cod Regional Technical School a Renewable Energy Pioneer
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Multiresistant Microorganisms of Sewage from Leaky Sewers Pass the Urban Underground and Enter the Groundwater
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Microbial Toxicity of Manufactured Nanomaterials

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Nanotechnology is considered as one of the world's most promising new technologies in this century. When materials are made in nanoscale (smaller than 100 nm), their properties and applications change vastly from ordinary materials with a same composition. Due to the expected wide use and large quantity production, manufactured nanomaterials will be inevitably released into the environment. The small size and unique properties of nanomaterials make them active in unusual ways in the environment and reacting with living organisms. Therefore, there are serious concerns about their adverse impacts in the environment including their toxicity. In this study we examined the toxicity of three oxide nanoparticles, i.e. zinc, aluminum, and silicon oxides as well as C60 fullerene to three bacteria: Bacillus subtilis, Pseudomonas fluorescence, and Escherichia coli. Bulk oxide particles and activated charcoals were used as control. Bacteria were grown in TS broth for 24h. Then the bacteria were separated from the broth, washed with an electrolyte solution and incubated with prepared sterilized nanoparticle water suspension for three hours. A decrease in bacterial population compared to that of control treatment was used as a toxicity indicator. All nanoparticles showed signs of toxicity compared to control. Toxicity of nanoparticles was independent from the dissolved elemental concentration. Sensitivity of different bacteria to each nanoparticle was different. Zinc oxide nanoparticles were most toxic among the studied particles. AFM and TEM images confirmed the attachment of nanoparticles to the surface of bacteria. We concluded that the studied nanoparticles were significantly more toxic than their bulk counterparts. Further work is needed to study the effect of natural environmental parameters on nanoparticle toxicity. This study emphasizes the important environmental implications of manufactured nanoparticles.

Teaching Green – Upper Cape Cod Regional Technical School a Renewable Energy Pioneer

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Upper Cape Cod Regional Technical School (UCT) is a regional school district in the Commonwealth of Massachusetts. For more than thirty years, high school students and adults seeking continuing education from the towns of Bourne, Falmouth, Marion, Sandwich, and Wareham have turned to UCT for quality educational opportunities. Recently, the school has developed an impressive curriculum focusing on renewable energy. Weston & Sampson has been working with UCT to enhance their already stellar renewable energy curriculum with real-world renewable energy and engineering projects related to the design of a Leadership in Energy and Environmental Design (LEED) accredited marine sciences building. This building will utilize green energy generated from an onsite commercial-scale wind turbine to be designed by Weston & Sampson and UCT students. Student involvement will be a main focus during the design and construction of these projects to ensure that the next generation of UCT graduates embraces renewable energy and understands the basic science behind these technologies. The Massachusetts Technology Collaborative (MTC) recently selected UCT to receive a Large Onsite Renewables Initiative (LORI) grant for the completion of a wind power feasibility study at the Site. In addition, UCT has recently installed photovoltaic cells at the school to power domestic hot water heaters and biodiesel fuel is being generated in the school's laboratories to fuel a student-converted school vehicle.

This paper will discuss the renewable energy curriculum developed by the school and will present the recent design of the LEED-accredited marines sciences building and the results of the wind power feasibility study. The paper will also present the many student involvement opportunities that were available during the completion of these projects. Students used these opportunities to learn about the science and engineering evaluations associated with renewable energy projects and LEED design/construction techniques.

Multiresistant Microorganisms of Sewage from Leaky Sewers Pass the Urban Underground and Enter the Groundwater

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Background: In Europe sewers are more than 50 years old and leaky. Raw sewage is trickling through the vadose zone and is entering the groundwater after “soil filtration”. Since sand filters are used to remove bacteria from purified wastewater as the final treatment step, we investigated whether trickling of raw sewage through 1 – 2.5 m of sandy soil would be enough to prevent groundwater contamination with feacal bacteria or pharmaceuticals.

Research tools: The fate of trickling sewage was investigated in water-saturated and nonsaturated, aerobic or anaerobic sand columns and in-situ in a number of groundwater wells which were thrilled close to leaking sewers.

Results of study: Long-term trickling of sewage through different sand columns as well as in-situ investigations of groundwater from urban underground revealed the following results:

1. 99 – 99.9 % of the aerobic and anaerobic sewage population was eliminated after 1.25 m trickling in sandy soil, leaving a to high residual population of coliforms and enterococci as requested by the European bath water regulation. More than 3000 bacteria/ml of “sand-filtered” sewage reach the groundwater, containing still enterococci and coliforms.
2. It takes about 20 days in a closed glass coulmn, before methane generation begins. Whereas the number of aerobic bacteria in the biofilm of sand columns decreases, the number of anaerobic bacteria increases on top and with depths. The highest density of anaerobes is found to a depth of 20 - 50 cm. Then carbon sources are no longer available for an unlimited growth of anaerobic bacteria.
3. In anaerobic sand columns sulfate reduction leads to heavy metal precipitation and no metals are released with the effluent. Desulfovibrio is the predominat sulfate reducing species.
4. Escherichia is part of the biofilm and is initially present only in the upper part of a sand column. With increasing leakage time it is also found in the biofilm of deeper zones.
5. Multiresistant sewage bacteria are entering the groundwater and may lead to a distribution of antibiotics resistance gene cassettes.
6. Several antibiotics in sewage are passing the underground and enter the groundwater, there inducing even more antibiotic resistances.

Trickling sewage may cause an increase of antibiotic resistances within groundwater bacteria by introducing antibiotic-resistant feacal bacteria and non-metabolized antibiotics into the groundwater.

Poster Session- MTBE

Anaerobic MTBE and TBA Biodegradation under Different Terminal Electron Accepting Processes

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Anaerobic MTBE and TBA Biodegradation under Different Terminal Electron Accepting Processes

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The fuel oxygenate methyl tert-butyl ether (MTBE) is a prevalent groundwater contaminant, and its key degradation intermediate tert-butyl alcohol (TBA) often accumulates in subsurface environments. Although studies have reported potential for aerobic microbial degradation of MTBE and TBA, in situ conditions within proximity of source areas are typically anaerobic, and moreover, oxygen introduced artificially can be consumed quickly by chemical oxidation of Fe (II) and sulfides. Source area bioremediation strategies must encompass anaerobic conditions from nitrate reduction, Fe (III) reduction, sulfate reduction to methanogenesis, as these processes shift from higher to lower redox processes. This research has investigated the mechanisms and kinetics of MTBE and TBA biodegradation under shifting anaerobic conditions.

Microcosm experiments were initiated using petroleum contaminated sediment, river sediment, and anaerobic digester sludge. Radiolabeled (14C) and non-radiolabeled MTBE and TBA were amended to different incubations to quantify MTBE/TBA biodegradation. Different electron acceptor amendments and electron shuttling amendments were added to identify the MTBE degradation (and potential TBA accumulation) dynamics as conditions shift from one dominant process to another. To date the microcosms are in acclimation stage with up to 5% recovery of [U-14C]-MTBE or [U-14C]-TBA as 14CO2. Data suggest that fumarate and electron shuttles increase the extent of MTBE biodegradation; however, TBA degradation is slower than corresponding MTBE incubations. Sulfate increases the rate of MTBE and TBA biodegradation, but is very dependent on the starting material. Liquid enrichments with petroleum contaminated sediment degraded MTBE and TBA in less than one month under nitrate reducing, Fe (III) reducing, sulfate reducing and fumerate reducing conditions. These liquid enrichments may provide a model, anaerobic microbial culture for investigating basic cellular processes related to anaerobic MTBE and TBA biodegradation – currently, no such anaerobic culture has been reported. These data suggest that anaerobic MTBE/TBA biodegradation is influenced by shifting electron accepting processes, and the effects of these geochemical factors on MTBE/TBA degradation continue to be investigated.

Poster Session- Radionuclides

Inexpensive Removal of Waterborne Radon From Private Wells

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Inexpensive Removal of Waterborne Radon From Private Wells

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Single measurements of waterborne radon in several hundred homes with private water wells, plus years of multiple measurements in tens of homes, reveal that in northern Virginia, private wells deliver potable water with most dissolved radon concentrations at less than 10,000 pCi/L, with an average of about 2,500 pCi/L (the US-EPA recommended Maximum Concentration Level is 300 pCi/L). Experiments were conducted in many homes over several years to determine if activated charcoal installed in commonly used water treatment tanks (@ 1 foot diameter, @ 5 foot tall) could successfully reduce the concentration of waterborne radon for many months or years. It was found that most types of activated charcoal available to water treatment specialists lost their ability within weeks or months to retain radon long enough to keep the radioactivity decay activity contained to inside the treatment tank. However, activiated charcoal made from coconut shells worked the longest. It was also found that larger amounts of charcoal worked better. Taken together, it was found that 2 1/2 cubic feet of coconut activated charcoal worked so well that in most homes, the radon decay was contained to the treatment tanks for years.

Poster Session- Risk Assessment

Derivation of Soil Ecotoxicity Guidelines for Petroleum Hydrocarbons Derived Using the Target Lipid and Equilibrium Partitioning Models

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Somerville Community Exposure to Contaminants from Wood Treatment Facility Emissions

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Risk Assessment of Sewage from Leaky Sewers in Urban Underground for Soil and Groundwater

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Derivation of Soil Ecotoxicity Guidelines for Petroleum Hydrocarbons Derived Using the Target Lipid and Equilibrium Partitioning Models

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Soil predicted no effect concentrations (PNECs) for a series of equivalent carbon (EC) number total petroleum hydrocarbon (TPH) fractions or "hydrocarbon blocks" were calculated using representative structures from a database of physicochemical properties for nearly 1500 individual petroleum hydrocarbon structures. Equivalent carbon numbers correspond to boiling point intervals referenced to *n*-alkanes of a given carbon number. The blocks were categorized as aliphatic or aromatic and covered EC numbers of 6 to 20 for aliphatic hydrocarbons and 6 to 30 for aromatic hydrocarbons. The individual hydrocarbon structures in the database were assigned to the selected hydrocarbon blocks by boiling point and general hydrocarbon class. PNECs were calculated with a modified Target Lipid Model (TLM) combined with a statistical extrapolation (HC5) to calculate dissolved hydrocarbon concentrations in soil porewater that are protective of 95% of all species in the TLM database. The TLM was modified to make use of estimated organism lipid membrane-water partition coefficients (log K_{MW}) for very hydrophobic compounds (log $K_{\mathrm{OW}} > 5.5$) where there is an observed deviation from the normally log-linear relationship between membrane- and octanol-water partition coefficients for less hydrophobic compounds. The soil PNECs were calculated from porewater PNECs by using Equilibrium Partitioning theory. The PNECs calculated with this approach are compared to measured soil toxicity data for terrestrial plants, microbes and invertebrates. This approach offers improvement for environmental site assessments by allowing the composition of TPH in contaminated soils to be taken into proper consideration.

Somerville Community Exposure to Contaminants from Wood Treatment Facility Emissions

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A wood treatment facility in Somerville, Texas has been operating for approximately 100 years treating railroad ties and telephone poles. During the wood treatment process, a significant amount of toxic creosote, pentachlorophenol and copper chromium arsenic (CCA) was used. Much of the chemicals used during the wood treatment process were released into the atmosphere and deposited on the Somerville community. To evaluate the historic exposure to the community, chemical analysis of attic dust was conducted. Attic dust was analyzed for dioxin/furans (dioxin TEQs), polychlorinated biphenols (PCBs), polycyclic aromatic hydrocarbons (PAHs), copper, chromium, arsenic, and hexavalent chromium. The results from the analysis show a dioxin total TEQ maximum, upper confidence limit (UCL), mean, and minimum of 1229, 1178, 189, and 11 ng/kg, respectively. For benzo[a]pyrene TEQs, the maximum, UCL, mean, and minimum were 708, 658, 112, and 0.98 mg/kg, respectively. For arsenic, the maximum, UCL, mean, and minimum were 51, 22, 8.9, and 2.8 mg/kg, respectively. The chromium maximum, UCL, mean, and minimum were 145, 46, 31, and 8 mg/kg, respectively. The UCLs were calculated using ProUCL software.The results of this field investigation demonstrate that the community was exposed to elevated concentrations of contaminants from the wood treatment facility.

Risk Assessment of Sewage from Leaky Sewers in Urban Underground for Soil and Groundwater

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Background: Many sewers are more than 50 years old and leaky, and often release more than 20 % of the total sewage into the underground. The raw sewage is trickling through the vadose zone and non-adsorbed/non-degraded residual compounds enter the groundwater. To assess the risc of groundwater contamination by sewage the German Research Foundation (Deutsche Forschungsgemeinschaft) funded laboratory, pilot and in-situ studies at the University of Karlsruhe.

Research tools: The fate of trickling sewage was investigated in water-saturated and nonsaturated, aerobic or anaerobic sand columns, in a 3x3x4 m “model soil compartment with a leaking sewer” at the sewage tretatment plant in Karlsruhe and in-situ in a number of thrilled groundwater wells in the neighbourhood of leaking sewers.

Results of study: Long-term trickling of sewage through different sand columns and the model channel, as well as in-situ investigations of groundwater from urban underground revealed the following results:

1. Leaking rates in sandy soil vary with concentration and leaking time within a wide range. No permanent colmation was observed.
2. Most of the COD of sewage is degraded within the first 50 cm trickling stretch in sandy underground. Even after a trickling stretch of 2.5 m 8-10 % of the COD of raw sewage remain as non-biodegradable compounds, containing (new) humic acid-like and xenobiotic substances, as well as inorganic sewage compounds.
3. In the center of an anaerobic sewage plume heavy metals are precipitated and immobilized under anaerobic conditions by sulfide steming from sulfate reduction. However, when trickling rates are decreasing and the plume gets aerobic, metal sulfides are reoxidized by aerobic conversion to sulfates and these are dislocated to deeper layers.
4. A biofilm and EPS is formed on the sand grains, leading to an increased moisture content and thus to a longer contact time of the sewage with microorganisms. This leads to a somewhat better removal of pollutants.
5. Although the sandy soil acts as a filter for microorganisms, more than 3000 bacteria/ml from the sewage reach the groundwater, containing many faecal microorganisms, such as enterococci and coliforms.
6. Boron can be used as an indicator of sewage pollution of groundwater.

Lab-scale and field studies revealednthe above results and indicated that trickling sewage contaminates soil and groundwater considerably.

Poster Session- Site Assessment

The Value of Characterizing the Hyporheic Zone at a Variety of Contaminant Sites
Mark Emmons, Resource Laboratories, LLC, Portsmouth, NH
Richard S. Behr, Maine Department of Environmental Protection, Augusta, ME
Troy Smith, Maine Department of Environmental Protection, Augusta, ME
Brian Beneski, Maine Department of Environmental Protection, Augusta, ME

Utilizing LNAPL Laboratory Testing Methods to Evaluate Mobility for Site Characterization & Selection of Remedial Alternatives
Brandon J. Fagan, Haley & Aldrich, Inc., Boston, MA
Michael Brady, PTS Laboratories, Inc., Santa Fe Springs, CA

No-Purge Groundwater Sampling Evaluation at the Massachusetts Military Reservation
Matthew Greenberg, CH2M HILL, Otis ANG Base, MA
Nigel Tindall, CH2M HILL, Otis ANG Base, MA
Rose Forbes, Air Force Center for Environmental Excellence, Otis ANG Base, MA

The Trace Metals and Natural Radionuclides in Seawater from around Oil Field Offshore Platforms. Environmental Study
Sergio F. Jerez Veguería, Universidade Federal Fluminense, Niterói, RJ, Brazil
José M. Godoy, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ, Brazil and Comissão Nacional de Energia Nuclear, Rio de Janeiro, RJ, Brazil

Cleanup Standards and Goals For Urban Fill Soil
Bill Swanson, CDM Inc., Cambridge, MA
Pam Lamie, CDM Inc., Cambridge, MA

Can Fractured Bedrock Sites be Characterized Sufficiently to Recommend Viable Remedial Technologies?
Jim Vernon, ENSR, Westford, MA
Mark Kauffman, ENSR, Westford, MA
Patrick Haskell, ENSR, Westford, MA

Phosphorus Enrichment in Weihe River of China
Jialong Lu, Northwest Agriculture and Forestry University, Shaanxi, China and University of Massachusetts, Amherst, MA
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The Value of Characterizing the Hyporheic Zone at a Variety of Contaminant Sites

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In New England, groundwater flow paths generally terminate in the vicinity of surface water bodies. Groundwater discharges often manifest themselves as distinct springs or as wetlands adjacent to a stream or river while in other instances the groundwater may discharge directly to the stream through the underlying sediments. This zone of discharging groundwater is called the 'hyporheic zone.' Characterizing the chemistry of this discharging water provides useful information about upgradient contaminant sources and impacts to surface water bodies. Using a push point ™ sampler, an inexpensive sampling device, one can assess the chemistry of discharging groundwater. We discuss hyporheic zone characterization data from several contaminant sites to illustrate a variety of reasons why it is a useful component of a site investigation. We present data from two sites where characterization of the hyporheic zone provided invaluable data about upgradient groundwater quality before installation and sampling of monitoring wells. Evaluation of the hyporheic zone can also optimize subsequent monitoring well placement. In one example, groundwater data from a small network of bedrock monitoring wells demonstrated the existence of a contaminant plume associated with a sludge filled quarry but limited funds precluded the downgradient delineation with additional bedrock wells. However, the subsequent chemical characterization of the hyporheic zone along a small brook identified groundwater discharges more 1200 feet from the source. Perhaps most importantly, historically investigators have largely relied on surface water samples to assess the impact of discharging contaminant plumes. Characterization of the hyporheic zone may reveal the biota residing in the stream sediments are exposed to a very different chemical environment. We present data from two sites where the hyporheic zone water quality data clearly demonstrates the surface water chemistry yields little about the chemical environment within stream sediments, the portion of the stream in which benthic organisms live.

Utilizing LNAPL Laboratory Testing Methods to Evaluate Mobility for Site Characterization & Selection of Remedial Alternatives

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Current progress by the EPA, API, RTDF and a wide array of researchers over the last 20 years have developed tools and models to characterize the potential mobility of NAPL, more specifically LNAPL for petroleum impacted site assessment. Conventional methods and modeling for the potential mobility has relied heavily on indirect indicators of LNAPL plume stability and mobility in soil utilizing well information, fractional concentration of organics in soil characterized with EPA methods, saturation profile modeling and other. Laboratory test alternatives under consideration for direct quantification of LNAPL mobility in soil coupled with lines of evidence for the site are reviewed for practitioners use ranging from comparison of field saturation relationships to residual saturation capacities of the soil to methods to obtain results with more direct methods that include capillary pressure drainage relationships, analysis of the relative permeability of the LNAPL to flow in soil in the presence of groundwater, and methods for measurement using unsteady state constant flow testing and water flood pore volume exchange methods to quantify LNAPL drainage and imbibition. Methods of analysis such as these reinforce field observations and develop the understanding of the migration potential of a plumes source and boundaries with more direct quantitative procedures to support risk based approaches for land reuse. Further, for feasibility analysis of site treatment, they can be instrumental in quantifying the potential performance of a remedial technology for LNAPL containment, recovery, and evaluation of the impacts of amendment and thermal modifications to LNAPL.

No-Purge Groundwater Sampling Evaluation at the Massachusetts Military Reservation

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The no-purge groundwater sampling methodology enables the passive collection of a groundwater sample from a discrete interval within a monitoring well screen without the pumping or purging required by conventional techniques such as low-flow sampling. No-purge sampling relies upon the natural advective movement of groundwater through an open wellscreen. After sufficient time has elapsed for the sampling device to stabilize, the resulting sample is considered to be representative of the aquifer conditions immediately adjacent to the wellscreen. The primary advantage of using the no-purge technique is the cost savings associated with reduced sampling time, reduced equipment and materials, and elimination of purge water when compared to sample collection through conventional methods using pumps. The feasibility of integrating the no-purge sampling methodology into a large groundwater monitoring program was evaluated at the Massachusetts Military Reservation (MMR) where at least 1,500 monitoring wells are sampled each year. With this many wells to sample, the cost benefits of integrating this technology into the monitoring program could be considerable. Two types of no-purge sampling devices were tested and evaluated: the passive diffusion bag sampler (PDB) and the HydraSleeve® sampler. A series of "side-by-side" sampling tests were performed that evaluated the performance of: (1) PDBs versus the traditional low-flow pump sampling techniques; and (2) PDBs versus HydraSleeve® samplers. The testing consisted of a comparison of the analytical data generated using each sampling technique, a qualitative assessment of the useability of the sampling devices, and an evaluation of the potential cost savings of using no-purge techniques against the conventional low-flow pump methods. In addition, the evaluation reviewed the overall benefits and limitations of the no-purge samplers tested against the traditional low-flow pump sampling techniques currently being utilized at the MMR.

The Trace Metals and Natural Radionuclides in Seawater from around Oil Field Offshore Platforms. Environmental Study

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Offshore oil and gas production can cause a potential impact to the marine environment. Large volumes of aqueous waste are produced during oil and gas production and, normally, these are discharged, following treatment on the platform, to the sea. In this produced water the high concentrations of metals and naturally occurring radioactive materials (NORM) are often found and this contaminants are being introduced or have entered the sediment and water column near production sites. In this work the offshore seawater samples from the Bacia de Campos oil field were analyzed for As, Ba, Cd, Co, Cu, Mn, Mo, Ni, Pb, V, Zn, U, 226Ra, ^{228}Ra and ^{210}Pb. In this paper, a procedure for multielement determination of Cd, Co, Cu, Mn, Ni, Pb, V and Zn in seawater using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is described. The method involves chelation of the metals onto a iminodiacetate resin (Toyopear® AF Chelate-650M) in a column with the simultaneous matrix removal. U and Mo determinations were performed by ICP-MS with ultrasonic nebulizer in quantitative mode (external calibration) using ^{205}Tl as internal standard. The samples (salinity ≥ 3.5% p/v) were diluted 1:100 with Milli-Q water and acidified with HNO_3 sub-distilled. Arsenic was determined by HG-ICP-MS. Using twenty liter of seawater, after radiochemical separation, the ^{210}Pb was determined by beta counting of ^{210}Bi, and ^{226}Ra and ^{228}Ra were determined by gross alpha and beta counting rate using a proportional 10-channel low-level proportional counter. In general, except for the sampling point immediately at the place of discards of produced water, the trace metals and radionuclides concentrations in the analyzed samples of seawater around de platforms are in agreement with the expected values for unpolluted water.

Cleanup Standards and Goals for Urban Fill Soil

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Understanding background contaminant concentrations in urban soil is critical to expediting and economizing cleanup at urban/brownfield properties. The objective of this paper in support of a poster presentation is to examine metals and polynuclear aromatic hydrocarbons (PAHs) common to urban soil and to identify natural soil concentrations, historic fill soil concentrations and those concentrations that clearly indicate a site of release of contaminants or an outlier. This effort will detail common historic fill background concentrations versus distinct release concentrations or outliers in a form that can be readily used by a site assessment professional to screen urban sites.

The objective was accomplished by using approximately 5,000 samples of urban soil available to the authors and primarily subjecting the data to statistical analysis. The database available to the authors has generally been derived from sites in urban New England and, in particular, Boston. Moreover, findings elsewhere in terms of background concentrations of these contaminants in soil will also be provided to enhance the poster presentation. The mean values derived for key parameters were incorporated into risk assessment calculations to determine if the defined urban fill soil was also a significant risk. By incorporating a large data set into an analysis, the authors developed a tool that can readily be overlaid by an analyst using a smaller, site specific data set particular to a given property or site under consideration. This overlay approach using a short list of key parameters provides the analyst with a powerful tool to determine how many data points, if any, occur beyond normal urban soil limits. A ninety (90) percent cut off point was selected as an allowable maximum and an upper confidence limit on the mean was calculated. The metals addressed include arsenic, beryllium, chromium, nickel and lead. PAHs are represented by benzo(a)pyrene and dibenzo(a,h)anthracene.

Can Fractured Bedrock Sites be Characterized Sufficiently to Recommend Viable Remedial Technologies?

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Despite advancements in biogeochemical data and geophysical tools, the distribution and transport of groundwater contaminants through crystalline bedrock fractures remains challenging to conceptualize. Groundwater flow can be restricted to a discrete subset of connected bedrock fractures, while contaminant transport may not be well correlated with the degree of fracture-zone hydraulic activity. While characterizing hydraulic interconnectivity between source areas and receptors and between individual wells is a desired component of a conceptual site model (CSM), scale issues may prevent the identification of specific contaminant pathways or the prediction of contaminant concentrations throughout a site. This predicament extends into the identification of remedial technologies and the common lack of confidence in recommending a truly viable option.

This particular case study has been the subject of prior papers, demonstrating the sophisticated array and sequencing of investigatory tools applied to developing the CSM. The site is coastal Maine, dominated by shallow metavolcanic and intrusive bedrock, with little overburden material. Groundwater flow is controlled by bedrock fractures, lithologic contacts, or faults. CVOCs discharged on site from past operations have been detected in wells at concentrations up to 4,000 micrograms per liter, with a heterogeneous and somewhat unpredictable and unexplainable spatial distribution.

Investigations have included: geologic and fracture mapping, surface and borehole geophysical surveys, whole-well and packer sampling, monitoring well installation and angled coring, rock matrix analysis for CVOCs, rock mass characterization, soil sampling, photolineament analysis, borehole radar investigation, hydrophysical logging, packer sampling, and water level monitoring. A combination of conventional and less frequently-applied techniques has allowed an assessment of contaminant transport pathways in the source area, a refinement of the CSM for the overall site, and a more direct evaluation of remedial options. However, despite the use of these tools and well-executed investigatory program, there are no remedial technologies that appear to have the potential to restore aquifer conditions. This creates a situation where the optimum approach could be to simply continue protecting receptors from coming in contact with contaminated groundwater. This paper critically evaluates what level of investigation is essential, before such a finding can be concluded.

Phosphorus Enrichment in Weihe River of China

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Phosphorus (P) is an essential element for plant growth, but it also is a key element for eutrophication of water bodies. The loss of P from agricultural soils leads to not only reduced utilization efficiency of fertilizers and high cost of agricultural production, but also to the P enrichment in surface and ground waters. In this study, water samples were collected at seven sampling locations along Weihe River on eleven occasions between March 2004 and March 2005. Total P (TP), molybdate reactive P (MRP) and total dissolved P (TDP) of the water samples were measured. Dissolved organic P (DOP) and total particulate P (PP) were calculated by the difference between TDP and MRP, and between TP and TDP, respectively. The results showed that the average concentration ranges of TP, MRP, DOP and PP in Weihe River were 0.18~1.48 mg P L-1, 0.018~0.38 mg P L-1, 0.019~0.23 mg P L-1and 0.074~1.28 mg P L-1, respectively. The average proportion of PP (58%) was higher than that of MRP (22%) and DOP (20%). The data of TP and MRP in this study exceeded the eutrophication threshold levels (0.1 mg L-1 for TP and 0.01 mg L-1 for MRP). Most likely, P in Weihe River is coming from the agricultural soils along the river banks, particularly in September due to the amount of rainfall. Therefore, it is important to have appropriate soil management to reduce soil runoff, thus, the output of P to Weihe River.