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The 22nd Annual International Conference on Soils, Sediments and Water

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ABSTRACT BOOK

The 22nd Annual International Conference on

Soils, Sediments and Water

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22nd Annual International Conference on Soils, Sediments and Water

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Analytical Considerations for Applying EPA Method 1668A for PCB Analysis on Soil and Sediment Investigations

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Numerous groundwater, surface water, soil, and sediment investigations include characterization and subsequent remediation of PCBs in the environment. Historically, environmental samples have been analyzed for PCB Aroclors using GC/ECD analytical methods. Comparison of GC/ECD chromatographic patterns of samples to laboratory-generated PCB Aroclor standards has led to a variety of problematic reporting issues because PCBs released to the environment decades ago can undergo weathering, alteration or degradation to varying degrees depending on the environmental conditions. For example, a common situation has been observed when a laboratory analyst believes PCB congeners are present in a sample but a chromatographic match to an Aroclor standard is not reasonable and the sample result is somewhat “inappropriately” reported as not detected. Additionally, identification of Aroclor concentrations may not provide the best information for use in human health or ecological risk assessments.

As a result of these misleading Aroclor reporting problems and the need for congener specific information for risk assessment, application of high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) isotope dilution techniques to characterize and quantitate individual PCB congeners is gaining popularity. Since 1999, significant attention has been focused on use of the US EPA’s Method 1668A for PCB congener analysis. This costly performance-based method is often viewed as the gold standard for PCB congener analysis; however, a number of pitfalls and limitations exist in the method that should be understood at the earliest stages of the project planning phase when US EPA Method 1668A is being considered. The work presented will summarize the historic development of the US EPA Method 1668A, including the results of US EPA’s inter-laboratory validation study to validate the method, as well as the ramifications and current limitations of this analytical technique.

Perfluorinated Compounds in Surface Waters of the Pacific Northwest by HPLC/MS/MS Detection

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Perfluorinated compounds are widely used in manufacturing throughout the world for application of coatings on textiles and plastics, as surfactants and for insecticide applications. These compounds have been shown to be persistent in the environment and bioaccumulate. An HPLC electrospray-tandem mass spectrometry method has been developed to investigate the level of contamination of a number of perfluorinated compounds. Eight compounds including perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) were included to investigate the extent of contamination in surface waters throughout the Pacific Northwest. Sixty sites were chosen from five different regions of the Pacific Northwest. This allowed for comparison of areas with various levels of manufacturing and commercial activities. A range of sources from lakes, small streams and large rivers were also included for comparison. By utilizing liquid-liquid extraction coupled with HPLC/MS/MS, ultra-low detection limits have been obtained. The limit of quantitation was 1.0ng/L for all reported compounds. This was the first study that examined the extent of contamination by perfluorinated compounds in waters of the Pacific Northwest of the United States.

Mass DEP's Evaluation of Laboratory Performance based on a Large VOC Double-Blind Study

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The Massachusetts Department of Environmental Protection (MassDEP) regulates the cleanup of contaminated sites in the state under a privatized program begun in 1993. In the past 12 years, over 20,000 sites have been assessed and cleaned up under this system. However, assessment and cleanup decisions are based upon test data from labs that are not specifically approved or monitored for this work. That has lead to concerns over the quality of the analytical data used to support site cleanup decisions. To address these concerns, MassDEP conducted a large double-blind laboratory evaluation study, involving 19 commercial laboratories located throughout New England that provide the majority of analytical support services to parties assessing and cleaning up hazardous waste sites in Massachusetts. A "double-blind" study is one in which a laboratory is unaware that they have been sent samples that contain known concentrations of contaminants. This study, believed to be one of the largest "undercover" investigations of analytical testing laboratories ever conducted in the United States, was undertaken by MassDEP as part of a multi-year/multi-component data enhancement effort, in order to obtain a *direct, real world* sense of data quality and reliability in its waste site cleanup program.

Obtaining Representative PCB Site Data – Overcoming Common Field and Analytical Pitfalls

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The Toxic Substance Control Act (TSCA -40 CFR 761) contains stringent regulations for assessing and remediating sites contaminated with polychlorinated biphenyls (PCBs). These regulations include very detailed requirements for the collection and analysis of PCB samples. This paper will discuss common field and laboratory errors that could be detrimental to the goals of the assessment/remedial program and the usability of the analytical data including the following:

Field Sampling issues:
- Improper investigation sequence causing cross contamination
- Mismanagement of vehicular or heavy equipment traffic across the Site
- Improper decontamination methods
- Missing information on laboratory Chain of Custody such as field observation of odor (e.g. sulfur, petroleum, organic) sheen, or staining, concentration range assessed from previous Site data, and the required detection limits
- Lack of field Quality Assurance/Quality Control (QA/QC) samples such as field duplicates, MS/MSDs, and temperature, field and equipment blanks
- Failure to obtain the required approvals from USEPA
- Incorrect grid alignment for cleanup verification

Laboratory issues:
- Improper extraction methods (Sonication not allowed by TSCA)
- Interferences caused by sulfur or naturally occurring organics
- Excess water in sample requiring additional cleanup
- Unresolved mixtures of Aroclors and estimation of PCB concentrations
- Inability to meet project required data turn-around times (TAT) due to instrument down time, sample interferences, or unexpected high PCB concentrations
- Inability to meet required detection limits
- Poor batch QA/QC results including surrogate recoveries

We will present chromatograms from active TSCA-regulated cleanup sites that illustrate key issues presented above and discuss how proper field planning can result in the attainment of data quality objectives, regulatory compliance, and site closure.

Using Quadrupole ICP MS Generated Stable Lead Isotope Ratios in Environmental Risk and Forensic Studies

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Stable lead isotope ratios can be used to identify sources of environmental contamination because the isotopic composition of lead varies depending on where it was obtained. Decay of naturally occurring radionuclides to the stable lead isotopes Pb-206, Pb-207 and Pb-208 over geologic time scales changes the abundance of these isotopes in the ore from which the lead was processed. A source of environmental lead contamination can be characterized based on these differences in isotopic ratios and used to identify contributions to far field sites. Thermal Ionization Mass Spectrometry (TIMS) has typically been used to determine isotope ratios, however, Quadrupole ICP MS is becoming increasingly more common in environmental laboratories and can also be used to generate isotope ratios, though the precision may not be as good. Two case studies are presented using quadrupole ICP MS generated isotope ratios to identify sources of lead contamination or using lead as a tracer associated with other contaminants. In the first case, two sea water samples, an effluent and far field sample, were shown to have different isotope ratios indicating that the effluent was either not the source of lead to the far field sample or significantly diluted. In the second case study, sediment cores were collected to examine the extent of contamination from a source containing high concentrations of lead, copper and zinc. Isotope ratios from the source lead were characterized and used to indicate the contribution to a far field core with high lead concentrations in the surface layer and periodic depositions at lower depths.

Improved PAH Field Screening Method & Fluorescence Fingerprinting Hydrocarbon Sites

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Field screening soils and sediments for Polyaromatic Hydrocarbons (PAHs) has improved using on-site innovative technology, such as Sitelab's new UVF-3100D model. Sitelab's portable ultraviolet fluorescence spectrometer, which has been widely used to test volatile and semi-volatile aromatic hydrocarbons for their gasoline and diesel range fractions, can now be used to help assess and clean up sites contaminated with Benzo[a]Pyrene and other carcinogenic PAHs of concern commonly found in coal tars, coal ash and weathered fuel oils typically encountered at manufactured gas plants, power plants or other petroleum sites.

Sitelab has recently developed optical filters that are more sensitive and selective to the target PAH compounds reported by EPA Method 8270 performed by certified laboratories, a very time consuming and expensive analysis. Samples are first extracted in methanol solvent using disposable test kits and then measured on the analyzer, which is calibrated to a standard containing 17 PAH compounds, the same compounds reported by the off-site GC/MS method. The equipment is easy to operate and quality controlled. From start to finish, results only take 5 to 10 minutes. Correlation is very good, as illustrated in the case studies attached (see PDF file).

In addition, the new PAH optics have become an integral part of Sitelab's fluorescence fingerprinting method for hydrocarbon identification. The ratios, or proportions, of a sample's VPH, EPH and Target PAH fractions vary depending on how old and what type of petroleum contamination is there. The signatures exhibited provide environmental professionals forensic information in the field within minutes, allowing them to delineate contaminated sites more cost effectively.

Arsenic

Using Multiple Lines of Evidence to Demonstrate that Elevated Arsenic Groundwater Concentrations are Naturally Occurring

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Derivation of Site-Specific Arsenic Background in Soil: A Case Study

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Risk and Background Evaluation for Arsenic in Soil at a Planned Residential Development

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Living With Arsenic in Hawai'i – Case Study of a Former Sugar Cane Plantation

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Novel Technique for Sustainable Brownfield Remediation of Arsenic Contaminated Soils

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Using Multiple Lines of Evidence to Demonstrate that Elevated Arsenic Groundwater Concentrations are Naturally Occurring

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It has been widely documented that in many parts of New England, background concentrations of arsenic in groundwater may exceed existing and/or proposed standards. Consequently, the need to document that concentrations detected above the standard values are, in fact, representative of naturally occurring arsenic concentrations and not the result of an anthropogenic release of arsenic to the environment has become increasingly important in recent years.

The study site is located in central Massachusetts, adjacent to a tributary to a public water supply reservoir. During the course of an investigation to evaluate the potential for subsurface discharge of non-contact cooling water, groundwater samples were collected from overburden and bedrock aquifers. Laboratory analysis indicated that elevated concentrations of arsenic were present in several samples. At some of those locations, detected concentrations in overburden and bedrock groundwater exceeded the reportable concentration for arsenic under the Massachusetts Contingency Plan of 0.050 mg/l (subsequently decreased to 0.010 mg/l), which triggered the need for further evaluation of subsurface conditions.

In this study, multiple lines of evidence were used to support the position that elevated concentrations of arsenic were due to natural dissolution of arsenic-bearing minerals in the overburden and bedrock aquifers. These lines of evidence included: historical information that did not support any use or disposal of arsenic-bearing materials; available geologic mapping; field observations of overburden and bedrock encountered during well drilling; total concentrations of arsenic, iron, and manganese and microprobe analyses indicating the presence of arsenic-bearing minerals in overburden materials; and evaluation of geochemical characteristics (pH, dissolved oxygen, oxidation/reduction potential) of groundwater samples.

Derivation of Site-Specific Arsenic Background in Soil: A Case Study

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During the course of environmental investigations of sites where arsenic is one of the principal contaminants, it often becomes necessary to determine arsenic background in soil in order to define the extent of the arsenic contamination from the site and, in many cases, to help establish an appropriate cleanup level. Arsenic background in soil often has two components, one being "natural" background from the formation of the earth's crust, and the other being "anthropogenic" background from human activities not associated with the site. For sites located in mostly pristine areas, it is likely that only natural background is involved, which in the eastern half of the United States is fairly consistent over a very limited range of arsenic concentrations. For these sites, arsenic background in soil can be established fairly easily through use of existing regional data or from a limited sampling of soil in areas unaffected by the site. However, for sites where the arsenic contamination is extensive over a large off-site area and other anthropogenic sources are suspected to have contributed to arsenic levels within that area, the determination of arsenic background applicable to the site becomes more complex. This case study describes how arsenic background in soil was established at one such site.

Arsenic based pesticides were produced or handled at the New York site from the 1930s through the 1970s. During that period arsenic released through air emissions was deposited on soil in areas surrounding the site, and arsenic was also discharged into a nearby stream which contaminated sediment and floodplain soils. The land surrounding the site has historically been used for residential and agricultural purposes (including orchards). Due to the possibility of historic arsenic pesticide usage in area orchards and other possible non-site related sources of arsenic in the area, it was necessary to consider other anthropogenic sources in evaluating arsenic background for this site.

This case study will discuss how land use categories were established based on suspected degrees of historic arsenic usage and the development of a soil sampling strategy based on the relative size of each land use type in the area surrounding the site. The arsenic results from the background sampling will be presented for each land use category, and differences discussed. The statistical methodologies used to help estimate the arsenic background concentrations for this site will be presented along with an uncertainty analysis. Finally, the case study will explore the complexities involved in estimating arsenic background for use as a cleanup criterion, where human health and environmental risks must be considered.

Risk and Background Evaluation for Arsenic in Soil at a Planned Residential Development

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Arsenic soil concentrations at many Florida environmental investigation sites have been reported above the current U.S. Environmental Protection Agency (EPA) soil screening level (0.4 mg/kg) and above the recently modified Florida default residential exposure Soil Cleanup Target Level (SCTL) of 2.1 mg/kg. At a site in west central Florida, arsenic soil concentrations were observed site-wide during early routine sampling. In a Chen et al. (2001) study of background concentrations of arsenic in Florida soils, 27 out of the 51 Florida counties that were evaluated contained arsenic soil concentrations above the EPA soil screening level. Ten out of the 51 counties that were evaluated had arsenic concentrations in soil regularly above the contemporary residential exposure SCTL of 0.8 mg/kg. That study also identified elevated arsenic concentrations above FDEP's residential exposure SCTL in a geographic "belt" from Leon and Madison counties in NW Florida to Lee and Charlotte counties in SW Florida. This belt includes Hillsborough County, in which the Site is located. Based on a very extensive database for surface and subsurface soil, it was apparent that the observed arsenic concentrations at the Site represent a naturally occurring condition (2.4 mg/kg average and 2.8 mg/kg 95% UCL concentration drawn from over 2,000 samples collected across the Site). The close agreement between the mean and the 95% UCL concentrations indicates a low degree of statistical variability across the Site, and is supportive of the conclusion that the observed distribution represents naturally occurring background. Further, while the 2.8 mg/kg UCL exceeds the Florida default residential cleanup target of 2.1 mg/kg, it does not represent a significantly increased human health risk. While there was no regulatory involvement, preparation of the initial background survey, a site risk evaluation, and a local background evaluation allowed the Site owner and prospective developer to determine that the site was suitable for residential improvement.

Living With Arsenic in Hawai'i – Case Study of a Former Sugar Cane Plantation

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Environmental investigations at a planned hotel site and former sugar plantation camp in Kea'au, Hawai'i led to the discovery of significant arsenic contamination in soil (>500 mg/kg total arsenic). The arsenic is related to the use of sodium arsenite in sugar cane fields during the early 1900s. During this time, over 100,000 acres of land were under cultivation for sugar cane. The arsenic is sorbed to iron hydroxyoxide, allophane and imogolite particles in thin Andesols. The soil investigation was expanded to include multi-incremental sampling of eighteen other areas in Kea'au. The highest levels of total arsenic were reported for community gardens (mean 331 mg/kg), followed by undeveloped land adjacent to residential subdivisions (mean 278 mg/kg), parks (mean 121 mg/kg) and schools (mean 37.0 mg/kg). Background total arsenic is typically <20 mg/kg.

The elevated arsenic posed several initial concerns, including leaching and impacts to groundwater, uptake in produce and direct exposure of residents. Elevated levels of arsenic have not been reported in local water supplies. Lab-based leaching studies are underway. Total arsenic in produce from community gardens is similar to marketplace data compiled by the USFDA. Bioaccessibility tests were conducted on soil samples to further evaluate direct-exposure concerns. Reported bioaccessibility ranges from 1.5% to 22%, with the highest levels of bioaccessible arsenic reported for the hotel site (186 mg/kg) and the community gardens (111 mg/kg). Bioaccessible arsenic in other areas ranges from <1 mg/kg to 27 mg/kg. An in-vivo study carried out on soils from the hotel site yielded a bioavailability of only 5-6%, however, or approximately 35 mg/kg bioavailable arsenic. A urine investigation carried out on residents appears to rule out unusual arsenic exposure from living in the area. Measures are being taken to minimize long-term exposure and educate the community on chronic risks posed by high arsenic in soils.

Novel Technique for Sustainable Brownfield Remediation of Arsenic Contaminated Soils

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Contaminated land is increasingly becoming an important issue worldwide. Many metal contaminants are persistent in soil for a large number of years. Immobilisation of metals has proven to be a challenging task and a cost-effective, non-invasive and socially acceptable technology is required for its remediation. The present study involves the *in-situ* immobilisation of heavy metals using compost enhanced with iron oxide and/or zeolite (up to 20% w/w) the assessment of their effectiveness with respect to metals containment and greening capability. The preliminary results illustrated that the combination of compost/iron oxide yielded better results for reducing the leaching of As (95%), Cu (97%), and Cd (73%) and the compost/zeolite treatment has reduced the leaching of Zn (97%), whereas compost treatment alone reduced leaching of Pb (90%) from the contaminated soils. The sequential extractions results show that the untreated soils contain Cu, Zn, Co and Cr associated with the organic bound fractions (42-81%) whereas Cd, Fe, As and Pb are predominant in the residual fractions (41-82%). All the metal fractions were associated with a lesser extent to the exchangeable fractions, indicating that the metals are not relatively mobile. It was also evident from the nursery trials that higher biomass production was achieved when using compost/zeolite amendments. Overall, this study has demonstrated that zeolite/iron enhanced composts amendments have a significant potential in reducing leaching of metals and improving plant growth.

Bioremediation

Combined Abiotic and Biotic Dechlorination of TCE in a Low Permeability Aerobic Aquifer

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Combined Use of EHC^{TM} plus KB-1^{TM} Dehalococcoides Inoculant for Accelerated ISCR – First Full-Scale Field Application in Ohio, USA

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James W. Smith, T H Agriculture & Nutrition, L.L.C., Lenexa, KS

Bioremediation of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitroperhydro-1,3,5,7-tetrazocine (HMX)-Contaminated Sediments

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Bioremediation of Soil Contaminated with Organolead Compounds - Laboratory and Field Studies

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Anaerobic Bioremediation Results Lead to Alternative Cleanup Levels for Chloroethene Contaminated Groundwater at Connecticut Site

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Bioremediation of VPH and EPH Contaminated Groundwater Using *in-situ* Submerged Oxygen Curtain (iSOC) Technology

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Combined Abiotic and Biotic Dechlorination of TCE in a Low Permeability Aerobic Aquifer

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A pilot study was conducted using nanoscale zero valent iron (nZVI) and emulsified soy oil to promote dual abiotic/biotic degradation of TCE in groundwater at a site in New Jersey. Most of the contaminant mass is bound within a low permeability silt unit situated at a depth of approximately 20 feet. Aqueous TCE concentrations of up to 230 mg/L were present within the silt unit whereas concentrations in the overlying more permeable sandy unit were two orders of magnitude lower. Prior to the injection of the amendments ORP and DO levels indicated aerobic conditions, there was little to no evidence that biodegradation was occurring and low pH levels were likely inhibiting microbial activity.

The nZVI and emulsified oil were injected into three injection points which targeted the silt unit. Pneumatic and hydraulic fracturing techniques were used to enhance the distribution of the amendments. Within days after the injections, ORP and DO levels dropped significantly to levels as low as -500 mV and indicated anoxic conditions in the range of sulfate reduction to methanogenesis had been achieved. In addition, pH levels had increased to near neutral.

Six months after the injection ORP levels were still below -100 mV and continue to decrease downgradient of the pilot study area, and DO levels are still anoxic. Post-injection VOC data showed a significant drop in TCE concentrations in the injection area deep well (MW-17D) from 241 mg/L to 13 mg/L by month six. Concentrations of c-DCE increased from ND to 450 mg/L in MW-17D indicating the near complete transition of TCE to c-DCE had occurred at that location by month six.

Post-injection TCE concentrations increased significantly in the sand unit (from 1.4 mg/L to 220 mg/L by month two) indicating that the fracturing techniques and/or the surfactant properties of the oil emulsion had mobilized TCE mass from the silt unit. An electrical imaging (EI) survey and molar concentration trends confirmed that TCE mass had been mobilized. However, by month six, TCE concentrations had dropped significantly to 0.12 mg/L. Concentrations of c-DCE and ethene increased appreciably indicating the complete dechlorination of the mobilized TCE mass is taking place.

Fluorescence in-situ hybridization (FISH) and microscopic counts of *Firmicutes* (suspected fermenting bacteria), *Deltaproteobacteria* and *Dehalococcoides ethenogenes* (*D. ethenogenes*) indicated that an anaerobic consortium capable of microbial dechlorination of TCE developed in response to the nZVI-oil injections. Total cell counts (DAPI staining) indicated that microbial populations increased by one to two orders of magnitude in the treatment zone groundwater after the injections. After the initial increase, *D. ethenogenes* counts were seen to decrease in months three through six of the study. The decrease in *D. ethenogenes* counts combined with an increase in CO_2 and methane concentrations could indicate that anaerobic oxidation of VC and c-DCE may be occurring.

Combined Use of EHC^{TM} plus KB-1TM Dehalococcoides Inoculant for Accelerated ISCR – First Full-Scale Field Application in Ohio, USA

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Groundwater at a former manufacturing facility in Ohio is impacted by TCE (370 to 750 ug/L; remedial objective = 5 ug/L) and its recognized anaerobic daughter products 1,2-DCE (2,800 to 5,200 ug/L; remedial objective = 70 ug/L) and VC (390 to 510 ug/L; remedial objective = 2 ug/L). Groundwater collection trenches totaling over 330 ft in length were previously constructed downgradient of the suspected source areas. The trenches measure about 2 ft wide and are filled with washed river gravel from about 5 to 12 ft bgs. The groundwater table is generally at 6 ft bgs. EHC^{TM} was injected into the gravel zone to convert the existing trenches into in situ permeable reactive barriers (PRB) that would treat the groundwater as it flows through the reactive zones. In February 2006, a total of 11,850 lbs of EHC was injected into a total 30 injection points strategically located about 10 ft off-center throughout the existing trenches. Each injection point received about 400 lbs of EHC delivered as 170 to 230 USG of slurry containing between 19 to 25% solids, resulting in an EHC application rate of 2.7 to 5.3% to soil mass within the trenches.

Immediately, following the EHC injections, KB-1TM Dehalococcoides inoculum (SiREM) was added to better ensure fast removal of cis-DCE. Approximately 800 ml of concentrated cell KB-1 inoculant was injected close to each of 26 EHC injection points within two depth intervals of the trenches. The KB-1 injections employed a Geoprobe® and a drop-hose (PEtubing). Argonne gas was used to pressurize the system and the volume injected was measured using a "syringe-type system".

Details of the EHC and KB-1 injection processes will be presented along with remedial performance and cost data associated with the remedial strategy.

Bioremediation of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitroperhydro-1,3,5,7-tetrazocine (HMX)-Contaminated Sediments

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The explosives RDX and HMX are significant contaminants in soil and groundwater at DoD facilities. Adsorbed mass continuously leaches into groundwater and migrates to distal areas. This study investigated electron shuttling mediated-biodegradation of RDX and HMX from two environments.

Batch experiments were performed with RDX-contaminated aquifer sediment from Picatinny Arsenal, NJ and with shallow-depth sediment contaminated by both RDX and HMX from Joliet, IL. Several different electron acceptors/shuttles including humic substances (HS) and anthraquinone-2,6-disulfonate (AQDS), an HS analog, were incubated with acetate as an electron donor.

In aquifer sediment catalytic concentrations of AQDS and HS stimulated RDX reduction; RDX was below detect in 20 and 45d with AQDS and HS, respectively; nitroso metabolites did not accumulate in these incubations. Acetate alone did not stimulate the same rate of RDX degradation; 58µM RDX decreased to only 45µM during the first 60d and the nitroso metabolites accumulated in the absence of electron shuttles. RDX was not reduced in sterilized or unamended sediment incubations.

In Joliet sediment RDX has been reduced by 20% within 45d in the presence of both acetate and HS, likely due to higher initial RDX concentration. The initial concentrations of RDX (150mg/kg) and HMX (28mg/kg) are higher than their water solubility (RDX: 40mg/l; HMX: 6mg/l). Therefore adsorbed mass may continuously partition into the aqueous phase until equilibrium. HMX has not been reduced, suggesting that HMX is more recalcitrant than RDX. These results indicate that indigenous microorganisms in sediments can utilize electron shuttles to stimulate RDX/HMX biodegradation. This strategy will provide rapid and effective reduction of explosives in contaminated systems. Upcoming experiments will include DNA quantification using real-time PCR and total microbial community analysis using amplified rDNA restriction analysis (ARDRA) to identify the dominant microorganisms associated with HS-mediated RDX/HMX biotransformation.

Bioremediation of Soil Contaminated with Organolead Compounds - Laboratory and Field Studies

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Tetraethyllead (TEL) and tetramethyllead (TML) were produced world-wide as anti-knocking additives for gasoline to increase octane numbers, causing an ubiquiteous pollution with tetraalkyllead (TAL) compounds and derivatives. For gasoline production in 1970 in the United States of America 279000 metric tons of organolead were comsumed. Another 326000 metric tons of organolead compounds were added worldwide to improve the burning quality of gasoline. Since the 1980´s the TAL in gasoline was replaced by methyl-tertiary-butylether (MTBE). In future the MTBE in unleaded gasoline presumably may be replaced by ethanol. Whereas an ubiquiteous distribution of low concentrations of organolead compounds and of much higher amounts of inorganic lead was caused by car exhaustive gases in the upper layers of soil, spillages of highly toxic tetraalkyllead (TAL) compounds during production, transportation or blending at oil refineries and petrol stations caused more severe soil and groundwater contaminations.
In Germany TEL and TML were manufactured by two chemical factories until the end of the 1980´s. At both production sites significant amounts of organolead compounds were spilled and drained into the underground and still endanger the aquifer. The subsurface soil contains mainly fluvial sand deposits with a hydraulic conductivity of 3.5×10^{-4} m s^{-1}. On average, groundwater saturation starts about 3 m below the ground level and the groundwater flow is about 70 m$\cdot$year^{-1}. Little oxygen is found in the groundwater upstream and no oxygen in the groundwater downstream of the industrial site.

Spillage of tetraethyl lead (TEL) and tetramethyl lead (TML) caused severe soil and groundwater contaminations at all TEL manufacturing sites and at gasoline distribution stations not only in Germany, but also in other gasoline producing countries (e.g. in Italy, etc.). During the regular production process volatile alkyl lead compounds were absorbed from the off-gas of TEL or TML production sites by the use of heavy-boiling oil fractions (hydrocarbons). The oily TEL or TML concentrates or TEL-/TML-containing production fluids were apparently spilled by inaccurate handling and migrated into the underground.

The nonionic TEL is stable in heavy oil phases but is unstable in moist soil and, once it is dispersed in the water phase, is subjected to chemical and/or biological dealkylation reactions. The first dealkylation products are very stable ionic, water soluble tri- and dialkyl lead compounds, which are motile in the water-saturated zone and cause a severe groundwater problem. The conversion of organolead compounds by degradation of the alkyl moieties into inorganic, less toxic lead (succeded by immobilisation of the Pb-ions to $PbCO_3$ or Pb_5PO_4Cl) reduces the environmental risk.

Bioremediation

Suitable conditions for chemical and microbiological transformation of alkyl lead to inorganic lead may allow in situ remediation of contaminated sites. Microbiological dealkylation of organolead compounds was reported in laboratory and field studies. However, the biological oxidation required an electron acceptor such as oxygen.

In a laboratory study, 10-L glass columns were filled with TEL contaminated soil (~ 300 mg TEL/kg soil and ~ 530 mg oil hydrocarbons/kg soil) from a TEL/TML-manufactoring site and dealkylation activity was monitored. In each of three parallel columns oxygen-saturated water (ca. 30 mg O_2/L; saturation with pure oxygen) or oxygen-saturated water plus a mineral mix to supply essential minerals for the microorganims was circulated to improve the conditions for the autochthonic soil microflora. At a pumping rate of 2.2 l per day and a retention time of the water/mineral mix in the columns of 1.4 days oxygen limitation was prevented. The formation and degradation of the tri- and dialkylated species in the circulating water was observed with time. Measurement of oxygen levels in the water leaving the columns with mineral addition revealed a much lower residual oxygen concentration of 2.8 – 3.6 mg/l compared to the leachate of the columns with just water circulation (13.4 mg/l). This indicated an accelerated respriation activity and therefore an enhanced microbial activity in the nutrient-enriched soil environment. The soil columns were run more than two years at different alkyllead concentrations. Most of the tetra- and trialkyllead was chemically converted and microbiologically degraded to inorganic lead precipitates, carbon dioxide and water. A significant viable population of microorganisms was found in the columns desipte of the alkyllead toxicity and the poor supply with nutrients and a suitable carbon source even after 3 years.

At the contaminated site, the groundwater was enriched with oxygen by air injection through air-injection wells. Air injection caused a groundwater circulation and the oxygen-enriched groundwater led to a degradation of the TEL/TML-contaminants.

For final sanitation of the alkyllead-contaminated site, the hot spot of the contamination was excavated and thermally purified. The heated soil was refilled in order to reduce the time requirement for biological sanitation. The residual groundwater pollution downstream of the polluted site was treated by pumping out the groundwater through groundwater wells at the end of the industrial area, oxygen-treatment of the groundwater that contained still low levels of tri- and di-alkyllead compounds in a special basin and re-infiltration at the upstream end of the area for final microbial purification in the soil.

Anaerobic Bioremediation Results Lead to Alternative Cleanup Levels for Chloroethene Contaminated Groundwater at Connecticut Site

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Trichloroethene (TCE) in the groundwater beneath a manufacturing facility in Connecticut is being treated utilizing a combined system of in situ enhanced anaerobic bioremediation (EAB) and groundwater control with the old pump and treat system. EAB was initiated by injection of sodium lactate (carbon source) into the upgradient third of the contaminant plume. Simultaneously, groundwater control was maintained with an extraction well located at the downgradient property boundary, with tray aerator and activated carbon treatment. Horizontal wells from the old pump and treat system were also utilized to enhance delivery of the carbon source. At the start of biostimulation, TCE concentrations ranged from 5,000 ug/L to 20,000 ug/L. Within one year, more than 50% of the TCE was transformed into cis-1,2-dichloroethene and vinyl chloride, while final daughter product ethene concentrations reached as high as 700 ug/L. The pilot test results indicated that the treatment time could be reduced by over 20 years and save up to $600,000, in comparison to continued operation of the original groundwater pump and treat system. Similar application of EAB to the remainder of the plume is planned.

A conceptual site groundwater model was constructed to predict chloroethene concentrations at multiple monitoring locations throughout the remediation process. The model and the EAB results were used to negotiate with the state regulatory agency a series of cleanup standards for the following sequential stages in groundwater cleanup: (1) termination of groundwater pumping, (2) ending active bioremediation, and (3) conducting monitored natural attenuation (MNA). The integration of the remaining components of the old pump and treat system and the EAB process was effective in maintaining regulatory compliance, while expediting source area treatment with a defined regulatory closure goal. The bioremediation system design and results will be described, as will the groundwater model, the negotiated cleanup goals and cost/benefit analysis.

Bioremediation of VPH and EPH Contaminated Groundwater Using in-situ Submerged Oxygen Curtain (iSOC) Technology

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An iSOC bioremediation system for residual aliphatic and aromatic volatile and extractable petroleum hydrocarbons (VPH and EPH) contaminated groundwater was installed and operated at a Massachusetts site. While more soluble petroleum compounds such as BTEX are know to be readily degraded under aerobic conditions, the degradation of other less soluble and less bioavailable VPH and EPH compounds is not as well understood. This case study will examine the performance of an in-situ bioremediation system for residual VPH and EPH contaminated groundwater in an area downgradient of a source area excavation.

Brownfields

Cascades Park: Remediation and Beneficial Recreational Redevelopment of a Former Manufactured Gas Plant Site

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Urban Fill Soil Characterization and Risk Based Management Decisions- A Practical Guide

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Regulatory Incentives to Promote Private Sector Brownfield Remediation and Reuse

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The Cascades Park site in Tallahassee, Florida is unusual in that it is listed both on the National Register of Historic Places and on the state Brownfields inventory for cleanup. The environmental impacts of principal interest relate to use of the site from the late-1800's though the 1950s as a manufactured gas plant (MGP), with typical accompanying contamination by metals, PAHs and BTEX. Impacts to groundwater are extensive both horizontally and vertically. Addressing soil impacts and deposits of free MGP product (i.e., coal tar residues) has proven to be a challenge, with obvious site contamination present at high levels to a depth of over 25 feet, and site-related chemicals found at depths greater than 90 feet. Remediation is further complicated by urban infrastructure, underground utilities, a storm water drainage channel, and major rail line. Remedial strategies and lessons learned regarding characterization and remediation of contaminated soils, sediments and ground water will be presented in detail. Extensive air monitoring results collected during remedial activities have demonstrated a general lack of off-site airborne substances of health significance, though detectable odors have been reported from time to time by site personnel and local residents. Following remediation of soil, sediments and ground water under requirements of Florida DEP and U.S. EPA, future land use of the site is to be a park, one piece of a long-range vision for enhancement of downtown, developed through cooperation among the City of Tallahassee, Leon County and local citizens. The site represents an excellent showcase of mutual environmental and social benefits that may be achieved by cooperative efforts among responsible parties, state and federal agencies, consultants and local development programs.

Urban Fill Soil Characterization and Risk Based Management Decisions- A Practical Guide

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The objective of this paper is to examine a number of common contaminants found in urban fill soil by presenting urban fill background concentrations, disposal facility parameters and limits, and no significant risk limits for site closure. This effort will provide a practical guide in consideration of what might be expected at numerous brownfield sites and how the findings at a particular site can be compared to the information provided to make practical soil management decisions.

It has become evident over the passage of years that urban fill soil may be expected to contain certain contaminants, in particular heavy metals and polynuclear aromatic hydrocarbons, from specific releases as well as background sources. Natural concentrations and background concentrations are an important sorting and selection criteria as to what chemicals should be selected for additional analysis and those that should be considered background to the analysis, partcularly the risk assessment. The authors propose to present a paper that deals with specific contaminants; lead, arsenic, carcinogenic polynuclear aromatic hydrocarbons, dioxins, and asbestos. The authors will provide a listing of each contaminant, its usual range in natural and urban fill soils, and its risk based or related thresholds, with emphasis on the New England area. The outcome will be a range of concentrations that can be used as a guide by persons considering Brownfields sites such that their information can be compared to the ranges and brought into meaningful focus.

Regulatory Incentives to Promote Private Sector Brownfield Remediation and Reuse

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Governments of growing industrial economies are faced with two substantial sources of urban environmental degradation—one from past activities and one from ongoing activities. The interior of mature urban communities often contain large areas of environmental contamination from past industrial activity. These sites often sit unmarketable and vacant, allowing the contamination to spread into the surrounding groundwater, land and air environments. Urban growth is diverted to envelop open space agricultural land and wildlife habitat on the borders of the urban area, creating a second front of degradation commonly known as urban or suburban "sprawl."

Resolution of both environmental problems created by historical contamination and non-sustainable land-use can be achieved by private sector redevelopment of brownfields. However, environmental laws and government policies intentioned to restore or protect the environment often inhibit or prevent brownfields redevelopment. Commonly this is attributable to (1) laws assigning legal liability for the past contamination to those purchasing or undertaking the remediation project, and (2) the high transaction costs of and long time delays associated with government oversight. This paper reports on five governmental policies that could facilitate the remediation and reuse of brownfields.

(1) Necessity – Government lawmakers and regulators must recognize the necessity of immediately addressing these two significant sources of environmental degradation in urban communities.
(2) Immunity – Environmental laws should be amended to provide immunity to innocent parties who undertake the remediation of past contamination.
(3) Efficiency – Regulatory oversight agencies should implement streamlined processes for cleanup and regulatory oversight to reduce the time and transaction cost of brownfields redevelopment.
(4) Certainty – Government should enhance predictability of the final cleanup remedy required for any discrete set of environmental contaminants.
(5) Flexibility – Regulatory oversight agencies should provide flexibility to brownfield redevelopers in the scope and level of cleanups through utilization of institutional controls appropriate for varied end uses.

Opinions represented here are those of the author and do not necessarily reflect any policy, finding or opinion of the State of California, Cal/EPA or DTSC.

Chemical Oxidation

Adaptive Remediation: Using a Membrane Interface Probe to Define Permanganate Distribution and CVOC Concentrations during a Pressure Pulse In-Situ Chemical Oxidation Application to Enhance Remedial Results

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The Effects of In-Situ Oxidation of Organic Contaminats on Metals Mobility in Sediments

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Successful Application of Activated Persulfate Chemical Oxidation Followed by Bioremediation in a Tight Soil Matrix

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Persulfate Decomposition Kinetics in Presence of Aquifer Materials

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Cyclodextrin Enhanced Iron Activated Persulfate Oxidation of TCE

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Case Study: Bench, Pilot and Field Scale ISCO with Activated Persulfate of Chlorinated Benzenes

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Adaptive Remediation: Using a Membrane Interface Probe to Define Permanganate Distribution and CVOC Concentrations during a Pressure Pulse In-Situ Chemical Oxidation Application to Enhance Remedial Results

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In an effort to enhance the efficacy of oxidant contact in an in-situ chemical oxidation (ISCO) application in a chlorinated volatile organic compound (CVOC) source area (primarily Trichloroethene (TCE)) in a heterogeneous overburden deposit, a membrane interface probe (MIP) was used to determine the vertical and horizontal distribution of permanganate in relationship to CVOC concentrations. Traditional dual screened and single screened pressure pulse wells were installed in the CVOC source area based on historical data collected in the area using traditional investigation techniques. An initial application of sodium permanganate was injected into the traditional pressure pulse wells using pressure pulse down-hole technology. Following an initial source zone injection of sodium permanganate, MIP borings were advanced in the area surrounding each pressure pulse injection well. The electrical conductivity (EC) dipole array on the MIP was used to determine the presence or absence of unreacted sodium permanganate in the subsurface in real time. The MIP was also used in conjunction with a photo ionized detector (PID) electron capture detector (ECD) and a field gas chromatograph (GC) to determine the distribution, relative concentrations and speciation of CVOCs in the subsurface. The real time data provided by the MIP during the mid permanganate injection characterization stage, was used to pin point remaining high concentration CVOC zones in the subsurface that were not in contact with permanganate. A direct push pressure pulse tool was used to apply sodium permanganate or potassium permanganate in the remaining high concentration zones that were not in contact with the initial sodium permanganate injection. The real time data provided by the MIP allowed the second permanganate applications to be conducted without site breakdown or remobilization.

The Effects of In-Situ Oxidation of Organic Contaminats on Metals Mobility in Sediments

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In-situ oxidation is increasingly being used as a treatment mechanism for organically polluted soils. However, the oxidation reagents and their byproducts will impact the surrounding sediment and groundwater chemistry. A change in the oxidative/reductive environment of the system could possibly increase metals mobility and also impact the toxicity of those metals by changing their oxidative state (e.g. Cr(III) to Cr(VI)). It is also possible that the end products of oxidation can reduce the mobility of metals in a treated system. For example, in-situ oxidation using a permanganate solution yields MnO_2, which has been found to bind and precipitate metals. It is possible that this binding and stabilization could counter-act the increase in mobility caused by the change in the oxidative/reductive environment.

The effects on metals mobility of in-situ oxidation of organically-impacted soils and sediments are tested by comparing the total metals concentrations, speciation, and extraction profiles both before and after chemical oxidation for a suite of metals including As, Ba, Pb, Mn, Cr, Se, and Hg. Two extraction methods are tested: the US EPA 1312 Synthetic Precipitation Leaching Procedure (SPLP), and a selective sequential extraction (SSE). Each fraction of the SSE uses a sequentially stronger extractant, and represents a range of metals mobility. In addition, natural organic fractions (humic and fulvic acids and humin) will be interrogated for associated metals to understand the fate of metals from an ion exchange standpoint. The results of these experiments will be discussed, along with conclusions regarding the fate of metal mobility and toxicity after in-situ oxidation of organic pollutants.

Successful Application of Activated Persulfate Chemical Oxidation Followed by Bioremediation in a Tight Soil Matrix

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An innovative sequential three step remediation approach has been developed to successfully treat contaminants in a tight soil matrix. The first step is to pre-condition low permeability soils using both chemical and mechanical means. During the pre-conditioning step, “unactivated” sodium persulfate and other conditioning agents are chemically injected and/or mechanically applied into the formation. The second step is to “activate” the sodium persulfate thus enabling a chemical oxidation process to desorb the contaminant mass from the tight soil matrix and reduce the biotoxicity in the source area. Field experience has demonstrated that persulfate can successfully be “activated” using a combination of hydrogen peroxide, transition metal catalysts, temperature, and pH adjustment. After the second step (chemical oxidation process) is completed, a third step (bioremediation polishing) is applied to treat the remaining contaminant mass.

Bench scale studies have indicated that use of high temperature (greater than 180°F) chemical oxidant applications in the saturated zone negatively impacts the subsequent bioremediation polishing step (third remediation stage). Use of low temperature (less than 100°F) chemical oxidant applications in the saturated zone have resulted in significant dissolved phase rebound problems. When the saturated zone temperature is optimally maintained consistently between 140°F and 170°F, contaminants are still effectively desorbed from the tight soil matrix through a mass transfer partitioning process without overly stressing the indigenous biological species needed for subsequent bioremediation while avoiding subsequent dissolved phase rebound problems.

The second chemical-oxidation/desorption-extraction step facilitates the third treatment step used to reduce total contaminant mass transferred from the soil matrix into the dissolved phase within the saturated zone. The final treatment step is an aerobic and/or anaerobic biostimulation process, which cost-effectively completes the innovative sequence of complementary treatment technologies needed to optimize the reduction of total contaminant mass in a tight soil matrix.

Persulfate Decomposition Kinetics in Presence of Aquifer Materials

STUDENT PRESENTER

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Persulfate is an emerging oxidant for *in situ* chemical oxidation (ISCO) applications with a high oxidation potential on activation ($E^o = 2.6$ V). The design of an oxidant remedial system involves a comprehensive understanding of a number of underlying physical and chemical processes. One of these processes, which impacts oxidant efficiency, involves the stability of the oxidant in the presence of natural aquifer materials. To improve our understanding and develop predictive relationships a series of batch and column experiments were designed to quantify the interaction between persulfate and aquifer materials. Well-characterized aquifer materials collected from seven sites across North America were used in this investigation. The batch experiments, run in triplicates for each aquifer material, were conducted to primarily observe and derive decomposition kinetic parameters for an experimental system comprising of 100 g of solids, and 100 mL of solution with an initial persulfate concentration of 1000 mg/L. The column experiments, which were more representative of *in situ* conditions, consisted of 40 cm long columns packed with aquifer material and flushed with a 1000 mg/L persulfate solution. The decomposition of persulfate followed a first-order mass action law in the presence of all aquifer materials used in this study although the reaction rate coefficient varied by an order of magnitude (10^{-4} to 10^{-3} hr^{-1}). As expected the column experiments yielded a higher reaction rate coefficient relative to the corresponding batch test data, suggesting that persulfate decomposition is a function of the persulfate to solid mass ratio. In general, the observed reaction rate coefficients were small indicating that persulfate will have a high stability in these aquifer systems. Dissolved organic carbon, iron, and manganese concentrations decreased relative to background conditions; however, no correlation with the reaction rate coefficients was determined.

Cyclodextrin Enhanced Iron Activated Persulfate Oxidation of TCE

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In situ chemical oxidation (ISCO) is an innovative remediation technology that shows promise as a method for destroying dense nonaqueous phase liquids (DNAPLs) such as trichloroethylene (TCE) in soil and groundwater. Sodium persulfate is often used as an oxidant for ISCO because the persulfate anion ($S_2O_8^{2-}$) can be activated with ferrous ions (Fe^{2+}) to generate a strong oxidant known as the sulfate free radical ($SO_4^{-}\cdot$) ($E^o = 2.4$ V). ISCO methods are usually most successful for the remediation of dissolved contaminants. Therefore, if DNAPLs are present, the effectiveness of the oxidation process is highly dependent upon mass transfer from non-aqueous (i.e., DNAPL) to aqueous phases (i.e., dissolved phase). Moreover, an increased concentration of an oxidant results in accelerated oxidation of a contaminant in the aqueous phase, which in turn could lead to an increase in the concentration gradient driving the mass transfer (i.e., dissolution) of DNAPL into the aqueous phase. The use of cyclodextrins such as hydroxypropyl-β-cyclodextrin (HP-β-CD) in conjunction with iron activated persulfate offers several advantages. For example, HP-β-CD is able to complex metal ions such as Fe^{2+} for persulfate activation while simultaneously complexing an organic molecule such as TCE. Laboratory experiments revealed that increases in HP-β-CD concentrations resulted in increased solubilization of TCE. This increase was linear and indicated formation of a 1:1 binding complex. Moreover, the presence of Fe^{2+} did not affect the solubilization of the contaminant by HP-β-CD. Comparison of the use of ferrous ion activated persulfate with and without HP-β-CD demonstrated that HP-β-CD can regulate the availability of Fe^{2+} and this resulted in a gradual controlled decomposition of persulfate. In the presence of HP-β-CD and ferrous ions, TCE solubility can be increased above its normal aqueous solubility (i.e., 1,100 mg/L) and its degradation by persulfate can be accelerated.

Case Study: Bench, Pilot and Field Scale ISCO with Activated Persulfate of Chlorinated Benzenes

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A field scale insitu Chemical Oxidation (ISCO) project was performed with activated persulfate in July through August 2005 at the Eastland Woolen Mills Superfund site (site) in Corinna, Maine. The ISCO application was designed to treat chlorinated benzene compounds present as residual DNAPL contamination. The site is managed by the U.S. Army Corps of Engineers for the U.S. EPA with Nobis Engineering (Concord, NH) as the primary contractor and Xpert Design and Diagnostics, LLC (XDD, Stratham, NH) as the ISCO specialist.

Preliminary work included bench tests designed to compare Modified Fenton's and activated persulfate and pilot scale tests. The results of bench tests indicated the Modified Fenton's system would be superior but persulfate was a close enough second that both systems were retained for the full scale field program.

For the pilot tests, Modified Fenton's reagent and activated persulfate were applied in two separate test areas (each area consisting of two injection wells at approximately 20 foot on center spacing). A comparison of baseline and 60-day post-treatment sample results indicated that the application of hydrogen peroxide had minimal effectiveness or was effective for a limited radius of influence (ROI). Conversely, the concentration of chlorinated benzenes in soil and groundwater was observed to significantly decrease in the persulfate area. The post-treatment soil data indicated approximately 50 percent to 80 percent of chlorinated benzenes were degraded with a ratio of 8 lbs of persulfate per lb of contaminant degraded. Carbonates are suspected to have been the deciding factor in influencing reactant system effectiveness. The results of these pilot tests underscore the importance of site specific characteristics when applying ISCO technologies.

Persulfate was selected for the field scale test and the results of these tests are described in detail in this paper. ISCO was applied to two areas on the site, with similar but significantly different subsurface soil/contaminant conditions. The results show that the persulfate system is effective for oxidation of the recalcitrant chlorobenzenes in typical New England soils and that a successful application is dependant on consistent application of bench and pilot scale testing with actual site soils to provide the proper basis for oxidant selection.

Combining Chemical and Biological Technologies for Soil and Groundwater Remediation

Overview of Technical and Policy Developments in Combining In-Situ Remedies to Address Non-Aqueous Phase Liquid Contamination

Jim Cummings, USEPA, Washington, DC

Impacts of Chemical Oxidation on Aquifer Conditions and Microbial Activities

Robert Luhrs, Raytheon, Waltham, MA

Sequential Application Of Chemical Oxidation Using Permanganate And Bioaugmentation

David Major, GeoSyntec Consultants, Guelph, Ontario, Canada
Eric Hood, GeoSyntec Consultants, Guelph, Ontario, Canada
Philip Dennis, SiREM, Guelph, Ontario, Canada

Molecular Biological Tools for Determine Strategies for the Transition from Chemical Oxidation to Bioremediation

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Tools for Designing and Monitoring the Performance of Combined Remediation

Thomas M. Christy, Geoprobe Systems, Salina, KS

Overview of Technical and Policy Developments in Combining In-Situ Remedies to Address Non-Aqueous Phase Liquid Contamination

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While environmental remediation literature has contained references to 'treatment trains' for a decade or more, the last 3-5 years have seen a significant increase in actual field deployments to address Non-Aqueous Phase Liquid (NAPL) contamination. In some cases, combining remedies is post-hoc -e.g.,, practitioners notice something 'interesting' in the latter stages of a project or supplement or replace older systems such as pump and treat with other technologies in an effort to enhance performance and achieve site closure. In other cases, as familiarity with combining remedies has increased, practitioners are designing treatment trains from the outset of remedial design and remedial action. Effective combination of technologies to improve ability to achieve remedial action objectives and/or to reduce cost and performance uncertainties requires both technical and policy adjustments to historical practice. This presentation will provide a national overview on current practices and policies, discussing prevalent technology combinations and needed policy adjustments in the area of more flexible decision documents.

Impacts of Chemical Oxidation on Aquifer Contaminants and Microbial Activity

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In-situ chemical oxidation has become an accepted remedial approach for projects containing an assortment of volatile organics. As this technology has gained industry acceptance, the results from some projects have begun to become public, with varying levels of success. Some found little to no contaminant degradation and claimed failure, while others have shown remarkable results. This presentation has been prepared to review the topic from a broad perspective, using lessons learned from multiple projects around the country to better understand chemical trends, impacts to the microbiology, and contaminant rebound after large injection programs.

Sequential Application Of Chemical Oxidation Using Permanganate And Bioaugmentation

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ISCO using permanganate and in situ bioremediation/ bioaugmentation are promising technologies for the treatment of DNAPL source areas. Both technologies have completed laboratory research and development and have been successfully demonstrated in pilot tests and full-scale applications; however, each technology has limitations that can affect the cost or duration of the approach. Enhanced bioremediation is being implemented at sites previously treated using permanganate, typically in response to post-ISCO monitoring data indicating that a rebound in contaminant concentrations has occurred. A research program was recently completed to demonstrate the efficacy of coupling in situ chemical oxidation (ISCO) to rapidly remove accessible DNAPL mass with in situ bioremediation via biostimulation or bioaugmentation to degrade and contain the remaining mass.

The results of this study provide several significant conclusions including: a) while permanganate may have strong disinfecting properties, recolonization of the permanganate treatment zone by indigenous microorganisms appears to occur rapidly (i.e. weeks to months) with only subtle differences between the pre- and post-treatment microbial communities which are not readily distinguished using widely available microbial characterization tools (e.g., PLFA, plating, MPN etc.); b) the extremely high manganese oxide (MnO_2) concentrations (1,000 to 10,000 mg/kg) in the permanganate treatment zone is unlikely to be significantly mobilized into groundwater during bioremediation; and c) the deposition of manganese oxide (MnO_2) is particular problematic since MnO_2 (an alternate electron acceptor) competitively inhibits reductive dechlorination of both cis-DCE and VC, limiting the performance of enhanced bioremediation in zones where MnO_2 is present.

This presentation will provide an overview of the results from these three aspects of the research program, draw conclusions for the applicability of the technology for DNAPL remediation and provide recommendations for a best-practice approach for future work with the sequential technologies.

Tools for Designing and Monitoring the Performance of Combined Remediation

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Chemical and biological technologies for in-situ remediation have grown markedly over the past decade. Never before have so many tools been available to effect the remediation of subsurface contaminants. However, as the list of successful remediation projects grows, so does the list of projects in which remediation materials were misapplied or wasted via application in essentially uncontaminated areas. Nearly every remediation specialist can cite a case that failed because treatment materials and contaminant mass failed to meet. In a similar manner, almost every remediation specialist can cite projects in which the final efficacy of a treatment regime remains unknown due to lack of appropriate follow-on performance monitoring. This paper will discuss methods for logging subsurface lithology, contaminant distribution, and permeability that can aid in site characterization and thereby enhance remediation efficiency. The logging methods discussed will include MIP, which has been used both in remediation design and performance monitoring; CPT, which has been used extensively in lithologic characterization; and a new tool, HPT, which gives very useful permeability information and can be used to direct mater injection efforts. Examples will be presented from the use of these tools on remediation sites.

Contaminated Sites Research in Canada & the Contaminated Sites Action Plan

Overview of Research Sponsored by Health Canada's Contaminated Sites Program/ Metal Concentrations in Indoor Dust

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Pat Rasmussen, Health Canada, Ottawa, ON, Canada
Nellie Roest, Health Canada, Halifax, NS, Canada

The Mutagenic Hazards of Complex PAH Mixtures in Contaminated Soils

Paul White, Health Canada, Ottawa, ON, Canada
Christine Lemieux, Health Canada, Ottawa, ON, Canada
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Dermal Penetration of Carcinogenic PAHs in Contaminated Soils

Richard P. Moody, Health Canada, Ottawa, ON, Canada

The Toxicity of Complex Metal Mixtures in Contaminated Soils

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Bioaccessibility: Improving Risk Assessments for Contaminated Sites

Megan Lord-Hoyle, Royal Military College of Canada, Kingston, ON, Canada
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The Assessment and Remediation of Contaminated Sites in Canada's Arctic

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Overview of Research Sponsored by Health Canada's Contaminated Sites Program/ Metal Concentrations in Indoor Dust

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The Canadian *Federal Contaminated Sites Action Plan* (FCSAP) was created to accelerate the assessment and remediation of contaminated sites owned by the federal government. To date over 4000 federal sites, including mines, military bases, harbours, airports, and lighthouses, have been listed in the federal inventory. Health Canada, as an Expert Support Department, provides guidance, training, advice, and tools for assessing the human health risks of contaminated sites. To help meet these responsibilities, Health Canada has initiated and sponsored research on risk assessment methods, toxicological reference values, soil quality guidelines, sampling methodologies, bioavailability, and other health-related issues at contaminated sites.

One of the FCSAP-sponsored research projects is investigating indoor exposures to toxic metals commonly found in contaminated soils, and the ability to predict indoor exposures from outdoor geochemistry. The study, which examined 48 homes in the Ottawa area, evaluated indoor/outdoor ratios in the concentrations of lead, cadmium, and nickel. Indoor (i.e., indoor dust) elemental concentrations were not spatially correlated with outdoor (i.e., garden soil) elemental concentrations. Moreover, indoor/outdoor ratios of total metal concentration were consistently higher than unity: 5.5 for Pb, 16.4 for Cd, and 3.4 for Ni. Considering only the migratable fraction, the indoor/outdoor ratios were found to be 24.8 for Pb, 20.7 for Cd, and 40.4 for Ni. Relative bioavailability factors (migratable/total metal) were also found to be higher in indoor dust as compared to outdoor soil. The high values appear to be related to the ability of the organic-rich indoor dust matrix to accumulate metals.

The Mutagenic Hazards of Complex PAH Mixtures in Contaminated Soils

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This FCSAP-funded project is evaluating risk assessment methods employed to assess the carcinogenic hazards of PAH mixtures. Methods for mutagenic carcinogens often employ an assumption of additivity and express total hazard as the cumulative hazard of priority PAHs. In this study, organic components of PAH-contaminated soils were extracted using pressurized fluid extraction and subsequently separated into polar (e.g., nitroarenes) and non-polar fractions (e.g., PAHs and alkyl-PAHs). Synthetic mixtures of priority PAHs were prepared using the results of chemical analyses. The mutagenic potencies of complex soil extracts/fractions, synthetic PAH mixtures, and individual PAHs were evaluated using the *Salmonella* mutagenicity assay. All soil extracts/fractions and synthetic PAH mixtures yielded significant mutagenic responses in at least one of *Salmonella* strains TA98 and TA100; however only 8 of the 16 PAHs yielded a mutagenic response. The predicted mutagenic hazard of the non-polar fraction, whether based on (a) its synthetic mixture or (b) the sum of the effects expected from the identified PAH constituents, was frequently greater than the mutagenicity of the non-polar PAH-containing fraction. Furthermore, a significant response was obtained for the polar fraction in *Salmonella* YG1041, a strain that is sensitive to N-containing heterocyclic compounds. These results suggest that a targeted risk assessment approach focusing on priority PAHs may provide useful, although conservative, assessments of mutagenic hazard for PAH-contaminated soils. However, a priority substance approach cannot account for hazards associated with unidentified polar compounds. Validation of the *Salmonella* results using an *in vitro* mammalian cell mutation assay is ongoing.

Dermal Penetration of Carcinogenic PAHs in Contaminated Soils

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Due to their recreational activites, children are especially vulnerable to dermal exposure to soil contaminants. Our laboratory at Health Canada has recently determined that the carcinogenic PAH benzo[a]pyrene (B[a]P) was quite well-absorbed in human skin exposed to gardening soil spiked with ^{14}C-B[a]P. This study followed our in-house *in vitro* dermal absorption test using fresh viable human skin tissue. Teflon® flow-through type diffusion cells were used to hold skin specimens cut by dermatome to about 0.3-0.4 mm thickness, perfused at 32 ^{0}C with a 'receivor' solution consisting of Hanks HEPES buffered (pH 7.4) Bold's basal saline solution (HHBBSS) containing 4% BSA. Including the % of the applied dose detected in the HHBBSS receivor solution summed together with the % in the skin 'depot' which contains the ^{14}C-B[a]P residues remaining in skin following soap washing, the total % absorption was 14.8 ± 6.17% (n = 5) and 15.8 ± 8.30% (n = 4) after 24 hr and 42 hr exposure to ^{14}C-B[a]P spiked soil, respectively. For use of such data in risk assessment the concept of the skin depot and the basic essentials of *in vitro* dermal absorption test methods need to be clearly understood. We will present an overview of our test protocol and briefly discuss the skin depot in relation to the bioavailability of soil contaminants.

The Toxicity of Complex Metal Mixtures in Contaminated Soils

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Current guidelines for soil contaminant levels are based on toxicological data from individual contaminants and estimated exposure in humans. There is little data available on combined exposure to metal contaminants found at contaminated sites and little toxicological information on the effects of exposure to mixtures of soil-bound heavy metals. The current study examined the neurotoxicological, systemic and pathological effects of *in utero* and lactational exposure to a metal mixture in the rodent model. The mixture of metals was based on frequency and cooccurrence of metals found at contaminated sites. Relative concentrations of metals in the mixture were based on current Canadian soil quality guidelines. The metals included: lead, cadmium, chromium, Copper, Zn and Ni. Pregnant rats were dosed with 0.00094, 4.7, and 9.4 mg/kg bw/day from gestation day 1 to PND 21. The lowest dose reflected estimated exposure based on current soil quality guidelines. Reproduction, mortality and weight gains were not affected in mothers or offspring. The highest dose of the mixture produced small alterations in motor coordination at Day 35 but no dose affected any other measure of motor function. Measures of reactivity and sensorimotor integration were not altered by any dose. Similarly, the mixture did not affect measures of learning and memory. Overall, there was no indication that doses at up to 1000 times the estimated exposure from current soil quality guidelines exerted any significant effects on neural system functioning. Analyses are currently underway to evaluate residue levels in mothers and offspring, pathology and systemic toxicity.

Bioaccessibility: Improving Risk Assessments for Contaminated Sites

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Regulations and guidelines for contaminated site remediation in Canada are currently based on the total concentration of the target substance in a particular substrate (soil, sediments or water). Contaminants in soil, however, maybe be tightly bound and thus there is a growing trend to consider bioavailability – the fraction of a substance that is absorbed by the organism – in determining suitable risk based endpoints for site remediation in Canada. Bioavailability is usually measured by using *in vivo* methodologies, which tend to be expensive and time consuming; bioaccessibility measurements using simulated gastrointestinal conditions to estimate the soluble fraction of a substance are increasing in desirability for incorporation into risk assessment. Bioaccessibility measurements can be carried out with a simple extraction procedure and hence are more accessible, less expensive and quicker than *in vivo* studies to estimate bioavailability. For these measurements to be meaningful, however, it is important to compare bioaccessibility to *in vivo* bioavailability results and determine their accuracy. This talk will focus on the development of bioaccessibility methods for arsenic and nickel, validation of the results using soils that have been subjected to *in vivo* testing, as well as the effect of more realistic exposure scenarios on risk assessment outcomes. It will also provide insight into the acceptance of the bioaccessibility results by Canadian regulators. It will conclude with a description of activities of Bioaccessibility Research Canada (BARC) – a newly formed network of parties interested in furthering the development and implementation of bioaccessibility in Canada.

The Assessment and Remediation of Contaminated Sites in Canada's Arctic

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Procedures for the investigation and remediation of contaminated sites in temperate parts of North America are well developed, but similar activities in cold, remote locations with short work seasons such as the Arctic present unique challenges. It is essential, for example, to obtain a complete understanding of contamination issues during the site assessment so that the specifications for the remediation phase can be complete and not give rise to costly and difficult 'extras' during the actual cleanup. The cost of reaching the site with chartered aircraft, as well as the expense of supporting the team, requires the optimal use of field analytical and data management methods. The unique ecosystem, with a more linear food chain, rather than food web, requires a careful assessment of ecological risk. Similarly, the reliance of Inuit on country foods (caribou, seals etc) poses special concerns with respect to human health. The Environmental Sciences Group (ESG) is the Scientific Advisor for Canada's largest environmental remediation project – the Distant Early Warning (DEW) Line project – and has conducted site assessments at over 100 Arctic sites. As well, they have worked extensively with Inuit in better understanding the risks posed by contaminants in the north and in communicating these risks effectively. This talk will provide an appreciation of the special concerns of working in the Arctic and will describe some of the tools that have been developed for both site assessment and remediation.

Emerging Contaminants

Status of the Environmental Council of States/Department of Defense National Dialogue on Emerging Contaminants

Gary S. Moran, Massachusetts Department of Environmental Protection, Lakeville, MA

Tungsten: Emerging Heavy Metal

Mark J. Begley, Massachusetts Environmental Management Commission, Camp Edwards, MA

Overview of Perfluorooctanoic Acid (PFOA)

Brooke Moore, ENSR Corporation, Westford, MA
Cynthia Cogan, ENSR Corporation, Westford, MA
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Biodegradation and Bioremediation of N-Nitrosodimethylamine (NDMA) in Groundwater

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Status of the Environmental Council of States/Department of Defense National Dialogue on Emerging Contaminants

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Each of the 50 states and every U.S. territory is home to at least one military facility of some kind. While the sustainability of the environment at these ranges is a shared goal and interest of states and the Department of Defense (DOD), there are also great pressures stemming from conflicting uses, mission, and priorities.

In 2004, recognizing the significant challenges and tensions arising between important military activities on DOD installations and need to ensure environmental protection, the Environmental Council of States (ECOS)— a national non-profit, non-partisan association of state and territorial environmental agency leaders, working with DOD, established the ECOS-DOD Sustainability Workgroup. This Workgroup serves as a focal point for discussions between ECOS and DOD regarding issues related to sustainability, and to foster cooperation and coordination in better planning and environmental management.

The Workgroup was divided into 3 major Task Groups, including the Emerging Contaminants in Groundwater Task Group. In recent years, one of the most challenging issues confronting states and DOD has been the response to and management of emerging contaminants. The recent experience with perchlorate illustrates some of the difficult issues surrounding emerging contaminants.

The Emerging Contaminants Task Group was formed to define the issues and challenges posed by emerging contaminants, and to develop plans of action to address such challenges. In November 2005, the Task Group organized a forum involving state and federal stakeholders to identify and prioritize proposed actions. Based on the Forum's recommendations, the Task Group is currently working on the highest priority actions, including a survey of states on emerging contaminants and papers on the following issues related to emerging contaminants: risk communication; pollution prevention strategy and workplan; use of provisional values in risk assessment; and initiation of actions and funding for emerging contaminants.

Tungsten: Emerging Heavy Metal

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The search for alternatives to lead ammunition for small arms and to depleted uranium penetrators has been a challenge for the military and the ammunition industry. Care must be taken that the environmental fate and transport of alternative materials, as well as the human health consequences are adequately examined and communicated to users before the material becomes widely distributed. Based on solid science and risk assessment principles, best management practices for ranges and pollution prevention techniques covering manufacturing, deployment, use and demilitarization must be developed along with the projectiles. The recent experience with tungsten at the Massachusetts Military Reservation is examined to demonstrate some of the information needed to make knowledgeable decisions regarding the use of alternative materials that are also emerging contaminates.

Overview of Perfluorooctanoic Acid (PFOA)

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The US Environmental Protection Agency (EPA) has been reviewing data and developing a draft risk assessment for Perfluorooctanoic Acid (PFOA). PFOA is a synthetic chemical, sometimes referred to as “C8”, used by chemical companies and manufacturers to make non-stick cookware (including Teflon®), water repellant coatings for all-weather clothing and fabrics, food packing, gaskets, O-rings, and hoses. It is chiefly used in producing fluoropolymers which are employed in almost all commercial industry segments including aerospace, automotive, building/construction, chemical processing, electrical and electronics, semiconductor, and textile industries. The durability of PFOA due to its specific chemical structure prevents breakdown in the environment. This leads to widespread bioaccumulation in the food chains. It is this bioaccumulation which prompted the EPA to conduct a further evaluation of PFOA and its potential to adversely affect human health. Scientists do not yet know how PFOA is transported within the environment; however, studies in adult rats show that the ammonium salt of PFOA is absorbed following ingestion, inhalation, and dermal exposure.

This presentation presents a brief overview of the chemical and discusses toxicological research results, the EPA’s current status on developing a risk assessment, and the future of PFOA going forward.

Biodegradation and Bioremediation of N-Nitrosodimethylamine (NDMA) in Groundwater

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N-Nitrosodimethylamine (NDMA) is a potent carcinogen and an emerging groundwater contaminant in the U.S. The objective of this research was to study NDMA biodegradation and to explore *in situ* and *ex situ* bioremediation strategies for this contaminant. Initial studies revealed that specific propanotrophs and toluene-oxidizing strains were capable of degrading NDMA. Two different biodegradation pathways were observed. The toluene-oxidizer *Pseudomonas mendocina* KR1 initially added a single oxygen molecule to the nitroso group of NDMA to form N-nitrodimethylamine, which was subsequently metabolized to N-nitromethylamine and trace amounts of formaldehyde. In contrast, the propanotroph *Rhodococcus ruber* ENV425 degraded NDMA into formaldehyde, methylamine, nitrate, nitrite, carbon dioxide, and methanol. Both degradation pathways will be presented. To evaluate the potential for *ex situ* treatment, a suspended growth reactor was seeded with *P. mendocina* KR1 and continuously fed toluene as a primary growth substrate. NDMA was fed to the reactor at concentrations ranging from 25 to 250 µg/L to represent typical groundwater levels. Strain KR1 consistently removed greater than 99.9 % of the added NDMA, and effluent concentrations below 0.09 µg/L (the MDL for the experiment) were achieved during the 4-month study. In addition to bioreactor studies, the potential for *in situ* treatment of NDMA was examined using aquifer samples from three locations around the U. S. Microcosm data indicated that indigenous bacteria capable of mineralizing ^{14}C-NDMA to $^{14}CO_2$ under aerobic conditions are indigenous in some aquifers. However, the biodegradation process appears to be largely co-metabolic and dependent on the presence of one or more additional carbon and energy sources. NDMA mineralization was also observed under sulfate-reducing conditions but not under denitrifying, iron-reducing or methanogenic conditions in one set of aquifer samples. The results from this research provide a basis for the further development of *in situ* and *ex situ* biological approaches for NDMA treatment.

Environmental Benefits and Risks of Nanomaterials

A Very Brief History of Nanotechnology: Implications for the Environment

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Alan Kennedy, U.S. Army Engineer Research and Development Center, Vicksburg, MS
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Igor Linkov, Intertox Inc., Brookline, MA

Brave New World: Strategies for Navigating the Uncertainties

Melissa A. Hoffer, Esq., Wilmer Cutler Pickering Hale and Dorr LLP, Boston, MA

Use of Nanoscale Zero-Valent Iron (NZVI) Particles for Groundwater Remediation: A Qualitative Risk Assessment

Barbara D. Beck, Gradient Corporation, Cambridge, MA
Noelle M. Cocoros, Gradient Corporation, Cambridge, MA

Impact of Nanoparticles on Aquatic Species: Invertebrates and Fish

Patricia McClellan-Green, North Carolina State University, Morehead City, NC

Inhalation Exposure to Nanoparticles

Michael Ellenbecker, University of Massachusetts, Lowell, MA

Multi-Criteria Decision Analysis and Environmental Risk Assessment for Nanomaterials

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A Very Brief History of Nanotechnology: Implications for the Environment

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As part of nanotechnology development, a wide variety of materials and material functionalizations are being researched. The unique properties of these materials make this a promising area for the enhancement of military technologies and threat reduction applications. Emerging toxicological evidence suggests these particles may pose an ecological risk and their unique properties may preclude use of existing approaches to assess their risk (exposure and effects). We present a conceptual model, substantiated by existing knowledge and emerging research, to assess the potential ecological impacts of nanomaterials. As part of the presentation, areas where data gaps contribute to the uncertainty in the assessment of this class of materials will be identified. The purpose of such a conceptual model is to help direct future research to focus on relevant materials, exposure pathways, and receptors. Ultimately the goal of such studies should be to assist the developers of this technology focus their research on materials that provide an optimal benefit to the military while minimizing the potential for adverse environmental implications.

Brave New World: Strategies for Navigating the Uncertainties

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The first half of this presentation will survey current developments in U.S. federal environmental regulation of nanomaterials, with a specific focus on the Toxic Substances Control Act. The presentation will review other potentially applicable environmental regulatory schemes, and contrast the U.S. regulatory approach with the more precautionary approach employed by the European Union. The presentation will review the role of voluntary standards, such as those developed by ASTM and ANSI, in environmental regulation, and discuss the relevance for stakeholders of the current voluntary standards development effort with respect to nanomaterials. The presentation will summarize general trends emerging from research on potential health and environmental effects in connection with exposure to certain nanomaterials and highlight existing uncertainties with respect to long term implications for human health and the environment. The second half of the presentation will identify practical approaches that currently may be employed to mitigate potential risk.

Use of Nanoscale Zero-Valent Iron (NZVI) Particles for Groundwater Remediation: A Qualitative Risk Assessment

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We have used a risk assessment framework to evaluate use of NZVI in the remediation of groundwater trichloroethylene (TCE). Data are not available for a formal risk assessment; however our approach should help identify approaches for evaluating risks from use of NZVI. Our aims are to: identify hazards and exposure routes potentially associated with this application; identify key data gaps and make recommendations for toxicity testing; and compare NZVI to conventional ZVI. The potential hazards associated with this form of remediation include exposure to the ZVI nanoparticles themselves, as well as by-products of the reduction/dechlorination process. Compared to traditional remediation of TCE, the primary benefits derived from NZVI include increased efficiency in remediation and by-products of little or no concern, although benefits are dependent on optimized remediation conditions. Primary routes of exposure would be ingestion and dermal contact for the general community and potentially, occupational exposure *via* inhalation and dermal contact. One important data gap is the limited data for the dermal and ingestion pathways compared to inhalation. Further, very few toxicity data are available regarding NZVI specifically and it is unclear whether toxicity information from divalent and trivalent forms of iron can be extrapolated to assess toxicity of nanoparticles of zero-valent iron. If toxicity data on Fe^{2+} or Fe^{3+} are relevant to NZVI, the natural protective mechanisms of the body against excess iron must be considered. The multiple forms of NZVI with different physical/chemical characteristics (*e.g.*, environmental persistence) should be considered with respect to toxicity. Efforts being made in the field to reduce agglomeration of NZVI particles should consider potential increases in hazard. Overall, based on the lack of hazardous by-products, the increased remediation efficiency, and the tendency of the particles to agglomerate, therefore likely reducing uptake, the risks of NZVI appear to be low with a positive risk-benefit ratio, but important data gaps remain.

Impact of Nanoparticles on Aquatic Species: Invertebrates and Fish

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Nanomaterials have recently experienced an exponential growth in their production and usage. Applications of these materials are dramatically expanding because of their small size and their unique physical and chemical properties. Nanomaterials are currently used in cosmetics, as environmental remediation agents, employed in various pharmaceutical formulations, for the development of semi-conductors, electronics, and in the development of alternative energy sources. Recently, studies have shown that many nanomaterials possess cytotoxic properties in both *in vitro* and *in vivo* systems. While many of these materials do not appear to be acutely toxic, organisms exposed to nanomaterials, e.g. fullerenes, do experience increased levels of lipid peroxidation and altered mitochondrial and enzymatic protein levels and activities. The goal of this study was to examine the behavior of fullerenes in the marine environment and determine the impact of exposure on pelagic and benthic organisms. Two invertebrate species as well as the benthic estuarine teleost *Fundulus heteroclitus* were exposed to increasing concentrations of fullerenes for 96 hours. Their uptake levels were monitored and the levels of antioxidant enzyme activities measured. No acute toxicity was observed in either species up to 20 ppm nC60. Uptake of fullerenes in the invertebrates was similar to that previously observed for daphnia (Oberdorster et al., 2006). The levels of antioxidant enzyme activities are currently being analyzed. In a companion study, it was determined that the extraction techniques of Oberdörster (2004) were not adequate to detect fullerenes in seawater. C60 in combination with certain oxidizers, such as magnesium perchlorate, caused materials to “salt out” as the overall salinity of the aqueous media increased. Additional studies were conducted comparing the type and concentration of oxidizing agents, including magnesium perchlorate, sodium hypochlorite (bleach), and hydrogen peroxide, in order to achieve maximum fullerene recovery from waters with varying salinities.

Inhalation Exposure to Nanoparticles

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Workers and the general public may be exposed to airborne nanoparticles during the manufacture of the nanoparticles, their incorporation into nano-devices, the use of the devices, and in the end-of-life disposal of those devices. At this time, little is known about the potential for inhalation exposure to nanoparticles during each phase of their life cycle. In addition, very little is known about effective methods to control such airborne exposures.

These issues are the subject of ongoing research at the NSF-funded Center for High Rate Nanomanufacturing (CHN) located at the University of Massachusetts Lowell, Northeastern University, and the University of New Hampshire. The primary mission of CHN is to develop manufacturing processes that move nanomaterials and devices from the laboratory to the production phase. A unique element of this Center is the complete integration of occupational and environmental health and safety into its mission. CHN is committed to developing and using nanomaterials and nanomanufacturing methods that are environmentally beneficial and healthful for workers. As part of this work, we are characterizing worker exposure to nanomaterials being used in the CHN laboratories. For example, several laboratories are using carbon nanotubes (CNTs) and fullerenes in innovative applications. We are measuring both nanoparticle air concentrations and detailed size distributions, which will be used together with lung deposition models to predict regional lung deposition. We are also developing control strategies for all exposures to nanoparticles and other exposures deemed to be hazardous. For nanoparticles this may well include the development of novel ventilation and filtration systems, as well as improved personal protective equipment.

This paper will present the current state of knowledge concerning the hazards from inhalation of nanoparticles and effective methods to control such exposures. It will also recommend needed research initiatives to increase our understanding of nanoparticle inhalation.

Multi-Criteria Decision Analysis and Environmental Risk Assessment for Nanomaterials

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Even though nanotechnology application is widespread, understanding of the environmental effects and risks associated with nanomaterial use is very limited and often contradictory. Although it was originally thought that these materials were biologically benign, recent studies have suggested that inhalation and dermal absorption of these materials may have deleterious effects on mammals and a potential for adverse ecological effects. Nanoparticle production processes and nanomaterial uses in consumer products may result in exposures and risks. Regulatory experience with inorganic and organic chemicals may not be directly relevant to nanomaterials since their physical and biological properties are often determined not only by their size or structure, but rather by functionalization that was engineered to achieve specific manufacturing goals. Even though the risk assessment paradigm successfully used by EPA since the early 1980s may be generally applicable to nanomaterial regulation, its application requires incorporating an uncertainty in basic knowledge that is much larger than the uncertainty for other materials. An additional challenge is balancing environmental and societal goods and risks associated with nanomaterials. This paper proposes a risk assessment and risk management framework utilizing multi-criteria decision analysis (MCDA) and adaptive management for nanomaterial regulation. Given the uncertainty in all aspects related to nanomaterials, the structured, transparent, and justifiable tools offered by MCDA for quantifying both scientific and decision-makers' values and views, as well as for developing a system of performance metrics consistent with regulatory requirements, may be especially valuable for this emerging field. The development and implementation of such a framework will make clear what information should be collected to support decisions. MCDA tools, coupled with value of information analysis and adaptive management, could provide a good foundation for both bringing together multiple information sources to assess risks associated with nanomaterials and also for developing justifiable and transparent regulatory decisions.

Environmental Biotechnology

Obtaining Direct Evidence of Ongoing In Situ Reductive Dechlorination Using TCFE and RNA Analyses

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Monitoring the Metabolic State of *Geobacteraceae* during *in situ* U(VI) Bioremediation

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A Molecular Diagnostics "Smoking Gun" for Natural Attenuation

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Extracellular Electron Shuttling in Bioremediation and Biotechnology

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Bio-Trap^{TM} Samplers Document *In-Situ* Microbial Oxidation and Assimilation of ^{13}C-labeled Benzene under Denitrifying Conditions

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Improved Site Assessment of a Landfill-Leachate Plume using Microbial Community Profiles

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Obtaining Direct Evidence of Ongoing In Situ Reductive Dechlorination Using TCFE and RNA Analyses

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Ideally we would like to know the following three bits of direct information in order to evaluate anaerobic biodegradation of chlorinated solvents in groundwater: 1) is biodegradation occurring, 2) is it progressing to completion, and 3) how fast is it happening? However, with current methods we can only obtain insight enough to predict the answers to these questions. This work is an effort to refine existing molecular biological tools (MBTs) to the point where they can provide us with direct, unambiguous information including proof of ongoing reductive dechlorination. Bio-Traps impregnated with trichlorofluoroethene (TCFE) were deployed at a chlorinated solvent biostimulation site where ethene is routinely detected. It was previously determined in the laboratory that the fluorinated daughter products will adhere to the Bio-Sep material in the Bio-Traps. Bio-Traps are to be removed after 30, 60, and 120 days. The 60-day traps contained 4.0 ug/bead of cis-1,2-dichlorofluoroethene (which constitutes proof of ongoing biodegradation) and significantly more RNA compared to the 30-day traps (1.0 X 10^2 to 1.0 X 10^6 gene copies per bead), which suggests that the amount of TCFE metabolic activity overtime may have increased. The 60-day analysis also indicated TCE RDase at 1.0 X 10^2 gene copies per bead and VC RDase 1.0 X 10^3 gene copies per bead. This data will be compiled to track the rate of TCFE degradation on the Bio-Traps and correlate it to the expression of the functional genes involved in the degradation processes. The long term goal of this work is to determine the significance of the amount of degraders in the subsurface with respect to degradation rate. The 120-day results are pending.

Monitoring the Metabolic State of *Geobacteraceae* during *in situ* U(VI) Bioremediation

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Stimulation of metal reducing microorganisms such as *Geobacter* species is a promising strategy for the reductive immobilization of U(VI) in contaminated aquifers. An understanding of the rates of microbial metal reduction will help develop strategies for optimization of the bioremediation process. However, it is difficult to monitor *in situ* metabolic rates using geochemical techniques. Therefore, a strategy for monitoring expression of genes that are indicative of metal reduction rates and the associated metabolic states of microorganisms participating in U(VI) reduction was developed. Relevant *Geobacteraceae* genes were identified from microarray experiments conducted under a variety of environmentally relevant conditions. Field experiments were conducted at a uranium-contaminated site in Rifle, CO. Acetate was injected into the subsurface to stimulate the growth of metal-reducing microorganisms. During the active phase of U(VI) reduction, *Geobacteraceae* accounted for 90% and 57% of the bacterial sequences in the groundwater and sediments, respectively. The *in situ* metabolic state of *Geobacteraceae* was determined by tracking the expression of stress response, nutrient limitation, and chemotaxis and motility genes. Results show that the oxidative stress genes, *cydA* and *sodA*, as well as the gene heavy metal efflux gene, *cusA*, were expressed during bioremediation. Moreover, genes indicative of nitrogen (*nifD*), phosphorous (*phoU*), and Fe(II) (*feoB* and *ideR*) limitations were also expressed. Interestingly, expression of the chemotaxis and motility gene, *pilT*, was inversely correlated with Fe(II) concentrations in the groundwater. As was expected, the number of mRNA transcripts from genes involved in central metabolism (*gltA*, *mdh*, and *korA*) and electron transport (*mcpA* and *ompB*) was correlated with acetate concentrations in the groundwater. These results demonstrate that monitoring the *in situ* transcript levels of key genes can provide insight into the rates of metabolism and nutrient requirements of *Geobacteraceae* during *in situ* bioremediation of uranium.

A Molecular Diagnostics "Smoking Gun" for Natural Attenuation

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Demonstrating whether biodegradation of contaminants is occurring, or is likely to occur under a specific set of environmental conditions is a key factor in managing any site where biological processes are relied upon for remediation. We have developed a combination of molecular tests and reactive tracers that provide "smoking gun" evidence of *in-situ* degradation of contaminants. Field sampling and testing were used to investigate the relationship between baseline geochemical and microbial community data with in situ reductive dechlorination rates at a site contaminated with trichloroethene (TCE) and carbon tetrachloride (CTET). Ten monitoring wells were selected to represent conditions along a groundwater flow path from the contaminant source zone to a wetlands groundwater discharge zone. Background samples were analyzed for a suite of geochemical and microbial parameters; push-pull tests with fluorinated reactive tracers were used to measure in situ reductive dechlorination rates. A principal component analysis identified three groups of wells with similar geochemical and microbial characteristics. Push-pull tests were conducted using trichlorofluoroethene (TCFE) as a reactive tracer for TCE and trichlorofluoromethane (TCFM) as a reactive tracer for tetrachloromethane (CTET). Injected TCFE was transformed in situ to cis- and trans-dichlorofluoroethene, chlorofluoroethene and, in one test, completely dechlorinated to fluoroethene. Injected TCFM was transformed *in situ* to dichlorofluoromethane and chlorofluoromethane. Zero-order TCFE transformation rates ranged from < 0.05 to 1.00 nM/hr (< 0.44 to 8.76 µM/yr). A single TCFM transformation rate was estimated as < 0.05 nM/hr (0.44 µM/yr). The results indicate that it is possible to use push-pull tests with reactive tracers to detect and quantify reductive dechlorination of chlorinated ethenes and ethanes under monitored natural attenuation conditions. TCFE reduction rates were different for the three groups of wells identified by principal component analysis providing preliminary evidence that geochemical, microbiological, and in situ reductive dechlorination rates may provide complimentary information.

Extracellular Electron Shuttling in Bioremediation and Biotechnology

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Extracellular electron shuttling compounds are molecules that transfer electrons between microbial biomass (as electron acceptors) to electronegative molecules in natural or engineered environments. They are particularly useful to bioremediation applications in which the contaminant cannot be directly accessed by individual cells or in situations where Fe(III) reduction must be stimulated. The molecules that have been studied most intensively to date are extracellular quinones and humic substances, which are natural organic compounds with multiple quinone functional groups. Electron shuttling has been reported to promote biodegradation of numerous organic and inorganic contaminants. Our work has focused on extracellular electron shuttling by prokaryotes and eukaryotes, and its effects on electronegative contaminants in subsurface environments. In addition, our work has explored the novel biotechnology application of extracellular electron shuttling – increasing fermentative hydrogen production for hydrogen fuel. The results presented in this seminar will include work conducted with prokaryotic transformation of the cyclic nitramine explosives RDX and HMX, and transformation of chlorinated organic molecules in contaminated sediment. The talk will also address eukaryotic electron shuttling in aerobic environments, particularly amongst the white and brown rot fungi. Finally, it will discuss data for increasing the molar hydrogen yield in fermentative pure cultures, and the role that reduced electron transfer molecules play in the hydrogen fuel economy.

Bio-Trap^{TM} Samplers Document *In-Situ* Microbial Oxidation and Assimilation of ^{13}C-labeled Benzene under Denitrifying Conditions

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An *in-situ* denitrification-based bioremediation (“DBB”) program was implemented in the fall of 2004 to treat a gasoline-contaminated shallow aquifer at DoD-owned gasoline service station site in Maine. Sampling of “smear zone” aquifer media documented a sharp decline in the sorbed-phase gasoline hydrocarbons in response to DBB treatment (Liyang Chu, et al., in submission). Several molecular, culture-independent methods were used to characterize the denitrifying, gasoline-degrading microbial consortia stimulated by the DBB treatments, including denaturing gradient gel electrophoresis (DGGE), real-time polymerase chain reaction (qPCR) and multi-color fluorescence in-situ hybridization (“mFISH”) (Hince, 2005, U. Mass Soils Conf.; Hince and Ogles, 2005, IPEC).

A Bio-trap^{TM} study (http://www.microbe.com/biotrap.htm) was conducted from November to December 2005 to evaluate the intrinsic ability of the DBB-stimulated microbial consortia to degrade the aromatic hydrocarbons present in the aquifer. Two Bio-traps^{TM} containing Bio-sep^{TM} 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-traps^{TM} were suspended in these wells for approximately one month using floats to maintain the Bio-traps^{TM} at a fixed distance beneath the water table and within the zone of highest hydrocarbon contamination. Subsequently, the Bio-traps^{TM} were retrieved and shipped to Microbial Insights, Inc. (Rockford, TN) 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-traps^{TM}. The isotopic abundance of dominant fatty acids (those comprising greater then 1-2% of the total PLFA profile) was 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^{TM}. Approximately 78% and 43%, respectively, of the ^{13}C-labeled benzene was degraded in the Bio-traps^{TM} installed in DP-13 and DB-04 over a one-month period. Biomarkers associated with the *Proteobacteria* dominated the PLFA profiles from both wells, consistent with the dominance of Gammaproteobacteria (*Pseudomonadaceae*) and Betaproteobacteria (*Comamonadaceae*) in the DGGE profiles and mFISH assays. Whereas the DGGE profiles were dominated by 16s rDNA sequences related mostly to the family *Pseudomonadaceae*, quantitative mFISH analyses indicated that Betaproteobacteria were actually more abundant than the Gammaproteobacteria in site groundwater.

In DP-13, several lipid biomarkers exhibited δ-^{13}C enrichment values that approached the theoretical maximum values (based on the initial loading of ^{13}C-labeled benzene): e.g., +5,992 (biomarker *16:1w7c*) and +6,627 (biomarker *18:1w7c*). ^{13}C enrichment was also observed in two fungal biomarkers, *18:2w6* (+4,738 δ-^{13}C) and *20:4w6* (+5,106 δ-^{13}C). An unusual finding in DP-13 was the eukaryotic biomarker *20:5w3* (+5,133 δ-^{13}C) often associated with microeukaryotic "grazers." The Bio-sep^{TM} beads used in the Bio-traps^{TM} have small pore spaces that should limit access by the larger eukaryotic grazers. Given the presence of other fungal biomarkers, the presence of the *20:5w3* biomarker may also be associated with fungal growth. In DB-04, δ-^{13}C enrichment values of lipid biomarkers were lower but still quite high: e.g., +1,272 (biomarker *16:1w7c*) and +2,996 (biomarker *18:1w7c*). ^{13}C-labeled benzene degradation and δ-^{13}C enrichment of lipid biomarkers correlated closely with the PLFA biomass and total microbial cell counts (determined via epi-fluorescent microscopy, DAPI staining), which were proportionately higher in DP-13 than DB-04.

Improved Site Assessment of a Landfill-Leachate Plume using Microbial Community Profiles

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Many municipal landfills are unlined and have released leachate, or liquids that have come in contact with waste products, to the underlying soils and groundwater. Leachate-contaminated groundwater is rich in organic matter, nutrients, and metals, which distinctly changes the subsurface environment. Microbial communities are linked to changes in the subsurface hydrochemistry, and gaining quantitative information about the microorganisms to improve our knowledge of the movement and degradation of the leachate-contamination is not well researched. We sampled groundwater monitoring wells over time and space at a leachate-contaminated aquifer in northeastern New York using the 16S rRNA gene for Archaea, Bacteria, and Geobacteraceae. Community profiles were generated for each group of organisms using terminal restriction fragment length polymorphism (T-RFLP), and the community shifts over time were quantified using the Jaccard Index. Shifts in communities for three groundwater zones; unimpacted, plume fringes, and contaminated, followed distinct temporal trends and were significantly correlated to changes in groundwater hydrochemistry. Our results show how microbial community dynamics, monitored using molecular methods, can be used to improve our knowledge of the groundwater system at a leachate-contaminated site.

Environmental Fate

Behavior of Alkyl Leads in Gasoline NAPL During Long Term Contact with Water

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Pharmaceuticals and Personal Care Products in Solids: Analysis and Field Results for Sediment, Soil, and Biosolid Samples

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Detailed CVOC Source Area Investigation in the Context of a Fractured Bedrock Conceptual Site Model: A Case Study

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Behavior of Alkyl Leads in Gasoline NAPL During Long Term Contact with Water

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Tetraethyllead (TEL) has been added to gasoline as an antiknock agent since the 1920's. Its use in the United States peaked in the late 1960's, was phased down in the late 1980s and banned as an automotive fuel additive in the mid 1990s. The prohibition of lead alkyls in automotive gasoline has substantially reduced the human and ecological exposure to these toxic contaminants however health and safety concerns still persist today. One potential source of these compounds still exists within the large volume of leaded gasoline non aqueous phase liquids (NAPL) underlying legacy releases at former leaded gasoline stations, bulk fuel storage facilities and pipelines. Despite the potential problems associated with these contaminants, little is known regarding their ultimate fate in soils, and less is known about their environmental fate within the leaded gasoline NAPL present on the groundwater. At issue in this study is the chemical fate of TEL and related organic lead compounds (tetramethyl lead (TML), methyltriethyl lead (MTEL), trimethylethyl lead (TMEL), and diethyldimethyl lead (DMDEL) in NAPL while in contact with water. Laboratory studies designed to measure NAPL alkyl lead degradation on groundwater demonstrated that over a 20 month period greater than 90% of the TEL could be degraded by hydrolysis. For gasoline containing reactive alkyl lead mixtures relative degradation rates are as follows: TEL > TML > MTEL) ≥ TMEL and DMDEL. Field data from former gasoline station sites confirms the laboratory results and documents the composition and degradation of legacy gasoline releases. These field data demonstrate that the hydrolysis of alkylated lead compounds is particularly significant in thin NAPL formations due to the high surface area to volume ratio at the ground water interface. This work provides new information concerning the fate of alkyl lead compounds in NAPL samples and has significant implications regarding the use of alkyl lead concentrations in NAPL for age dating gasoline.

Pharmaceuticals and Personal Care Products in Solids: Analysis and Field Results for Sediment, Soil, and Biosolid Samples

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Pharmaceuticals and personal-care products (PPCPs) have been described as ubiquitous complex mixtures present at trace concentrations in surface- and ground-water samples throughout the United States and Europe. Sediment, soil, and biosolids have been much less studied, and might be important as sources of PPCPs to surface- and groundwater. The means for mobilizing PPCPs from solids will vary, but a critical evaluation of PPCP compositions and concentrations in these solids and a comparison between solids is necessary to evaluate their importance in the transport and fate of PPCPs in the geosphere and hydrosphere. In this study, a series of soil, sediment, and biosolid samples were extracted by accelerated solvent extraction and analyzed by high-performance liquid chromatography (HPLC) coupled with single or tandem mass spectrometry (MS or MS/MS) to identify and quantify PPCPs. Method recovery studies using naturally occurring organic matter (NOM)-containing and NOM-free sediments suggest that the primary effect of NOM is to sequester PPCPs and shield them from extraction. Staged amendment experiments indicate that the PPCP recoveries subsequent to extraction are not substantially diminished by the presence of NOM matrix components, suggesting incomplete extraction of PPCPs from NOM-containing soils, after equilibration for 24 hours and under extraction conditions previously determined to be optimal. In these samples, overall PPCP concentrations generally are similar in soils and sediments, and substantially greater in biosolids. The distributions of different PPCPs in all three matrix types were comparable. The PPCPs determined in solid matrixes differ compositionally from those most commonly detected in water, although physical properties, such as predicted partitioning coefficients commonly used to estimate solid/water distributions, are inadequate predictors of whether a PPCP will preferentially reside on solids. Mechanistic studies of PPCP partitioning and sorption behavior are necessary to understand the processes that bind PPCPs to solids.

Detailed CVOC Source Area Investigation in the Context of a Fractured Bedrock Conceptual Site Model: A Case Study

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Dissolved-phase transport of groundwater contaminants through crystalline bedrock fractures is often highly heterogeneous and 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. Detailed characterization in known or suspected contamination source areas, in the context of an existing CSM, not only guides remediation and monitoring strategies, but also enhances understanding of contaminant transport to potential off-site receptors.

The case study area in coastal Maine is underlain by fractured metavolcanic and intrusive bedrock, present at or near the ground surface. Water levels are as deep as 120 feet in some wells. Groundwater flow is restricted to fractures, lithologic contacts, or faults within the bedrock. Chlorinated volatile organic compounds (CVOCs) discharged on site from past operations have been detected in wells at concentrations varying from more than 3,000 micrograms per liter to below detection limits, with a heterogeneous spatial distribution. A variety of investigations has led to the development of a CSM for the site. Information obtained from detailed source area investigations may allow identification of specific contaminant pathways within the source area, but not at the greater distances that are present between the source area and some receptors.

Investigations, conducted or planned, that focus on the CVOC source areas include: 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, soil sampling, photolineament analysis, borehole radar investigation, hydrophysical logging, 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.

Environmental Forensics

Perchlorate Forensics - Sources and Investigation Methods: Theory and Application for Identification of New Sources

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Environmental Forensic Characterization of Chlorinated Hydrocarbon Sources

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Use of PCB Congener and Homolog Analysis in Source Apportionment at a Rail Yard Superfund Site

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Assessing the Extent and Distribution of a Crude Oil Spill in Chalmette, Louisiana following Hurricane Katrina – The Role of Chemical Fingerprinting

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Using the Abiotic Transformation Rate of 1,1,1-Trichloroethane to Estimate the Date of Discharge

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Integrated PAH Profiles and Compound-Specific Stable Carbon Isotope Analysis for Identifying Sources of PAHs in Urban Background near Former MGP Sites

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Perchlorate Forensics - Sources and Investigation Methods: Theory and Application for Identification of New Sources

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Perchlorate is rapidly gaining dominance as a global contaminant of the 2000's. Although manufactured and used for a long time (since 1940s in the U.S.), perchlorate has only recently emerged as contaminant of concern, in close connection with the advances in knowledge and analysis methods. The increasing number of perchlorate detections in water wells, vegetal and animal products, its alleged health impacts at low concentrations potentially affecting human metabolism, along with its environmental persistence and travel-capacity in water without retardation are all concurring, transforming the way we visualize the impact of perchlorate in the environment. Environmental forensics plays an important role in any investigations concerning perchlorate but our understanding of the sources and environmental fate of perchlorate is still limited.

This presentation will review the known sources of perchlorate (both natural and anthropogenic) and the available forensic techniques. Finally, the application of such knowledge in a forensic investigation leading to the discovery of a new source of perchlorate in Southern California will be presented and discussed. The main forensic techniques applicable to perchlorate include: stable isotopic analysis ($^{37}Cl/^{35}Cl$, $^{87}Sr/^{86}Sr$, $^{16}O/^{17}O$), surrogates analysis, historical information assessment (aerial photography, propellant use and chemistry, firing range usage), geologic analysis, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The application of some of these methods in a recent forensic investigation resulted in the identification of a new source of naturally occurring perchlorate associated with the Mission Valley Formation outcrop in San Diego California (a carbonate rich marine layer). Modification of existing agricultural soil sampling techniques USDA 60-6(26) and USDA 60-6(27a) were used for sample preparation along with EPA Standard Method 314.0 for extract analysis. No statistical relationship between major ions (sulfate, total nitrate, chloride) and perchlorate in soil was identified. The discovery of naturally occurring perchlorate in the marine layer within the Mission Valley Formation, CA in addition to its presence in Texas and New Mexico suggests that large portions of the southern United States or similar areas (i.e., semi-arid) may contain natural sources of perchlorate.

Environmental Forensic Characterization of Chlorinated Hydrocarbon Sources

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Environmental Forensics entails the application of various potential techniques for identifying and characterizing the historical sources of releases at sites with hazardous substances in the soil and/or ground water. They can be particularly useful in better characterizing chlorinated solvent sites. The techniques include 3-D examination of historical aerial photographs, chemical fingerprinting, interviews, research of historical documents and industrial processes, waste volume calculations, degradation studies and fate and transport evaluations. Currently, efforts are underway via an ASTM standards development subcommittee to develop guidance for the application of environmental forensic techniques. The authors are reviewers involved in the process and offer this paper to illustrate the importance of these techniques in scoping site characterization and remedial evaluation studies and, in particular, in characterizing sources of chlorinated hydrocarbons. By understanding the source of the chlorinated hydrocarbons, one can better interpret the effects of disposal and natural degradation processes on the material and predict the ultimate fate of the material at a site.

This paper provides an overview of how the field of environmental forensics has evolved and examples of various techniques to illustrate their application. The authors will provide examples of the misapplication of these techniques and note the importance of developing multiple lines of evidence to support conclusions. A recent case example of the application of these techniques in the identification, characterization and assessment chlorinated hydrocarbons is given to illustrate the importance of the techniques. These techniques were applied as part of site characterization and remedial evaluations and are discussed from both a technical and legally defensible perspective.

Use of PCB Congener and Homolog Analysis in Source Apportionment at a Rail Yard Superfund Site

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After almost two decades of cleaning up the PCB contamination at the Paoli Rail Yard, SEPTA, Conrail and Amtrak resolved their allocation claims against American Premier Underwriters (APU), the successor corporation to Penn Central, the prior owner/operator of the rail yard. Chemical analyses, records research, worker testimony, and other evidence were woven into a persuasive cost allocation that resulted in a recovery of $38 million. Congener specific chemical fingerprinting of the PCB molecules found in the soil at the Rail Yard: confirmed the Aroclor identification of historical investigations; found little weathering of either Aroclor 1254 or 1260; and confirmed that the vast majority (over ninety percent) of the PCBs were of a chemical formulation which dated from the Penn Central era, *i.e.*, before 1976. Applying a two-end member mixing model, both the congener analysis and the homolog analysis yielded equivalent results as to the relative proportion of Aroclor 1254 and 1260 present in the soil. These scientific findings, coupled with an allocation model which took into account the rail car histories and worker practices at the Yard, led to the historic settlement. Another key contribution was the testimony of several retired railroad engineers, who revealed a keen memory of the historic use and handling of PCBs at the site, including the deliberate PCB dumping there, which took place during the early Penn Central era.

Assessing the Extent and Distribution of a Crude Oil Spill in Chalmette, Louisiana following Hurricane Katrina – The Role of Chemical Fingerprinting

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Floodwater associated with the Hurricane Katrina's storm surge (August 29, 2005) displaced and damaged a 250,000 gallon above ground storage tank at Murphy Oil Corporation's Meraux Refinery in Chalmette, Louisiana. Crude oil was released and was dispersed into the nearby and evacuated residential and commercial area by the retreating floodwaters. The circumstances of this oil spill investigation are unprecedented – as was the subsequent environmental assessment. The assessment, which began September 18, involved biased sampling and "chemical fingerprinting" of interior and exterior wipe samples (from the visually-evident "bathtub rings" on structures) and interior and exterior sediments from over 3000 homes, businesses, churches, and schools. Crude oil from the failed tank was thoroughly characterized using chemical fingerprinting. Over 10,000 Tier 1 (GC/FID) chromatographic (EPA Method 8015B) analyses were conducted as a means of mapping the overall lateral extent, concentration, and continuity of the crude oil impact. These Tier 1 GC/FID analyses – when evaluated spatially using Geographic Information System (GIS) – largely revealed the extent of crude oil contamination in the area – as well as the widespread occurrence of (1) non-crude oil, petroleum-derived contamination (e.g., engine lube oils, hydraulic oils, diesel fuel, household lubricants) and (2) allochthonous natural organic matter (e.g., peat and plant materials) from surrounding marshes that was carried and dispersed by the floodwater. More advanced Tier 2 fingerprinting, involving quantitative petroleum biomarker data generated using GC/MS-SIM (modified EPA Method 8270), was conducted on a selected subset of samples. When the biomarker-based diagnostic ratios were evaluated statistically using the revised Nordtest oil spill identification protocol (Daling et al., 2002), the presence/absence of the crude oil, even at concentrations below residential standards, was established. This information was used to develop and govern a settlement and remedial program with the affected property owners, and to defend against claims brought by unaffected parties.

Using the Abiotic Transformation Rate of 1,1,1-Trichloroethane to Estimate the Date of Discharge

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The primary contaminant identified in a shallow water-bearing zone at an industrial site located in Central New Jersey was 1,1,1-Trichloroethane (TCA). The discharge date of TCA to ground water was established in order to evaluate the legitimacy of an insurance coverage claim.

The age of TCA in ground water was determined by employing the fact that when dissolved in water, TCA is transformed chemically (abiotically) into 1,1-Dichloroethene (1,1-DCE) via an elimination reaction, and acetic acid (HAc) via hydrolysis. The reaction yields 22% 1,1-DCE and 78% HAc.

The transformation rate (*k*) is a function of temperature ($k = Ae^{-E/0.008314K}$) where *A* and *E* are constants, and *K* is the temperature in degrees Kelvin.

Using the first order rate equation, $t = \frac{\ln \frac{C_o}{C_t}}{k}$, where C_t is the concentration of TCA at any time t, and C_o represents the initial TCA concentration at t=0, and then using the 1,1-DCE/TCA concentration ratio measured during ground water sampling to derive the C_o/C_t TCA ratio, the age of TCA in ground water (*t*) for each of thirteen monitoring wells was calculated.

The calculated age of TCA in each monitoring well was then subtracted from the sampling date to arrive at the date that TCA was first dissolved in ground water.

The earliest discharge date using this method was April 1984. The average discharge date using ground water data from three different ground water sampling events spanning a forty month period was July 1985 with a standard deviation of 9.5 months.

Potential interferences using this method include anaerobic biodegradation of TCA to 1,1-Dichloroethane (1,1-DCA) and production of 1,1-DCE from the biodegradation of Trichloroethene (TCE). However, these interferences were not a concern due to low TCE concentrations observed at the site, and the absence of anaerobic conditions as indicated by the presence of high dissolved oxygen concentrations and the absence of vinyl chloride.

Integrated PAH Profiles and Compound-Specific Stable Carbon Isotope Analysis for Identifying Sources of PAHs in Urban Background near Former MGP Sites

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Polycyclic aromatic hydrocarbons (PAHs) have been released into the environment from a number of natural and anthropogenic sources, particularly in urbanized areas. Because of the potential financial liability for cleanup, many parties find it important to be able to determine the source(s) of PAHs found on their property or neighboring properties. This need can be especially strong for owners of major industrial PAH sources, such as refineries, foundries, coke plants, and former manufactured gas plants (MGP), who often are considered the source of all PAHs in the vicinity of their properties. This presentation will summarize the results of a recent study of PAHs in urban background soil and neighboring former MGP sites. Over 100 randomly selected urban sites were sampled as well as 18 former MGP sites. The samples were classified by land use and analyzed by GC/FID, GC/MS, and GC/IRMS. In particular, the utility of integrated PAH profiles and ratios and compound-specific carbon isotope ratios by GC/IRMS will demonstrated. Also, the capabilities and limitations of the available methods and some of the triggers for success or failure will be discussed.

Ethanol Fuels

Ethanol Fate and Transport: An Updated Review of its Impact on Subsurface Gasoline Contamination

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The Fate of Oxygenates and BTEX from Gasolines Containing MTBE, TBA and Ethanol: Initial Findings from a Controlled Field Experiment, Borden, Canada

Erika Williams, University of Waterloo, Waterloo, ON, Canada
Marian Mocanu, University of Waterloo, Waterloo, ON, Canada
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The Impact of Fuel Ethanol on Groundwater: Source Behavior

Brent P. Stafford, University of Houston, Houston, TX
Natalie L. Cápiro, Rice University, Houston, TX
William G. Rixey, University of Houston, Houston, TX
Pedro J.J. Alvarez, Rice University, Houston, TX

The Impact of Fuel Ethanol on Groundwater: Microbial Response

Natalie L. Cápiro, Rice University, Houston, TX
Marcio L. B. Da Silva, Rice University, Houston, TX
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Ethanol Fate and Transport: An Updated Review of its Impact on Subsurface Gasoline Contamination

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The potential environmental effects of blending ethanol with gasoline have been studied extensively in recent years, and a June 2006 study concludes that our knowledge base on the topic has improved substantially since 2001. However, uncertainty remains in predicting the subsurface behavior of gasohol, particularly as it relates to formation of contaminant plumes in groundwater. This presentation assesses the current state of knowledge and directions for future research. Most studies agree that the issue of co-solvency inducing elevated levels of benzene in groundwater is real for neat (pure) ethanol spills, but not for releases of gasoline containing ethanol at 10% (E10) or lower. Yet to be answered, however, is the question of whether the ethanol in blended gasoline will enhance the transport of benzene in the subsurface. If so, a release of ethanol-blended gasoline might produce a larger subsurface benzene plume than a release of ethanol-free gasoline. Uncertainty regarding ethanol transport to the groundwater clouds the issue, and the body of field data from real ethanol-gasoline spill sites is still inadequate to refute or validate the models and theories. As such, until much more field data and supporting knowledge are gathered, uncertainty remains about the extent of benzene-plume lengthening at gasohol spill sites.

The Fate of Oxygenates and BTEX from Gasolines Containing MTBE, TBA and Ethanol: Initial Findings from a Controlled Field Experiment, Borden, Canada

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The development and fate of groundwater plumes derived from three emplaced oxygenate-gasoline residuals in the Borden Research Aquifer are being monitored with multilevel monitoring fences. One fuel contains 90% gasoline with 9.8% MTBE and 0.2% TBA (GMT); another contains 90% gasoline and 10% ethanol (E10); the third contains 95% ethanol and 5% gasoline (E95). Ethanol was found 15 m downgradient of the sources and after 250 days at concentrations of 300 mg/L (E10) and 3000 mg/L (E95). While ethanol from E10 appears to have undergone considerable biodegradation, ethanol from E95 underwent relatively less. Surprisingly, MTBE and TBA mass fluxes declined precipitously and very little MTBE or TBA mass flux was found downgradient. However, previous experience at Borden and the lack of stable C isotopes fractionation suggests this apparent decline in MTBE mass flux may represent uncertainties in monitoring short slugs (<100 days) with only a few mass flux measurements. Considerable bioattenuation of BTEX, trimethylbenzenes and naphthalene is noted and is consistent with past Borden experience. Ethanol appears to enhance the mass flux of benzene and toluene, but not trimethylbenzenes or naphthalene, as compared to the GMT case.

The Impact of Fuel Ethanol on Groundwater: Source Behavior

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In addition to concerns over the impact of gasohol on groundwater quality, there is concern over the potential impact of spills of fuel grade ethanol (E95 and E85). Two important spill scenarios are fuel grade ethanol spilled into the subsurface onto existing NAPL contamination and fuel grade ethanol spilled into the subsurface without existing contamination. This research assesses the extent of NAPL mobilization, phase separation and groundwater impacts for these two spill scenarios in both 2D bench-scale and pilot-scale (8-m^3 tank) systems. Complementary experiments (presented in a companion paper) are investigating the impact of these same two spill scenarios on microbial processes. Results from the pilot-scale E95 release (supported by 2D bench-scale visualization studies) indicate that significant migration of ethanol, BTX and other hydrocarbons occurred within the capillary fringe downstream of the source, and NAPL was redistributed in the capillary fringe. Low concentrations of hydrocarbons and ethanol were observed below the water table at several positions downgradient of the injection point. Higher concentrations of ethanol were found at the water table ($[EtOH]_{max}$ = 0.5% v/v) and at the tank outlet ($[EtOH]_{max}$ =1% v/v), suggesting that for the flow rate and media used in this study, downgradient migration of ethanol occurred above the water table. Ethanol was undetected in the outlet after 30 days. Analysis of vadose zone soil cores taken on day 60 yielded BTX and other hydrocarbons in soils downgradient of the injection point. For the E100 release onto pre-existing NAPL, ethanol concentrations were greatest in the capillary fringe ($[EtOH]_{max}$=20% v/v), with lower levels measured in the outlet ($[EtOH]_{max}$=0.6%) and in groundwater samples ($[EtOH]_{max}$=0.2% v/v). Ethanol was undetected in the outlet after ~90 days. The corresponding 2D bench-scale visualization experiments showed that ethanol flushed pre-existing residual NAPL emplaced above the water table, then redistributed the NAPL downgradient from the source following phase separation from the ethanol as it migrated through the capillary zone. These results suggest that ethanol spills (at least for the specific spill volumes considered in this research) can be expected to migrate primarily in the capillary zone and that physico-chemical effects will have a significant impact (in conjunction with microbial processes) on the observed concentrations of ethanol and hydrocarbons in groundwater at various points downstream of fuel ethanol spills. In addition, these results have implications for the longevity of the ethanol source as well as the distribution of NAPL at ethanol spill sites.

The Impact of Fuel Ethanol on Groundwater: Microbial Response

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The use of ethanol as a gasoline additive is rapidly increasing due to the phase out of methyl tertiary-buytl ether (MTBE), which despite helping to meet Clean Air Act requirements, has caused widespread groundwater contamination problems. Ethanol is also being widely used to meet renewable fuel requirements. This increases the probability of groundwater contamination by ethanol-amended gasoline, which requires an improved understanding of how ethanol affects microbial communities associated with the biodegradation of hydrocarbons in the subsurface.

In this study, a 8-m^3 pilot-scale aquifer tank packed with sandy soil was used to simulate two spill scenarios that are likely to occur in the field: 1) fuel-grade ethanol (E95, ethanol 95% v/v containing gasoline 5% v/v as a denaturant) into soil containing no existing contamination, and 2) neat ethanol (100% v/v) release onto gasoline-contaminated soil. Real-time quantitative polymerase chain reaction (RQT-PCR) and most probable number PCR were used to estimate the concentration of *Bacteria* (16s rRNA), *Archaea* (e.g., methanogens), nitrate-reducers (*nir*), sulfate-reducers (*dsr*), and iron-reducers (*Geobacter*). Additionally, bacteria-harboring benzylsuccinate synthase (*bssA*), phenol hydroxylase (*phe*) or toluene dioxygenase (*tod*) genes were also quantified as biomarkers for potential BTEX biodegradation, since these genes are ubiquitous in bacteria capable of degrading aromatic hydrocarbons under anaerobic and aerobic conditions, respectively.

The fuel-grade ethanol spill at the water table interface was unique, the high reaeration rate resulting from the shallow vadose zone (0.5 m) and high inflow rate (2 m day^{-1}) maintained aerobic conditions throughout experiment, inhibiting the growth of any anaerobic species. *Bacteria* concentration in the soil prior to E95 injection was $1.9 \pm 1.3 \times 10^3$ cells g-soil $^{-1}$. Within 6 months after the E95 pulse release (75-L), the *Bacteria* concentration increased significantly ($p \leq 0.05$) to $6.8 \pm 5.1 \times 10^4$ cells g-$soil^{-1}$, while the population of bacteria harboring *tod* genes also increased (0.13 ± 0.05 to $1.8 \pm 1.8 \times 10^3$ cells g-$soil^{-1}$). Even though bacteria-harboring *tod* increased by one order of magnitude, ethanol did not select for specific BTEX degraders (decreased *tod*/Bac ratio). These preliminary results suggest that ethanol stimulated the growth of total *Bacteria* and thus the fortuitous growth of putative aerobic BTEX degraders (*tod*), suggesting that higher BTEX degradation rates could occur in the presence of ethanol provided that oxygen is not limiting.

The spill of neat ethanol onto residual BTEX mimicked potential spills that could occur at bulk (blending) terminals. In this experiment, higher ambient temperatures (summer) associated with lower influent D.O. saturation and higher microbial activity, coupled with a slower flow rate (0.7 m d^{-1}), resulted in fast depletion of oxygen from the system. The high oxygen demand exerted by ethanol consumption lead to strongly anaerobic conditions (i.e., methanogenic) 20 days after ethanol addition. After ethanol had been washed out (50%), the system returned to aerobic conditions (rebound time of 60 days), which favored the growth of BTEX degraders (*tod*) by over two orders of magnitude. However, the short acclimation time limited the growth of other anaerobic communities, which was corroborated by the absence of their corresponding geochemical footprints. Microbial growth coincided with ethanol migration and availability, which was restricted to a relatively thin layer at the capillary fringe and water table interface, and toxic effects from ethanol exceeding 10,000 mg/L were not detected. These results suggest that releases of highly concentrated ethanol into the subsurface may not be as detrimental to microbial communities as previously believed because of short rebound times and minimal genotype dilution.

Evaluating and Management of Small Releases from USTs

UST Vapor Leak Research

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Monitoring Small Releases from USTs and Assessing Vadose Zone Infiltration

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Evaluation of Maryland’s Enhanced UST Regulations for Mitigating Groundwater Contamination Risk from Small Gasoline Leaks

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UST Vapor Leak Research

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The State of New Hampshire has encountered significant MtBE contamination problems at operating service stations that it has attributed to tank system vapor releases. State sponsored research is being conducted to foster understanding of the releases and practical ways to mitigate them. The research partnership includes DES, the University of New Hampshire, a large northeast/mid Atlantic oil company and equipment vendors (US EPA and API also provided supplemental funding and assistance). Seven operating service stations were instrumented to collect continuous data on groundwater levels, subsurface temperatures and tank internal pressure. On a weekly basis data was collected on groundwater quality in the well nearest to the tanks and soil vapor levels at the nearest monitoring well and tank pad well. Additional data was collected on gasoline deliveries, tank inspections, leak repairs and A/L ratio modifications. After an initial month long baseline monitoring period, six of the service stations were modified. The following modifications were evaluated: 1) SVE system installation and startup, 2) vent processor installation and operation, 3) ORVR compatible nozzle and clean air separator installation, 4) pressure decay test and leak repairs, 5) monthly inspection and leak repairs and 6) ISD system monitoring and repairs. After approximately three months of operation and data collection on the modified systems, the service stations transitioned from gasoline containing MtBE to gasoline with ethanol. The data collection continued to capture the response in the MtBE contamination levels in groundwater once MtBE was no longer present in the ongoing vapor releases. Preliminary findings will be discussed on: a) the main sources and relative size of vapor leaks, b) the impact of A/L and nozzle type on tank system pressures, c) the success of the technologies in controlling releases and d) the response time in various geologies once releases are reduced.

Monitoring Small Releases from USTs and Assessing Vadose Zone Infiltration

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In conducting near-field UST monitoring over several years, we have observed periodic spikes in MTBE ground water contamination in the absence of BTEX. MTBE levels may exceed thousands of parts per billions. Based on the work of others, the likely source of the MTBE contamination spikes is periodic vapor releases. Conceptually, MTBE vapors will rapidly partition into vadose zone soil moisture or a shallow water table, given its low Henry's Law constant. In these environments, BTEX constituents would readily biodegrade. Accumulations of MTBE in soil moisture can be periodically flushed from the vadose zone by direct infiltration beneath the asphalt, by a rise in the water table in response to precipitation and by infiltration in upgradient recharge areas. Direct infiltration may occur during precipitation events at downspout locations adjacent to on-site buildings, from dry wells beneath pump islands which drain station canopies, and from cracks in the asphalt. Furthermore, it is possible that water migrating downward at these locations rapidly moves laterally in the coarse subbase of the asphalt. We have implemented a monitoring program at several gas station sites to evaluate the magnitude, duration and configuration of the water table rise beneath the asphalt in response to precipitation events. The monitoring program entails the installation of pressure transducers in wells in the near field along with an on-site rain gauge to document the water table response.

Evaluation of Maryland's Enhanced UST Regulations for Mitigating Groundwater Contamination Risk from Small Gasoline Leaks

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The State of Maryland promulgated new regulations in January 2005 to require owners of new and existing UST systems in areas of the State defined as "High Risk Groundwater Use Areas" to implement groundwater monitoring and additional leak testing to prevent releases of petroleum products into groundwater sources used for drinking water.

ENSR conducted an evaluation of the new UST regulations in order to: 1) perform a cost evaluation for implementing the new regulations for existing sites; and 2) evaluate the effectiveness of the new regulation to better detect releases from existing gasoline UST systems in high risk groundwater use areas.

Maryland estimates that 750 UST systems are located in high-risk areas. ENSR evaluated a sample of 30 UST systems and estimated the cost to install monitoring wells and perform the first year testing requirements to be $13,500. The annual cost of compliance with the regulations was estimated to range from $5,640 to $6,300. It was also estimated that approximately 7% of the UST systems in the state will be required to comply with the new regulations.

ENSR used the simple BIOSCREEN model (EPA, 1996) and a number of assumptions to evaluate the effectiveness of the new UST regulations. Assumptions related to quantity and duration of release, concentration, specific gravity and solubility of MTBE, dilution factor, groundwater flow velocity and elapsed time and monitoring well distance relative to the point of release. The modeling suggested that small releases of reformulated gasoline will result in MTBE plume migration and the releases will be detected by the 180 day monitoring cycle required by the new regulations.

Maryland's new UST regulations will likely detect or prevent several different types of gasoline leaks that previously went undetected The regulations target a relatively small number of UST systems located within high risk groundwater use areas and are, therefore, considered to be cost effective.

Heavy Metals

Site Assessment for the Presence of Mercury in Soil using Passive Soil Gas Sampling

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Comparison and Critique of Selective Sequential Extraction Methods for Metals in Soils and Sediments

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Chemical Speciation of Heavy Metals in Wetland Sediments Treating Urban Stormwater Runoff

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Assessment of Ferrous Sulfate for the Remediation of Chromite Ore Processing Residue (COPR) in an Oxygen Limited System

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Mineral Enriched Composts for the Remediation of Heavy Metal Contaminated Sites

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A Case Study of Arsenic Regulations by a Local Board of Health Regarding Redevelopment in a Former Orchard

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Site Assessment for the Presence of Mercury in Soil using Passive Soil Gas Sampling

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Passive soil gas (PSG) methods have been used over the years for site assessment, but have been primarily limited to screening sites for the presence of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). Detection capabilities for PSG technologies, however, are only limited by the chemical and physical properties of the compound, design of the sampler, and the analytical technique used. Therefore, inorganic compounds with sufficient vapor pressure and limited water solubility such as mercury are viable candidates for detection.

PSG sampling was recently performed at the Engine Test Facility (ETF) at Arnold Air Force Base in Tennessee. PSG was chosen as a cost effective tool to investigate the large area of the facility (28 acres) for the presence of VOCs/ SVOCs and mercury.

This presentation will discuss the sampler design, general considerations for the use of PSG, and the design and results from the site investigation performed at Arnold AFB.

Comparison and Critique of Selective Sequential Extraction Methods for Metals in Soils and Sediments

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A metals' toxicity is often dependant upon speciation and not strictly upon total concentration. In addition, speciation can often predict metal mobility and potential exposure risk. Unfortunately, certain metal species are often difficult to measure directly, limiting analysis and interpretation. Selective sequential extractions (SSE) offer a way to interpret the potential compounds of metals by examining the solubility or leachability of metals under certain conditions. However, rather than direct species analysis, SSEs give indirect speciation information from which the biogeochemical behavior and toxicological implications of the metals present in the sample are inferred.

There are many SSE methods available, most of which are developed with a particular target metal in mind and for a select range of species. The range of species tends to be limited in order to minimize confusion when interpreting the data. Frontier has developed a SSE approach that examines the effect of behavioral chemistry and the resulting extraction effect on the target metals in the sample. This in-house method will be compared with the new EPA Method 3200 (Mercury species fractionation and quantification by microwave assisted extraction, selective solvent extraction and/or solid phase extraction), which is designed to assess the bioavailability of Hg in soils. In addition, more traditional SSEs, such as that developed by Greve for multiple metals in mine tailings, will be performed in parallel and the results compared. The interest of the study is not only in comparing and critiquing these methods for the original suggested target metals, but also in expanding to a larger suite of analyzed metals including Hg, As, Ba, Pb, Mn, Cr, and Se.

Chemical Speciation of Heavy Metals in Wetland Sediments Treating Urban Stormwater Runoff

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Heavy metals in urban stormwater runoff are primarily removed by sedimentation in stormwater best management practices (BMPs) such as ponds and wetlands. Heavy metals accumulated in BMP sediments have the potential to produce toxic effects in benthic invertebrates and aquatic microorganisms in wetlands. In order to evaluate the possible toxicity or risk of environmental pollution of heavy metals present in sediments, it is imperative to assess the types of chemical associations between heavy metals and the sediment solid phase. The geochemical forms of particulate heavy metals allow a qualitative assessment of metal lability/stability, metal bioavailability and toxicity, and ultimately evaluate the potential for environmental degradation of receiving water bodies. This research is a part of the ongoing research activity at U.S. EPA's Urban Watershed Research Facility in Edison, NJ, evaluating the relative efficiencies of pond and wetland BMPs for the treatment of heavy metals in urban stormwater runoff. The objectives of this research include: (i) evaluating the effects of two types of structural BMPs (cattail wetland and wet pond) on the removal of particulate-bound and soluble heavy metals from stormwater runoff; and, (ii) assessing the chemical associations between heavy metals and wetland sediments by a modified sequential chemical fractionation technique (Bureau Commun de Reference, BCR). Preliminary results showed that structural BMPs such as retention ponds and cattail wetlands are effective in attenuating particulate-associated heavy metal loads, especially, Al, Cu, Pb, and Zn in urban stormwater runoff, and could potentially improve the water quality of receiving water bodies. BCR sequential extraction results for wetland sediments showed that the residual fraction was the most dominant for Al and Fe; Cu, Pb, and Zn were most abundant in the potentially mobile phases. Cu was present as the oxidizable organic matter/sulfide bound species; Pb and Zn were bound to amorphous Fe/Mn oxides. The exchangeable fraction was the least dominant for all metals except Mn.

Assessment of Ferrous Sulfate for the Remediation of Chromite Ore Processing Residue (COPR) in an Oxygen Limited System

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This study investigated the remediation of Chromite Ore Processing Residue (COPR) using ferrous sulfate under oxygen limited conditions. It included a full factorial design experiment to evaluate the effects of water content, chemical dosage, treatment pH, particle size, and multifactor interactions on the performance and permanency of the treatment. Decreasing the pH of the COPR matrix from its natural value of 12.5 to 9 destabilized Cr(VI) bearing minerals and enhanced the release of Cr(VI) into solution. Reduction of particle size from mesh 4 to mesh 200 enhanced the leaching of Cr(VI) by 1.5 times. Chemical and mineralogical testing of the treated COPR combined with statistical analysis of the experimental data elucidated the mechanisms of the chemical treatment and pointed to possible causes of the non permanency of some COPR treatments using ferrous sulfate. The study indicated that the reappearance of Cr(VI) in the treated samples in some treatments can be attributed to incomplete reduction of Cr(VI) due to mass transfer limitations and scavenging of the reductant. Cr(VI) reduction occurred both during curing as well as during alkaline digestion and TCLP leaching. Ferrous extraction in the treated samples indicated that the non-stoichiometric reduction of Cr(VI) by ferrous and the apparent reversibility of the treatment was due to the scavenging of ferrous by molecular oxygen as opposed to the inactivation of ferrous due to sequestration in sparingly soluble ferrous precipitates, re-oxidation of Cr(III) by manganese present in the COPR matrix, or re-oxidation of Cr(III) during curing or alkaline digestion by oxygen. Low water content favored oxidation of the ferrous by molecular oxygen thus reducing its overall reduction effectiveness. To ensure successful treatment of the COPR material and to minimize mass transfer limitations the chemical reduction of Cr(VI) should be facilitated by pH adjustment, particle size reduction, high water content, and effective mixing.

Mineral Enriched Composts for the Remediation of Heavy Metal Contaminated Sites

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Soil contaminated with heavy metals can be remediated by reducing the bioavailability of the heavy metals in order to break the pollutant-receptor pathway. This kind of remediation can be used prior to establishment of vegetation to create green space. Compost is often proposed as a suitable material for the remediation of contaminated brownfield sites, vitalising the soil but also for its reported immobilisation of heavy metals. Through this immobilisation the contaminant receptor linkage pathway will be broken and the toxicity of the soil will be reduced. In addition of composts there are also inorganic soil amendments that are known for their immobilising effect on heavy metals and therefore may be suitable for soil remediation. In our research we have examined the usage of two composts enriched with zeolite to increase the immobilising behaviour of the composts. The two composts were composted garden waste and composted sewage sludge and a combination of both. Results show that the composted greenwaste reduced the leaching of metals from contaminated soil efficiently while composted sewage sludge increased leaching. In contrast however, the growth of ryegrass was much more improved by composted sewage sludge. This compost also reduced metal uptake by the grass leaves more efficiently than the composted greenwaste. The results have also shown that the additional effect of the minerals added to the compost is limited compared to the metal immobilisation effect of the compost on its own. Additional trials will be performed to demonstrate the sustainability of the technique with minerals addition. Overall, this study has clearly shown that the metal immobilising capacity of composts has to be examined for each soil separately and an increase in performance can be achieved by higher levels of minerals added to the composts.

A Case Study of Arsenic Regulations by a Local Board of Health Regarding Redevelopment in a Former Orchard

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A proposed mixed-use residential subdivision on over 100 acres of land in Central Massachusetts is on a former orchard, historically which had been treated with arsenical pesticides. The town is within a known area of high naturally occurring arsenic in soils. Under subdivision development rules in Massachusetts the planning board seeks advice from the local board of health on matters of public health. The board of health recommends to the planning board whether a development has public health issues and, if it does, conditions the development to mitigate those issues. Arsenic from pesticides applied in accordance with the directions on their label is not considered a release and is therefore not subject to the jurisdiction of the Massachusetts Department of Environmental Protection (DEP). Further, contaminants present at background levels are determined not to pose a risk to health. Consequently, the DEP Hazardous Waste Clean Up Regulations, known as the Massachusetts Contingency Plan, are not binding on a board of health. This Board of Health required extensive testing of the soils and subsoils on the site, resulting in one of the most intensely studied orchards. Equally intensive were the risk assessment analyses performed to study background conditions and assess risk under residential use. The conclusions of these tests and analyses furthers the knowledge of arsenic in these situations. Equally interesting are the Board of Health's attempts to devise remediation standards which it felt adequately protected the future residents of the subdivision from the perceived threat of arsenic in a town with naturally high occurring arsenic levels. The subdivision was eventually approved, conditioned on a remediation plan, the cost of which to develop and implement will be discussed in relation to the risk reduction achieved and, in contrast, what would have been achieved through application of the Massachusetts Contingency Plan, had it been applied.

Implementing Aggressive Remediation Strategies

Remediation Optimization Using Direct Sensing Technologies and SmartData Solutions® to Reduce Remediation Costs
John Sohl, Columbia Technologies, Baltimore, MD
Ned Tillman, Columbia Technologies, Baltimore, MD

Applying Visualization, GIS, and Modeling Tools to Optimize System Design and O&M
Mary Ann Parcher, ES&T, a division of GES, Blacksburg, VA

Real-Time Feasibility Testing to Properly Assess Multiple Remediation Technologies in One Event
Charles Blanchard, GES, Pleasant Hill, CA

Improving Well Efficiency to Enhance System Performance
Bill Morrow, Parratt-Wolff, Inc., East Syracuse, NY

System Optimization During System Design and Operation to Enhance Conventional Remediation Technologies
Charles Whisman, GES, Exton, PA

Optimization of Full-Scale Chemical Oxidation Systems to Improve Performance
William "Tripp" Fischer, DNREC, New Castle, DE
Peter Herlihy, Applied Process Technology, Inc., Pleasant Hill, CA

Remediation Optimization Using Direct Sensing Technologies and SmartData Solutions® to Reduce Remediation Costs

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Historically, some remediation efforts have failed due to inadequate site characterization and/or over-generalized and misleading conceptual site models (CSM). The need for total mass characterization including sorbed, dissolved, free-phase liquid and vapor phase site data, both pre- and post-application of the remedial technology, is critical to project success. With the emergence of direct sensing tools such as the membrane interface probe (MIP) and optical methods (fluorescence), much more information can be collected in a short time and more accurate site models can be built. These tools gather thousands of measurements on the geology, hydrology, nature, and extent of the subsurface contaminants. The data can be processed into high-definition two- and three-dimensional images of the site, providing much more detail than is normally available for designing a remediation approach. With this detail, one can better determine which areas to target for remediation, resulting in a more effective remediation effort. There are a number of enhancements to the basic MIP probe that make it even more effective as a tool for characterizing hydrocarbons. These enhancements allow for individual chemical species, such as benzene, naphthalene, and even the oxygenates to be identified and mapped to concentrations as low as the 10-100 ppb range. The real-time capabilities of direct sensing technologies combined with real-time information processing such as the patent-pending SmartData Solutions® enable project managers to identify and close data gaps early in site characterization and at much lower cost than would be incurred via mobilizations of personnel and equipment. In turn, these methods provide time and cost-effective improvements in the application of remedial technologies. MIP will be demonstrated at the conference.

Applying Visualization, GIS, and Modeling Tools to Optimize System Design and O&M

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To determine practical remedial endpoints and effectively design remediation systems, a thorough understanding of the subsurface conditions and distribution of the contamination is necessary. This can be achieved through the development of an appropriate Conceptual Site Model (CSM) that demonstrates relationships between the subsurface geology, hydrology, and contamination distribution. The CSM can be used to evaluate the extent and magnitude of contamination, assess potential data gaps, and form the basis for any future analyses. Approaches and tools to assist with developing and conveying a CSM include analytical and numerical models, visual imagery analyses, and Geographical Information Systems (GIS). Various spatial analysis tools can be used to delineate non-aqueous phase liquid (NAPL) distributions as well as dissolved and soil contaminant plume distributions, calculate mass and volume estimates, perform screening level risk assessments, and discern concentration trends across the site. NAPL mobility analyses can be performed spatially to identify and delineate migrating plumes from stable plumes so that remediation efforts can be prioritized and optimized for both efficiency and costs. Data visualization allows the audience to quickly and intuitively comprehend site information as well as difficult or abstract concepts and relationships. Through the use of visualization techniques, the CSM and progress of remedial activities can be easily conveyed to clients, regulators, and other stakeholders. Example applications of these approaches and tools will be presented, including the incorporation of modeling and visualizations during system operation to aid in the optimization of the remediation system.

Real-Time Feasibility Testing to Properly Assess Multiple Remediation Technologies in One Event

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Performing an effective feasibility test is essential in the selection of a remedial technology to address environmental impacts. Information gathered during the study is often used to design a full-scale remediation system, which may incorporate conventional and/or innovative remediation technologies, and result in reduced life-cycle costs for site cleanup. A unique pilot-testing platform allows for the evaluation of multiple technologies during one feasibility study. The pilot test vehicle enables engineers to collect accurate, real-time data to determine if a remedial approach is effective while the test is ongoing. A short duration (one to three days) feasibility test can be performed to evaluate up to eight different remediation technologies. Following an effective feasibility test, the data can be used to prepare life-cycle remediation costs for various technologies. This presentation will walk through the steps of performing an effective feasibility study including: gaining an understanding of the site conceptual model; planning an enhanced test strategy; performing the test with the appropriate equipment and supervision; and summarizing/evaluating the test results to develop a remedial plan. Feasibility testing equipment will be demonstrated at the conference facility.

Improving Well Efficiency to Enhance System Performance

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Maximizing remediation system performance requires optimizing well design, careful drilling method selection, and efficient well development. One must consider how geology impacts well performance and how the drilling method can cause formation damage. The well design and well development method should be selected to maximize the performance of the well for its designated purpose. To improve upon the traditional monitoring well design, consideration should be given to alternative screen design, such as slotted versus continuous slots, coarser sand packs, and more efficient slot sizing. Sand pack thickness is also a factor in determining well development rate: the thicker the sand pack, the more time is required for development. A drilling method should be chosen which least impacts the surrounding formation. Because every drilling method causes some damage to the formation, thus reducing its ability to transmit fluids, one should carefully select the proper drilling procedure and equipment to avoid under-performance and the need for additional well installation and time spent on well development. Various mechanical and/or chemical methods, such as a traditional surge block and eductor pump, can be utilized to mitigate the effects of formation damage. The presentation will discuss factors that impact design, and alternative approaches that have been shown to yield improved well performance and result in more effective remediation.

System Optimization During System Design and Operation to Enhance Conventional Remediation Technologies

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System optimization means more than just keeping remediation systems fully operational. Effective system optimization can subtract years off the remediation system life-cycle, resulting in expedited cleanup programs and significant cost savings. System optimization decisions can be made throughout the project, from remediation system design through the operation and maintenance (O&M) phase.

Design improvements will be discussed, from selecting appropriate equipment, to designing the appropriate flexibility and redundancy in a system to allow for variable operating conditions and improved run time. Other design features to be reviewed involved some of the latest system control features for remote system review/analysis, optimization, and adjustment.

The common steps of system performance evaluation will be discussed, including: identifying capital costs for system upgrades and modifications; determining the degree of system effectiveness; inspecting field O&M data; reviewing mass recovery, contaminant reduction, and O&M costs; and evaluating system run time. Evaluating system performance information is crucial in determining the optimal remediation equipment and instrumentation to utilize, how to improve remediation system up-time, what information should be collected in the field, and how to proactively optimize remediation systems. This presentation will evaluate optimization considerations for conventional remediation technologies (soil vapor extraction, air sparging, total-phase vacuum extraction, and vacuum-enhanced groundwater extraction). Case studies documenting several instances in which system optimization efforts resulted in the remediation of significant soil and groundwater impact in less than two years of system operation will be discussed. Topics of discussion will also include combining remedial technologies to reduce the remedial life-cycle, effective data evaluation to allow for system adjustments, interaction between office and field personnel to ensure optimization, and utilizing visual/modeling tools to help make optimization improvements.

Optimization of Full-Scale Chemical Oxidation Systems to Improve Performance

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Aggressive chemical oxidation technologies that combine liquid oxidants (such as hydrogen peroxide or persulfate) and a gas (such as ozone, oxygen, or air) for aggressive injection in soil and groundwater can be used to address significant source reduction in all contaminant phases (adsorbed, dissolved, and LNAPL). Case studies include remediation of thousands of pounds of contaminant mass, such as BTEX, MTBE, and TBA, in soil and groundwater via the injection of ozone, oxygen, air, and hydrogen peroxide. Aggressive oxidation systems can be optimized using field and analytical data, and system controls, including remote monitoring software. When appropriately applied, some chemical oxidation systems can aggressively remediate contaminated soil and groundwater within a short time frame. The technology can be applied to varying lithologies and at sites with significant contaminant mass. The discussion evaluates all of the processes that may be involved in measuring and enhancing system performance: chemical oxidation; enhanced air sparging; enhanced bioremediation; and soil vapor extraction. The discussion will review the data that should be collected during full-scale system operation and how that information can be used to maximize system performance. The bioremediation effects of chemical oxidation will also be discussed, from dissolved oxygen increases to the increased number of microorganisms in the subsurface.

Legal/Regulatory

A Brownfield Model Collapses Under the Weight of Litigation: City of Wichita v. Trustees of the APCO Oil Corporation Liquidating Trust

Neal H. Weinfield, Greenberg Traurig, LLP, Chicago, IL

Evaluating Data Usability and Representativeness Under the New MCP Guidelines

Susan D. Chapnick, New Environmental Horizons, Inc., Arlington, MA
Ian M. Phillips, Roux Associates, Inc., Burlington, MA
Nancy C. Rothman, New Environmental Horizons, Inc., Skillman, NJ

EPA's New "All Appropriate Inquiry" Standards: When Have You Done Enough?

John G. Nevius, Anderson Kill & Olick, PC, New York, NY

An Overview of DEP's Proposed Asbestos in Soil Regulations and the Implementation of Innovative Asbestos Impacted Soil Remediation Methods

James R. Fair, Weston & Sampson Engineers, Inc., Peabody, MA
George D. Naslas, Weston & Sampson Engineers, Inc., Peabody, MA

Dams and Contaminated Sediments: Regulation, Removal and Liability

Kathy Robb, Hunton & Williams, New York, NY
Andrew Skroback, Hunton & Williams, New York, NY

A Brownfield Model Collapses Under the Weight of Litigation: City of Wichita v. Trustees of the APCO Oil Corporation Liquidating Trust

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This presentation will focus on the City of Wichita's largely failed efforts to collect its response costs for remediating the Gilbert & Mosley Site ("Site"), one of the premier Brownfield redevelopment models. In *City of Wichita v. Trustees of the Apco Oil Corporation Liquidating Trust*, 306 F. Supp. 2d 1040 (D. Kansas 2003), the Court held that if properly used, computer models are invaluable in estimating the size of overlapping contaminant plumes. Both parties used computerized groundwater modeling to determine the plume sizes allegedly migrating from each source, and mathematical computations to allocate orphan shares within the Site. Both parties agreed that where plumes overlapped, the overlapped area should be divided by the number of PRPs whose plumes contributed to the overlap. However, the parties then parted ways. The City proposed two allocation models; the Trustees evaluated six allocation models. The City's groundwater modeling expert modeled parent CVOCs for some sources, and daughter CVOCs for others; the Trustees' expert modeled parent CVOCs for some sources, and daughter CVOCs for others; the Trustees' expert modeled both parent and daughter CVOCs for all sources. The City saddled the last two defendants remaining at trial with the entire orphan share; the trustees argued that they should be saddled with little if any orphan share. Both parties used the same computer model, but inputted different variables. Faced with competing modeling, the Court reasoned that "even in the best of circumstances, a model is only an estimate and the accuracy of the estimate depends to a considerable extent on the data selected for sue in the computer model, the quality and reliability of that data and, of course, the skill of the modeler." Ultimately, the Court rejected the City's modeling base don *Daubert,* holding that "To be reliable, the expert's testimony must be based on the 'methods and procedures of science' and reflect more than the witness'' 'subjective belief or unsupported speculation.'" After examining glaring errors in the City's modeling, the Court rejected the City's methodology because it was not based on any guidelines or standards, but rather on poor quality "professional judgment". The presentation will delve into groundwater modeling, modeling presentation, allocation, *Daubert* principles, and witness creditability.

Evaluating Data Usability and Representativeness Under the New MCP Guidelines.

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In April 2006, the Wave 2 updates to the Massachusetts Contingency Plan (MCP) were promulgated. Within these regulations (subpart K of 40.1056) is the requirement that all Class A, B, or C Response Action Outcomes (RAOs) include a Data Usability Assessment to document that the data used are scientifically valid and defensible and "of a sufficient level of precision, accuracy, and completeness to support the RAO". In addition, an evaluation of Representativeness must be included to demonstrate that adequate, usable data have been collected to represent the nature, extent, and risk from contamination at a Disposal Site. The Massachusetts Department of Environmental Protection (MADEP) formed a workgroup to develop guidance identifying the measures that need to be evaluated and documented in a Data Usability Assessment and Representativeness Evaluation. This presentation will illustrate the application of quantitative (analytical quality control results such as surrogate recoveries and laboratory blank spikes) and qualitative (conceptual site models, site history, etc.) measures that may be used to demonstrate data usability and representativeness. We will discuss the interpretation of the MADEP guidance for different site scenarios and offer recommendations to enhance the generation of data that will be considered both usable and representative to support a RAO.

EPA's New "All Appropriate Inquiry" Standards: When Have You Done Enough?

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No one wants to buy into a Superfund site. However, when buying or investing in property you can never be absolutely certain of what's in the ground. So how do you protect yourself and your clients? What does it take to meet a due diligence requirement? When have you done enough? It just got clearer as this presentation will explain.

The Environmental Protection Agency ("EPA") recently published a Final Rule establishing an "all appropriate inquiry" ("AAI") standard. The rule addresses minimum due diligence for so-called innocent or contiguous landowners as well as *bona fide* prospective purchasers seeking liability protection from the reach of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 ("CERCLA" commonly known as "Superfund"). The AAI Rule will take effect on November 1, 2006, but can be utilized now!

On January 11, 2002, President Bush signed into law the Small Business Amendments Liability Relief and Brownfields Revitalization Act (the "Act"). The Act provides for protection from liability under CERCLA for purchasers of properties ultimately found to be contaminated by Hazardous Substances. To qualify for the Act's protection, prospective purchasers must take reasonably diligent steps, including undertaking "all appropriate inquiry" to determine whether property may be contaminated.

Environmental Professionals hired to undertake all appropriate environmental inquiries must now conduct interviews with a wider range of individuals than they would have had to under the prior American Society of Testing and Materials ("ASTM") "Phase 1" guidelines. They must also undertake a more thorough visual inspection of properties adjoining the subject property, review a broader array of governmental records and expressly acknowledge areas of uncertainty that may have an effect on their conclusions.

The new AAI standards go further than the prior ASTM guidelines and have the advantage of being final EPA Rules promulgated pursuant to federal law. Properly undertaking all appropriate inquiry should go a long way toward alleviating the uncertainty associated with property contamination and potential Superfund liability. Environmental professionals of all stripes would be well-advised to become more familiar with this important new development.

An Overview of DEP's Proposed Asbestos in Soil Regulations and the Implementation of Innovative Asbestos Impacted Soil Remediation Methods

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The Department of Environmental Protection (DEP) is in the process of significantly revising the regulations governing asbestos contaminated soil. We will review the proposed changes to the Air Quality, Solid Waste and the Massachusetts Contingency Plan (MCP) Regulations, and will present examples of innovative remediation methods utilized at large scale Massachusetts asbestos contaminated sites. The presentation will cover current analytical methods for asbestos fibers in soil, and will review options for demonstrating No Significant Risk (NSR) for site closure under the MCP, including the use of Pilot Studies and quantitative risk assessments utilizing the Superfund (Elutriator) Method to measure asbestos in respirable dust. In addition, we will discuss Best Management Practices (BMPs) and a proposed Pilot Study at a local Municipal landfill to assess the use of soil containing low levels of unconsolidated asbestos fibers as landfill grading and shaping material or possibly daily cover.

Dams and Contaminated Sediments: Regulation, Removal and Liability

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There are tens of thousands of dams in the United States, more than 75,000 of which are greater than six feet high. Each of these dams is a potential repository for contaminated sediments from upstream sources that are washed into the waterbody it spans. These contaminants can include everything from pesticides to heavy metals to polychlorinated biphenyls ("PCBs"). An estimated eighty-five percent of the Nation's dams will be over 50 years old by 2020. As these dams age, and as pressure mounts to remove dams from the Nation's rivers, more and more regulatory attention will be paid to the contaminated sediments gathering behind them and to the potential liabilities associated with them.

The proposed article, "Dams and Contaminated Sediments: Regulation, Removal and Liability," would examine the sources of potential liability and its application to a variety of parties, including dam owners and operators, abutting property owners, and up-stream dischargers. The scope and application of liabilities associated with the contaminated sediments impounding behind the Nation's dams is not clear. Accordingly, the article will provide guidance on a number of questions, including:

- When are dam owners liable for the contaminated sediments gathering behind their dams?
- Are dam owners or operators – current and past – liable for releases of contaminated sediments through normal dam operation, including drawdowns that resulted in re-release of sediments gathered behind their dams?
- Who is responsible if a dam fails?
- What are the potential statutory and common law bases of liability?
- Does the Clean Water Act regulate discharge of water through dams?
- Are municipalities or other government agencies protected from liability through sovereign immunity?
- What liabilities do dischargers face for contaminants released upstream and now settled out in the sediments located behind the dams? Can this include POTWs?
- Can the liability protections adopted in the Brownfields Revitalization and Environmental Restoration Act of 2001 limit liabilities related to sediments gathering behind dams?
- How does the Endangered Species Act affect the fate of the Nation's aging dams?

Natural Resource Damage Assessments: Integrating Remediation and Restoration

Overview of Integrated Natural Resource Damage Assessment Process
Jen Lawton, ENVIRON International Corporation, Burton, OH
Tim Barber, ENVIRON International Corporation, Burton, OH
Mark Travers, ENVIRON International Corporation, Burton, OH

NOAA's Approach to Cooperatively Resolving Natural Resource Liability
Kenneth Finkelstein, National Oceanic and Atmospheric Administration, Boston, MA

Myths, Incentives and Challenges of Natural Resource Damage Assessments: A State Trustee Perspective
Dale C. Young, Massachusetts Executive Office of Environmental Affairs, Boston, MA

Natural Resource Damage Assessment: Lessons Learned from a Legal Perspective
Michael Daneker, Arnold & Porter, LLP, Washington, DC

Estimation of Natural Resource Damages for 23 Florida Cases Using Modeling of Physical Fates and Biological Injuries
Jill Rowe, Applied Science Associates, Inc., Narragansett, RI
Deborah French McCay, Applied Science Associates, Inc., Narragansett, RI
Nicole Whittier, Applied Science Associates, Inc., Narragansett, RI

Application of a Restoration Inventory to Natural Resource Damage Assessments
Sarah C. Watts, Northern Ecological Associates, Inc., Portland, ME
David J. Santillo, Northern Ecological Associates, Inc., Portland, ME
Derek Pelletier, ENVIRON International Corporation, Portland, ME
Miranda Henning, ENVIRON International Corporation, Portland, ME

Using DOJ's Database of Natural Resource Damage Settlements to Look Forwards and Backwards
Tim Barber, ENVIRON International Corporation, Burton, OH
Jen Lawton, ENVIRON International Corporation, Burton, OH

Overview of Integrated Natural Resource Damage Assessment Process

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Natural Resource Damage Assessment (NRDA) is a process to determine the appropriate amount and type of restoration needed to compensate the public for losses following the releases of hazardous substances. The NRDA process is most commonly performed under the authority of the Clean Water Act, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) as amended by the SARA, and/or Oil Pollution Act. Federal, state, and tribal natural resource trustees must use natural resource damage recoveries to restore, rehabilitate, replace, and/or acquire the equivalent of injured natural resources and services. The relationship of NRDA to CERCLA response and remediation activities has historically been somewhat disjointed. Agencies and stakeholders are required to coordinate, but not necessarily integrate activities where possible. This presentation will provide an overview of the NRDA process, federal statutes and regulations, and limitations.

NOAA's Approach to Cooperatively Resolving Natural Resource Liability

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NOAA's Office of Response and Restoration (OR&R) acts as a federal natural resource trustee whose principal mission is to protect and restore natural resources by countering and responding to environmental threats and promoting sound decision-making in the coastal zone. The integration of remedial and restoration investigations, planning, and activities is a successful paradigm for achieving restoration-based settlements. Because NOAA places a technical liaison respectively within or nearby federal and state remedial decision-makers, we effectively work to integrate the remedial and damage assessment process to protect natural resources, to reduce or eliminate residual natural resource injuries after cleanup, and to achieve restoration as part of a cooperative natural resource injury settlement with responsible parties.

There are two primary paths within OR&R that can lead to the resolution of natural resource damage liability under CERCLA; 1) a cooperative and integrated approach to remediation and restoration leading to a negotiated comprehensive settlement, the results of which are often included in the Consent Decree or 2) a formal damage assessment to assess injury that uses the codified regulations under 43 CFR Part 11. Both processes result in a Restoration Plan but the former provides the benefits of flexibility, speed, and cost efficiency. Nevertheless, the latter may be necessary when: 1) the responsible party is not cooperative, 2) there is a potential for large-scale economic and biological injury, or 3) the remedial action does not address significant natural resource injury. A similar approach is available at oil spills whereby the responsible party is invited to engage in natural resource injury assessment and restoration efforts under Trustee oversight.

The cooperative integrated remediation/restoration approach is characterized by 1) an integrated and streamlined process for data assembly to support planning for remediation and restoration, 2) development of protective cleanup strategies to minimize residual injury and enhance recovery of coastal areas, 3) injury assessment, restoration planning and scaling, 4) the negotiated release of natural resource liability through a Covenant Not To Sue, and 5) implementation and monitoring of restoration.

Cooperative comprehensive or universal settlements to resolve both cleanup and natural resource liability under CERCLA are becoming more common around the country. This presentation will include a discussion of such settlements in Connecticut, Rhode Island, and Massachusetts.

Myths, Incentives and Challenges of Natural Resource Damage Assessments: A State Trustee Perspective

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Pursuant to Federal Superfund (CERCLA), the Oil Pollution Act, and various state statutory authorities, Natural Resource Trustees are authorized to conduct Natural Resource Damage (NRD) Assessments and seek restoration of natural resources injured by releases of hazardous substances and discharges of oil. Trustees seek to identify the natural resources injured, determine the extent of injuries, recover damages from those responsible, and plan and carry out natural resource restoration activities. The ultimate goal is to restore natural resources injured by contamination. Cooperative NRD Assessments involving Responsible Parties, Trustees, and the remedial agencies, can be an efficient and effective approach to achieving restoration and resolving liability at sites. Benefits include innovative approaches to the NRD process, coordination of site remediation with restoration, and strengthened partnerships with industry and other stakeholders.

This presentation will discuss State perspectives on NRD issues, highlight NRD case settlements and program goals for Massachusetts, and explore the various “Myths, Incentives and Challenges" in achieving timely NRD restoration. Members of the NRD community including Trustees, Industry, and NGOs will gain a better understanding of the structure, challenges, and benefits involved in NRD.

Natural Resource Damage Assessment: Lessons Learned from a Legal Perspective

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Over the last 25 years, the natural resource damage (NRD) regulations and assessment strategies have evolved towards a cooperative approach that attempts to integrate remediation and restoration considerations. This presentation will discuss key legal issues associated with existing NRD regulations and the trend towards cooperative assessments. Additionally, this presentation will provide an overview of current trends such as the integration of remediation and restoration early in the CERCLA process, the state of New Jersey's NRD initiative, and the trustees' pursuit of damages at RCRA corrective action sites.

Estimation of Natural Resource Damages for 23 Florida Cases Using Modeling of Physical Fates and Biological Injuries

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Oil spill modeling was performed using the “type A” (simplified, with a minimum of field data requirements) modeling approach and SIMAP (Spill Impact Model Analysis Package) to assess marine biological injuries and natural resource damages (NRD) for 23 spill cases identified by Florida Department of Environmental Protection (DEP). The objectives were to provide (1) an assessment of the pathways and fate of the oil, and thus, estimate exposure to the water surface, shoreline and other habitats, water column, and sediments; and (2) estimates of injuries to wildlife, aquatic organisms, and habitats that were used to scale compensatory restoration. Compensatory habitat restoration for all quantifiable wildlife, fish and invertebrate injuries was scaled using Habitat Equivalency Analysis (HEA) and wetland habitat creation as mitigation. However, this is not a direct method of increasing sea turtle production. Therefore, scaling was performed to estimate the number of hatchlings needed to compensate for the sea turtle injuries. DEP then successfully submitted claims for NRD to the US Coast Guard Oil Pollution Fund.

Application of a Restoration Inventory to Natural Resource Damage Assessments

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A field-based inventory developed for the purpose of evaluating and documenting potential restoration opportunities was adapted to use in expedited Natural Resource Damage settlements. The outcome – an inventory of restoration projects with their associated resource service values – is well-suited to states with multiple smaller Natural Resource Damage claims. Background data collection provides useful information to assist in identifying potential wetland areas in need of restoration, but in-field evaluations are critical to ensure that all sites are identified and adequately documented. The interactive database allows exploration and expansion of the inventory, which is based on baseline field data, site restoration potential, screening and ranking criteria, and resource service levels, expressed as discounted service acre years (DSAYs). For any identified site, users can print out a summary report that provides detailed information regarding the environmental degradation observed on site, the severity of degradation, options for restoration, project cost, a list of project strengths and barriers to success, as well as information on land ownership, site location, and surrounding land uses. Thus, when responsible parties and Trustees are considering settlement options for a given Natural Resource Damage claim, the full range of restoration opportunities within that site's watershed, as well as their associated DSAY values, can be considered in order to more rapidly identify the most effective settlement. To date, the inventory details potential restoration opportunities along 150 miles of rivers, streams, and estuaries in four watersheds in coastal Maine, and more than 480 sites in need of restoration have been identified.

Using DOJ's Database of Natural Resource Damage Settlements to Look Forwards and Backwards

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Since 1982, more than 230 settlements for natural resource damages (NRD) have been reached at sites throughout the United States. The Department of Justice has recovered in excess of $3.35 billion from private and public entities. This total is likely to rise significantly in the near future as state, federal, and tribal trustees pursue NRD claims at hundreds of additional sites. Settlements can include primary and compensatory restoration and reasonable assessment costs; damages associated with compensatory restoration to address interim lost services generally are the largest share of the totals. Settlement costs have varied dramatically depending on a number of factors, including site size and location, chemicals of interest, affected resources, and the responsible industry. The large number of documented settlements provides an opportunity to predict the cost range of similar NRD cases for verification purposes. Coupling a nationwide settlement database with multivariate statistical methods allows the prediction of future settlement costs associated with NRD claims. This presentation will provide an overview of the NRD settlements database including structure and variables that can be used in the analysis. Statistical methods will be developed to predict a range and "most likely" NRD cost estimate based on the historical settlements.

Oxygenate Biodegradation

To Degrade or Not To Degrade: Isotopic and Microcosm Evidence for Anaerobic Biodegradation of TBA
Eric M. Nichols, LFR Inc., Braintree, MA

The Utility of Stable Isotope Analysis: Lessons Learned from Numerous Practical Applications to the Management of Fuel Oxygenate Contamination
Joseph E. Haas II, New York State Department of Environmental Conservation, Stony Brook, NY

Biodegradation of *Tert*-Butyl Alcohol by Mixed Culture *KR1*
Kimberly M. Reinauer, University of Illinois- Urbana Champaign, Urbana, IL
Xiaomin Yang, Atlantic Richfield Company, BP, Warrenville, IL
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U.S. Operating Experience with Biologically-Active GAC Systems for MTBE and TBA Treatment
Tatsuji Ebihara, LFR Inc., Elgin, IL

Ex Situ Bioreactor Treatment of Tertiary Butyl Alcohol at a New Hampshire Site
Joseph E. O'Connell, Environmental Resolutions, Inc., Lake Forest, CA

Pulsed Air Sparging for MTBE and TBA Source Zone Remediation
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The Utility of Stable Isotope Analysis: Lessons Learned from Numerous Practical Applications to the Management of Fuel Oxygenate Contamination

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The analysis of the ratios of the stable isotopes of carbon and the ratios of the stable isotopes hydrogen has gained creditability as a tool to assess and or to quantity the potential role of biodegradation at sites contaminated with fuel oxygenates such as Methyl Tertiary Butyl Ether (MTBE). The utility of such analysis to the management of such contamination is a function of many factors not the least of which are the cost and availability of analytical services, the reliability of the data and the usefulness of the data in revealing and or supporting the appropriate the role of biodegradation as a practical component of the overall management of the contamination.

Stable isotope data has recently been acquired and the analysis applied to the management of fuel oxygenates contamination at a number of well-characterized sites in Long Island New York. The stable isotope work was undertaken in conjunction with the management decision-making for the sites in which biodegradation was likely to be a component of varying importance. The importance of the analysis of the stable isotope data with respect to the management of the contamination ranged from a low of supplying an additional line of evidence of the functionality of biodegradation to a high of being the basis of the quantification of the biodegradation rate needed as a key component of a monitored natural attenuation strategy.

The methods and utility of the application of the analysis to the management of each site is detailed including information on the development of sampling plans, the cost and availability of analytical services, the reliability of the data and the usefulness of that data with respect to the role of biodegradation as a practical component of the overall management of the contamination.

Biodegradation of *Tert*-Butyl Alcohol by Mixed Culture *KR1*

STUDENT PRESENTER

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Tert-butyl alcohol (TBA), a metabolite of methyl *tert*-butyl ether (MTBE) and a fuel oxygenate, is often considered recalcitrant in contaminated groundwater and a rate limiting step in MTBE degradation. TBA is miscible in water; it is difficult to treat with traditional air sparging or adsorption techniques. Biofilms that form on granular activated carbon (GAC) units can degrade TBA. The goal of this work was to optimize TBA degradation in a Bio-GAC reactor as part of a pump and treat system for contaminated groundwater.

A mixed culture, *KR1*, was enriched from a GAC sample in a bicarbonate-buffered freshwater media. Transfers over a one month period enriched a culture that degrades TBA under growth conditions as the sole carbon and energy source and is physiologically different than other cultures enriched from the same GAC material. TBA was degraded to 10% of the initial concentration (2mM) within 5 days after initial inoculation and continuously degrades within 1 day of re-amendment. Resting cell suspensions mineralized 70% of the TBA within 12 hours. Mineralization data suggest that transformation will not stop at intermediate metabolites but rather continue to innocuous end products. Performance optimization with resting cells was conducted to investigate kinetics and extent of TBA degradation as influenced by oxygen, pH and temperature. Culture longevity was investigated, and cultures starved for periods of 7, 14, and 21 days were able to degrade TBA, indicating that the culture will recover after periods of no TBA loading.

Current work focuses on isolating a pure culture from the enrichment that effectively degrades TBA. A packed bed GAC reactor will be developed using KR1, or isolate, as an inoculum for continuous treatment of low concentration TBA. This work will investigate inoculation strategies, oxygen delivery and substrate interactions, which will then be extrapolated to a full-scale pump and treat system.

U.S. Operating Experience with Biologically-Active GAC Systems for MTBE and TBA Treatment

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Ten field applications of biologically-active granular activated carbon (BioGAC) systems were evaluated for the purpose of developing operating guidelines for reliable *ex situ* treatment of oxygenate-impacted groundwater. Average flow rates of these systems ranged from 1 to 65 gallons per minute (gpm). Average influent methyl tertiary-butyl ether (MTBE) concentrations ranged from 0.003 to 3.7 mg/L and average tertiary-butyl alcohol (TBA) concentrations ranged from 0.016 to 2.5 mg/L. These systems reliably achieved non-detectable effluent concentrations of petroleum hydrocarbons and ethers, and less than 30 to 40 µg/L TBA. In some cases high influent organic concentrations led to transient oxygen limitation conditions and temporarily elevated TBA concentrations in the effluent of the first or second stage of the BioGAC process. Despite these transient conditions, the effluent of the final stage of the BioGAC process achieved less than 30 to 40 µg/L TBA. The most critical parameter for proper operation of BioGAC systems was the maintenance of dissolved oxygen (DO) conditions within the lead BioGAC bed and subsequent GAC beds in series.

Pulsed Air Sparging for MTBE and TBA Source Zone Remediation

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The effectiveness of pulsed air sparging on MTBE and TBA removal from source area was investigated in a pilot scale study. The results suggested that pulsed air sparging is a viable, cost effective technology to remediate MTBE and TBA contaminated soil and groundwater. The data collected also provide reliable engineering design basis of a pulsed air sparging system to treat MTBE/TBA in soil and groundwater. Numerous parameters were monitored to evaluate the groundwater MTBE and TBA reduction rates and to understand the removal mechanisms – volatilization vs. aerobic biodegradation. The MTBE first order reduction rate constants ranged from 0.04 per day to 0.06 per day in the MTBE source area while the benzene reduction rate constants varied from 0.04 per day to 0.07 per day. The effectiveness of pulsed air sparging on benzene and MTBE treatment was approximately equal. MTBE at more than 10 ppmv level was also detected in the soil vapor collected from the headspace of groundwater monitoring points, indicating material contribution of MTBE volatilization to the total MTBE removal. As an intermediate product of MTBE aerobic biodegradation, TBA accumulated in groundwater in the first six months of the pulsed air sparging operation. MTBE carbon and hydrogen stable isotope ratio analysis was also conducted to verify the MTBE aerobic biodegradation. TBA concentration started to decrease after six months of air sparging, and its reduction rates were between 0.05 per day to 0.08 per day, and TBA aerobic biodegradation is the dominating mechanism of TBA removal. In addition, the field observations suggested that the pulsed operation dramatically eased, if not eliminated, the groundwater depletion created injecting air into subsurface, thus mitigating the risk of groundwater spread and alleviating MTBE rebound potential. We believe that this is the set of field supporting this speculation.

Oxygenates and Public Water Supplies

Volatile Organic Compounds in the Nation's Ground Water and Drinking-Water Supply Wells
Mike Moran, U.S. Geological Survey, Rapid City, SD

NH MTBE in Drinking Water Supplies Statewide Survey
Joe Ayotte, USGS, Pembroke, NH

Time Trend Analysis of MtBE Detections in Public Water Systems in Connecticut
Maureen C. Leahy, Environmental Resources Management, East Hartford, CT

Control and Closure of a Rapidly Moving and Diving MTBE/Benzene Plume in a Public Water Supply Area
Michael L. Scherer, Massachusetts Department of Environmental Protection, Springfield, MA

PM-1 and Beyond: Assessment of MTBE Biodegradation to Support Re-Injection into Drinking Water Aquifer
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Jeffrey M. Baker, Tesoro Petroleum Companies, Inc., Auburn, WA
Kristin Hicks, UC-Davis, Davis, CA
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Volatile Organic Compounds in the Nation's Ground Water and Drinking-Water Supply Wells

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Personnel from the National Water-Quality Assessment (NAWQA) Program of the United States Geological Survey (USGS) completed a national assessment of the occurrence of 55 volatile organic compounds (VOCs) in 98 aquifers across the United States used as important supplies of drinking water. The occurrence of VOCs in samples of ground water collected prior to treatment or blending from domestic and public wells also was included. VOCs were detected in aquifers across the Nation indicating the importance of monitoring the occurrence and trends of VOCs in ground-water resources. Monitoring of VOCs was performed at low analytical levels in order to fully characterize VOC occurrence. Twenty-four VOCs warrant further monitoring in ground water resources because they were detected relatively frequently or because they had concentrations greater than, or approaching, Maximum Contaminant Levels (MCLs). In-depth studies on VOC occurrence in aquifers ultimately could focus on these compounds. Thirteen VOCs were not detected in any aquifer samples and may not warrant further monitoring in ground water resources. The detection frequencies of most VOCs were higher in public well samples than domestic well samples. Less than two percent of samples from domestic or public wells had a VOC concentration of potential human-health concern. Further studies should investigate the source and transport of VOCs to wells that have VOC concentrations exceeding, or close to, concentrations of potential human-health concern. Chloroform was the most frequently detected VOC in aquifers and chlorination of drinking water may be an important source of chloroform in ground water. Methyl *tert*-butyl ether (MTBE), a gasoline additive, also was one of the most frequently detected VOCs despite its relatively short and recent period of use. Solvents like PCE and TCE also were frequently detected in ground water and were among the VOCs that most frequently had concentrations greater than MCLs. Some factors important to the occurrence of VOCs in aquifers included urban land use, septic systems, wet and dry climates, and dissolved oxygen. The natural and anthropogenic factors that explain the occurrence of a specific VOC in a particular aquifer need to be understood to effectively manage and protect aquifers.

Time Trend Analysis of MtBE Detections in Public Water Systems in Connecticut

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Methyl-*tert*-butyl ether (MtBE) was first reported detected in groundwater in Connecticut in 1987. By February 2000, Connecticut Department of Environmental Protection reported that MtBE had been detected in 4 public water supply wells at concentrations exceeding the State Advisory Level of 70 micrograms per liter (ug/L) and at trace levels in 51 other Public Water Systems (PWS). In response to the issue of MtBE in groundwater, Connecticut passed legislation in July 2000 to ban the sale and use of MtBE in gasoline. The ban became effective on 1 January 2004. Time trend analyses were conducted on monitoring data published by CTDEP to assess the overall effect of the ban on the detection of MtBE in PWS. Prior to the MtBE ban between 2000 and 2003, 208 PWS in Connecticut had reported the detection of MtBE at least once. Most of these PWS only reported the detection of MtBE in one reporting year with 60 to 114 PWS reporting MtBE detections annually. The majority of these detections were less than 3 ug/L and less than 20 of the PWS had reported the detection of MtBE above the State Action Limit. In the first reporting year after the MtBE ban in 2004,104 PWS reported MtBE detections. One year later, however, in 2005, the number of PWS reporting MtBE detections dropped to 54. Of the PWS that reported MtBE for the first time after the ban, only 5 PWS in 2004 and 1 PWS in 2005 reported the detection of MtBE at a concentration greater than the State Advisory Level. These data indicate a significant decrease in the frequency and magnitude of MtBE detections in Connecticut's groundwater within two years after the ban.

PM-1 and Beyond: Assessment of MTBE Biodegradation to Support Re-Injection into Drinking Water Aquifer

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This presentation will discuss the regulatory acceptance of a precedent-setting MTBE cleanup program involving re-injection of biologically treated groundwater into an important drinking water aquifer. The Former Fast Fuel Facility project in North Hollywood, California will be presented as a case study. Significant microbial analysis of the degradation potential of the aquifer have been performed by the University of California at Davis to support this project. These microbial evaluations and the role they played in gaining the regulatory acceptance for the overall remediation program will be highlighted.

The Former Fast Fuel Facility project exhibits successful treatment of a MTBE groundwater plume with a combination of ex-situ biological treatment and re-injection of treated groundwater back into the aquifer. This site presented significant challenges including: >10 mg/L MTBE in groundwater at over 200 feet below ground surface, high permeability aquifer with dynamic flow conditions, a disconnected plume located beneath a densely populated/developed residential neighborhood, over 70 water supply wells within a 1-1/2 mile radius of the site, and a plume traveling toward the closest municipal supply wells (less than 1,000 feet away) at a rate of approximately 100 feet per year.

The specifics of the ex-situ biological system will be discussed, focusing on the self-seeding of the treatment beds by the bacterial population naturally present in site groundwater. UC-Davis provided significant support to the project team by assessing the MTBE-degrading characteristics of the indigenous microbial population both in-situ and within the ex-situ treatment beds. Significant scientific advances were attained during the study that evaluated the adaptations of the microbes to the ex-situ environment and the improvement of the MTBE-degrading kinetics.

Ozone Remedial Barrier and Clean-up Systems for Fuel and Solvent Spills

Ozone, Hydrogen Peroxide, and Air Injection Systems for Aggressive Remediation
Charles B. Whisman, Groundwater & Environmental Services, Inc., Exton, PA

An Innovative Approach to Protecting a Municipal Supply Well - Air/Ozone Sparge Curtain Results
Kent Zenobia, URS Corporation, Sacramento, CA
Ed Tarter, URS Corporation, Sacramento, CA
Vern Elarth, URS Corporation, Sacramento, CA
Nicole Damin, Stanislaus County Department of Environmental Resources, Modesto, CA

Superoxidation Ozone Systems for Aquifer Restoration – A Michigan State Superfund Site
Andrew Brolowski, Kerfoot Technologies, Inc., Mashpee, MA
William B. Kerfoot, Kerfoot Technologies, Inc., Mashpee, MA

Ozone Oxidation for Source Removal and a Prevention Barrier at a Fire Training Academy
Thomas C. Cambareri, Cape Cod Commission, Barnstable, MA
Scott Michaud, Cape Cod Commission, Barnstable, MA

Successful Closure of an Industrial Site Adjacent to an Ohio Municipal Wellfield
William B. Kerfoot, Kerfoot Technologies, Inc., Mashpee, MA
Bruce E. Ehleringer, Washington Group International, Inc., Cleveland, OH
John Muncy, REM Investments, Enon, OH

In Situ Chemical Oxidation of Manufactured Gas Plant (MGP) using Ozone
Jeffrey C. Dey, The Resource Companies, Moorestown, NJ
Imtiyaz Kahn, The Resource Companies, Moorestown, NJ

Ozone, Hydrogen Peroxide, and Air Injection Systems for Aggressive Remediation

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Providing cost-effective and aggressive remediation solutions to sites impacted with BTEX, MTBE, and TBA compounds can be a great challenge. Innovative ozone, hydrogen peroxide, and air injection systems have been shown to remediate BTEX, MTBE, and TBA impact at costs significantly below conventional methods and within a comparatively short time frame. The technology results in three chemical oxidation species to aggressively remediate contaminated soil and water: ozone, hydrogen peroxide, and hydroxyl radicals. The technology can be applied to varying lithologies and at sites with significant contaminant mass. Proper application of this technology can result in effective in-situ remediation of dissolved, adsorbed, and separate phase hydrocarbons. Various ways to implement ozone, hydrogen peroxide, and air injection systems will be presented, including full-scale (24/7 operation) and short-term applications (weekly injection events). The discussion will also evaluate costs associated with these different options and compare them to conventional remedial technologies. Case studies will be presented where thousands of pounds of contaminant mass were remediated with the process.

An Innovative Approach to Protecting a Municipal Supply Well — Air/Ozone Sparge Curtain Results

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Petroleum contaminants released from a retail gasoline station in a California Central Valley town threatened a municipal supply well (muni well) immediately adjacent to the station. Methyl *tert*-butyl ether (MtBE) was present in groundwater at concentrations up to 30,000 micrograms per liter (μg/L) in the first encountered groundwater aquifer, between 30 to 45 feet below ground surface (bgs). The muni well is located approximately 200 feet downgradient from the source area. Quarterly groundwater monitoring results indicated MtBE had migrated off site, and remedial action would be required to protect the downgradient muni well. The project team designed an innovative remediation system comprising an aggressive source area treatment with soil vapor extraction (SVE) for impacted vadose zone soils and a downgradient *in situ* treatment barrier at the property boundary.

The *in situ* treatment barrier includes air/ozone sparge wells placed downgradient of the source area and upgradient of the municipal supply well. The barrier is intended to reduce/destroy the MtBE concentrations and other residual gasoline-range organic (GRO) contamination. The perimeter *in situ* treatment barrier—sparge curtain—comprises dual-completion air/ozone sparge points co-located in the aquifer's deeper and shallow portions.

URS developed a pilot test protocol for this process and agreed to share results with the Regulatory Agency prior to full system operation. Test results showed monitoring well MtBE concentrations were 780 μg/L initially, 50 μg/L after 8 days, and 1.5 μg/L after 35 days. Tertiary compounds were not generated. The pilot test protocol included employing a downhole video camera to record the intercept on the monitoring well from the sparge point locations. Contaminant concentrations in wells downgradient have shown further improvement and the system continues to protect the muni well. The site is currently in monitoring status, and installation of new confirmation soil borings is scheduled so final closure can be requested.

Superoxidation Ozone Systems for Aquifer Restoration – A Michigan State Superfund Site

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The term "superoxidation" refers to the combination of oxidative gases and liquids in such a manner as to maintain high oxidative states despite rapid reduction of target organics. Coatings of peroxides and perates on ozone microbubbles can continuously generate hydroxyl, perhydroxyl radicals, and persulfate. With fine microbubbles volatile organics are drawn into the gas bubbles, reacting with the hydroxyl radicals. The variety of organics which can be treated is substantially broadened over normal ozone to include alkanes, ethers, aromatics, and polyaromatics (PAHs). Even though the PAHs are poorly soluble semi-volatile compounds, the reactions with these compounds generate acetone and alcohols which serve to increase their solubility and reactivity. Although easy to isolate in the laboratory, monitoring during field remediation has shown low or nondetectable acetone or alcohol presence. This occurs because of reactivity with excess ozone and likely bacteriological activity.

An example of "super-oxidation" involves the case study of the former Thomas Solvents Company site, Ypsilanti Township, a Michigan Department of Environmental Quality (MDEQ) remediation cleanup which began in January, 2004. With treatment area soil consisting primarily of fine to medium and coarse sand, the remediation system was designed with ozone gas with a peroxide coating (Perozone™) to treat the following wide variety of source area and outlying organic ground water contamination exceeding applicable regulatory cleanup standards: ketones (including acetone and butanone), chloroethanes (CE, MC, CTC, and TCA), chloroethenes (PCE, TCE, DCE, and VC), and aromatics (BTEX, isopropylbenzene, trimethylbenzene, butylbenzenes, naphthalenes). Following 24 months of operation, with source area dissolved ground water total VOCs ranging in average above 20,000 ppb, total VOC ground water mass had been reduced greater than 93%.

Ozone Oxidation for Source Removal and a Prevention Barrier at a Fire Training Academy

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The Barnstable Fire Training Academy is a multi-plume site resulting from chronic releases of petroleum hydrocarbons during simulated fire-fighting conditions over several decades as an "industrial/commercial" use in a Zone II public water-supply area. Use of petroleum at the site was ceased in 1986. Multiple source removals were conducted over the last 20 years. A pump and treat containment system was successful in reducing the down-gradient extent of petroleum, a release of MTBE from a leaking gasoline tank and a chloroform plume from another up-gradient site. Although contamination migrating down-gradient of the site does not present an imminent threat or substantial hazard to public health due to natural attenuation, the smear zone continues to release slugs of contamination to groundwater. The site is located in a highly permeable aquifer suitable for an air-sparging system. The Kerfoot Technologies "C-Sparge/Perozone™" system was selected as the preferred remedy to treat the residual smear zone. The system consists of 12 sparge points capable of delivering air/ozone and peroxide to the smear zones and was configured with a secondary purpose of forming a barrier against unforeseeable events related to on-going training activities. Sparge points are duel-stacked in source/smear-zone areas in recognition that deep sparge points treat a wider lateral area, while the shallow sparge points concentrate treatment close to the source. The system was brought on line in April 2006 and continuous peroxide injection commenced in June 2006 following monitoring, repairs, adjustments and optimization of the system. Sparge times for each well are set to optimize the duration of ozone/air and peroxide delivery to each well. Initial results indicate a range of groundwater dissolved-oxygen concentrations around each sparge well up to supersaturated conditions. Concentrations of BTEX, naphthalene and associated volatile organics in groundwater samples collected in June 2006 remain within concentration ranges observed since 2002-3. Additional groundwater samples scheduled to be collected in August 2006 will provide further opportunity to evaluate system performance.

Successful Closure of an Industrial Site Adjacent to an Ohio Municipal Wellfield

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Ozone sparging using the KTI C-Sparge™ process was performed on an industrial site adjacent to a major water supply well site. Ozone sparging was initiated in February, 2000, and groundwater volatile organic compound (VOC) concentrations in downgradient wells decreased as much as 95% by the end of 2001. From 2003 to closure in 2006, the responsible party continued treatment with monitored attenuation and combined source treatment with a barrier region rather than more aggressively attack plant source areas. There were three reasons: 1) initial treatment showed reductions to near MCLs at the well site and boundary, and reductions were continuing; 2) monitoring costs were projected to closure at substantially less than addition of capital equipment; and 3) the current plant owner was separate from the responsible party, so access was limited, and interruption of work unacceptable.

The site geology consisted of a fluvial sand and gravel aquifer with discontinuous silt lenses, where near surface caused perched water conditions. Initial remedial actions included source excavation (1996), a Fenton's Reagent flood (1998), followed by ozone sparging.

The regulatory agency accepted ozone sparging for source treatment and temporary barrier as the most desirable alternative. Monitored attenuation was not acceptable without source reduction and elimination. Continued operation of the facility progressed during remedial treatment. Closure was obtained with the region achieving MCLs at the operational water supply wells and on the industrial site boundary. Final groundwater removal was in excess of 99%. No adverse water quality impacts were found during treatment at the water supply wellheads.

In Situ Chemical Oxidation of Manufactured Gas Plant (MGP) using Ozone

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A comprehensive pilot-scale field test of in situ chemical oxidation with ozone as a potential in situ remedial approach for Manufactured Gas Production (MGP) related contamination was conducted at an MGP site in the Northeastern United States.

The targeted treatment area occupies 2500 sq. feet, located 10 to 15 feet below grade. Residual MGP impact in subsurface soil and groundwater at the site included coal tar, coal fragments, Non Aqueous Phase Liquid (NAPL), TPH-DRO including elevated concentrations of polynuclear aromatic hydrocarbons (PAHs), and TPH-GRO with elevated concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX).

Injection activities were conducted for 90 days. Baseline, mid-treatment, and post treatment soil and groundwater sampling and analysis were completed as part of the pilot study. Post treatment sampling and analysis was conducted immediately after the completion of ozone injection and also 30 days after cessation. In monitoring well MW-103 (located within targeted area), a comparison of post test groundwater analytical results with the baseline analytical results indicated a reduction of total BTEX concentrations by 95% (from 10.99 to 0.56 ppm), total PAHs concentrations by 92% (from 7.93 to 0.62 ppm), TPH-DRO concentrations by 55% (from 20 to 9.0 ppm) and TPH-GRO concentrations by 93% (from 25 to 1.8 ppm).

Comparisons of soil sampling analytical results with the baseline analytical results were varied. The post test soil results (samples taken 30 days after cessation of ozone treatment) indicated that BTEX concentrations increased by 8% (an increase from 93 to 101 mg/kg) in samples collected from 10 to 15 ft depth, but show reduction of BTEX concentrations by 7% (from 145 to 134 mg/kg) in samples when depth varies, PAHs concentrations were reduced by 38% (from 4,069 to 2,531 mg/kg), C-PAHs concentrations were reduced by 39% (from 417 to 253 ppm), TPH-DRO concentrations were reduced by 22% (from 6,329 to 4,910 ppm), and TPH-GRO concentrations were reduced by 81% (from 922 to 179 ppm). The observed increase in BTEX concentration is due to abnormal variation of BTEX concentrations observed in preliminary samples. The SVE data indicated a total vapor phase VOC mass recovery of 78.94 lbs, and an average recovery rate of 0.021 lbs/hr.

Destruction of COCs within the test area indicated the viability of using ozone as a feasible approach to remediation of the MGP related COCs. However, as the post–remediation soil data suggests treatment activities should be conducted for a period greater than 90 days.

Perchlorate

Distinguishing Natural from Anthropogenic Perchlorate

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Column Studies on Perchlorate Reduction by Autotrophic Bacteria in the Presence of Zero-Valent Iron

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Perchlorate Reduction in a Packed Bed Bioreactor Using Elemental Sulfur

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Demonstration of Active and Semi-Passive Approaches to *In Situ* Bioremediation of Perchlorate in Groundwater

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Removal of Perchlorate from Drinking Water and Ion Exchange Regenerant Brines

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Lessons Learned for Future Designs from Thermal Treatment of Perchlorate in Soil

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Distinguishing Natural from Anthropogenic Perchlorate

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Until recently, it was assumed that all of the reported groundwater impacts from perchlorate resulted from historical disposal practices by the military, the aerospace and ordnance industries, and perchlorate manufacturers. However, new evidence suggests that Chilean nitrate fertilizer and natural mineral sources in the United States may also contribute to groundwater and drinking water contamination. The overall extent to which *natural* sources add to groundwater pollution is unknown, but there are numerous perchlorate plumes for which military or industrial sources are unlikely, and natural sources are suspected. Stable isotope ratio analysis has been widely used to document the origin and geochemical behavior of both organic and inorganic pollutants. Recently, isotopic methodologies have also been developed for perchlorate, and these techniques have been used to analyze a wide variety of man-made and natural perchlorate sources. The isotopic signatures of chlorine (^{37}Cl: ^{35}Cl) and oxygen (^{18}O: ^{16}O) in these materials have been observed to differ significantly between naturally-occurring and anthropogenic perchlorate. In addition, the natural perchlorate analyzed to date is characterized by a positive Δ^{17}O, which is not observed for any of the man-made material. A sampling procedure utilizing custom ion exchange columns has been developed to collect adequate quantities of perchlorate for isotopic analysis (i.e., 5 - 10 mg) from dilute groundwater plumes. Sampling is currently underway at several locations for which perchlorate origin is unknown. In combination with other key hydrogeological and geochemical parameters, stable isotope analysis is expected to provide critical evidence for perchlorate origin in groundwater. An overview of stable isotope analysis and its application for perchlorate forensics will be provided.

Column Studies on Perchlorate Reduction by Autotrophic Bacteria in the Presence of Zero-Valent Iron

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Recently, the presence of perchlorate contaminated ground water has been a rising concern in the USA. To treat perchlorate contaminated ground water, bioremediation is the preferred strategy as ClO_4^- is converted to chloride and eliminated from the environment. H_2 is the favored energy source for the perchlorate reducing microorganisms (PRMs) as it does not result in excess biomass growth and can be more cost-effective than organic compounds. As an alternative to supplying external H_2 gas, zero-valent iron (ZVI) can serve as the ultimate electron donor by supplying H_2 *in-situ* to PRMs via the iron corrosion process. In primary batch experiments of this research, combined ZVI-*Dechloromonas sp.* HZ successively reduced perchlorate at increasing degradation rates when perchlorate was added in successive cycles. Effects of pH, nitrate, cell density, and iron activity on the performance of ZVI-PRMs were also evaluated. As a follow-up to that study, flow-through column experiments were conducted to evaluate basic operation variables such as influent composition, flow rate, perchlorate concentration, nitrate concentration and cell density on the reduction process.

In the first column experiment, ZVI (570 g, 18/25 mesh) was packed into a glass column (2.5 cm ID. x 50 cm) and inoculated with a relatively small amount of biomass (OD_{600}=0.015). This was operated at a fixed flow rate of 3.6 mL/hr (Velocity=0.17 m/d, EBCT=63 hours) to simulate the movement of ground water in a field scale iron wall. At the influent concentration of 500 ppb, perchlorate removal (>99%) was achieved and maintained for both reagent-grade solution and perchlorate-amended tap water.

In the second experiment, ZVI-filled columns (3.8 cm ID. x 60 cm) were run at relatively high flow rates up to 4.5 L/hr (Velocity = 95 m/d, HRT = 9 min). Two columns were inoculated with relatively large amounts of biomass (OD_{600}=1 and 3, respectively). In a third column, soil obtained from a rapid infiltration wastewater treatment plant (Colton, CA) was placed in the first 20 cm of the column and followed by 30 cm of ZVI with no other bacterial amendment. The final column operated as a control containing only ZVI with no bacterial addition. Perchlorate degradation profiles along the flow path were monitored with time. At the influent concentration of 500 ppb, complete (RE >99%) perchlorate removal was observed in both of the bacterial-amended ZVI columns at flow rates ranging from 7 to 50 mL/min (HRT=14 to 98 min). In the

soil amended column, no reduction of perchlorate was observed in the soil layer; however, reduction through the iron layer was observed with complete removal of perchlorate at flow rates ranging from 7 to 30 mL/min (HRT=15 to 65 min). Minimal perchlorate reduction was observed in the control column, confirming that the reduction of perchlorate was biological rather than chemical. When influent perchlorate concentration was varied between 30 and 1000 ppb, the best overall results were achieved in the soil-amended column. At an influent perchlorate concentration of 30 ppb, perchlorate breakthrough (> 6 ppb) was observed only when the molar ratio of nitrate to perchlorate was greater than 1000:1 in the soil-amended column.
These studies demonstrate the feasibility of using biologically active ZVI for large-scale treatment of perchlorate-contaminated water.

Perchlorate Reduction in a Packed Bed Bioreactor Using Elemental Sulfur

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Perchlorate release in groundwater has affected water supplies to approximately 15 million people in the US and has primarily occurred in association with manufacturing of missiles, rockets, fireworks and industrial processes. Presently, perchlorate contamination has been recorded in drinking water in 38 US states[1]. The Commonwealth of Massachusetts has proposed limits on perchlorate of 1 μg/L because of adverse effects to the thyroid[2.] Although perchlorate is on the EPA contaminant list, no standards have been set so far.

Various researchers and have found that perchlorate can be used as an electron acceptor in anaerobic microbial metabolism[2]. A variety of electron donors including H_2, ethanol, acetate and sugar derivatives have been investigated for perchlorate removal using both mixed and pure cultures.

This study investigated a novel process for treatment of perchlorate contaminated water using elemental sulfur as an electron donor. A microbial culture capable of coupling sulfur oxidation with perchlorate reduction was enriched from a denitrifying wastewater inoculum under anaerobic conditions. Microbial biomass was added to flasks containing elemental sulfur, crushed oyster shell and 5 mg/L ClO_4^- . An initial acclimatization period of approximately 15 days was observed, after which perchlorate was reduced to below detection limits (500ppb). Subsequently, the cultures were inoculated into an upflow bioreactor packed with elemental sulfur and crushed oyster shell media. Groundwater containing ~5 mg/L of ClO_4^- was continuously fed to the column at an initial hydraulic retention time (HRT) of 53 hours. HRT was optimized to 13 hour over the first three months of operation. Intermittent recirculation resulted in faster degradation of perchlorate, possibly due to more uniform distribution of the biomass through the column. The column is presently being operated with low levels of perchlorate (100 ppb) and with other co-contaminants, which shall be discussed at the meeting.

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[1] MADEP 2005. *The Occurrence and Sources of Perchlorate in Massachusetts* . Draft report URL: http://www.mass.gov/dep

[2] Edward, T. U. 1999. *Perchlorate in the Environment.* Kluwer Academic/Plenum publishers, NewYork, NY.

Demonstration of Active and Semi-Passive Approaches to *In Situ* Bioremediation of Perchlorate in Groundwater

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In situ bioremediation is increasingly being used to treat perchlorate-impacted soils and groundwater. Groundwater bioremediation demonstrations have routinely reduced perchlorate from starting concentrations ranging from 250 to 500,000 µg/L to less than the practical quantitation limit (PQL) of 4 µg/L using a variety of electron donors and varying delivery configurations. Provided that electron donor addition is balanced with the electron acceptor demand, perchlorate biodegradation can be accomplished without unduly impacting groundwater redox and quality, maintaining the groundwater as a valuable resource. Approaches that inject large batches of soluble or slow-release electron donors (e.g., molasses, edible oils, HRC) tend to adversely impact groundwater quality by producing significant methane and sulfide, and by mobilizing metals such as manganese and iron making these approaches unsuitable for many sites.

GeoSyntec has received funding from ESTCP (Project CU-0219) to demonstrate semi-passive and active in situ bioremediation approaches for perchlorate-impacted groundwater. The semi-passive approach has been demonstrated at the Longhorn Army Ammunitions Plant (LHAAP) in northeast Texas. The data from the demonstration show that significant reductions in perchlorate concentrations can be achieved using the semi-passive biobarrier system for in situ bioremediation of perchlorate without having significant impacts on secondary water quality characteristics.

The active approach is being demonstrated at the Naval Industrial Reserve Ordnance Plant (NIROP) facility in West Valley City, Utah. Extraction and re-injection wells have been installed at the site in a line perpendicular to the direction of groundwater flow. Groundwater is being extracted, amended with electron donor and reinjected on a continuous basis. The concentration of electron donor is being limited to provide just enough electron donor for perchlorate degradation but not enough to have significant impacts on secondary water quality characteristics. Results from both demonstrations will be presented.

Removal of Perchlorate from Drinking Water and Ion Exchange Regenerant Brines

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Perchlorate ions from rocket fuel, flare and munitions manufacture and use have escaped into groundwater in several states in the USA. Perchlorate causes alarm because it mimics iodine physiologically and is adsorbed by the thyroid gland, subsequently interfering with the endocrine systems of the brain. Removal of perchlorate to very low ppb is difficult on two fronts: competing ions such as nitrate, sulfate, carbonate etc. are often present at 1000 times higher concentration than perchlorate, and perchlorate is surprisingly stable considering its reputation as a rocket fuel oxidant. Direct electrochemical reduction of perchlorate in the parts per billion range is too slow and expensive to be viable. Ion exchange produces a troublesome disposal problem: either a perchlorate laden ion exchange resin; or a brine stream containing high concentrations of perchlorate, nitrate, sulfate and bicarbonate. Electrochemical redox reduction of perchlorate, coupled to ion exchange capture and concentration is an economic and elegant method of dealing with both nitrate and perchlorate, particularly if the kinetics of the reduction process are fast. Perchlorate is surprisingly stable to reduction at a reducing cathode and with common reducing redox ions such as Cr^{2+} and Fe^{2+}. The reduction of perchlorate with Ti^{3+} is well documented in the literature, but the kinetics are slow in common solutions. In our latest study, we have discovered that the reaction of perchlorate with titanium ions in methanesulfonic acid is very fast. We describe the laboratory experiments and pilot plant field trials in California that demonstrate the utility of this method for removing perchlorate and nitrate directly from drinking water and from regenerant brines from ion exchange systems.

Lessons Learned for Future Designs from Thermal Treatment of Perchlorate in Soil

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A soil remediation project, using ex-situ thermal treatment to remove explosives, was modified at the latter stages of planning to include treatment of perchlorate. The design-build approach consisted of a bench scale study, and pilot testing. The bench-scale study verified treatability of perchlorate via thermal destruction and established baseline treatment conditions. Pilot scale studies, conducted with soil spiked with known concentrations of perchlorate, allowed confirmation of laboratory results and defined the process parameters for successful full-scale treatment.

The project specific treatment goal for perchlorate was 4 ppb. The pilot tests results revealed a reduction in treatment effectiveness at elevated perchlorate concentrations in the feed soil. During initial full-scale operations, a high rate of treatment failures was experienced. Analytical results of samples collected from various stages along the treatment train indicated a potential for a portion of the perchlorate-contamination to by-pass the primary treatment process. This potential would likely be higher with greater concentration of perchlorate in the feed soil, explaining the reduction in treatment efficiency. Slower feed rates and higher operating temperature did not show any conclusive positive impact on treatment efficiency. Recycling the particulates from the air pollution control equipment back into the feed soil was initially considered, but was deemed infeasible with the current equipment design. A cost-effective solution was achieved by reducing the size of the treated soil sample batch volume to analyze for perchlorate more frequently, thereby reducing the amount of soil requiring re-treatment. The initial re-treatment rate of 30% dropped to 1.33% after the process was modified, resulting in an overall 11% re-treatment rate for the entire project. Future plant designs intended for treatment of perchlorate to very low concentrations goals potentially improve destruction efficiency by recycling particulates to the beginning of the process instead of the treated soil discharge.

Pesticides

The Elimination of PCB Congener Interference in Organochlorine Pesticide Analysis Using Mass Spectrometry

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Degradation of Chlorinated Pesticides Using Stabilized Nanoscale Zero-Valent Iron Nanoparticles under Aerobic and Anaerobic Conditions

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Anaerobic Bioremediation of DDT and Toxaphene in Soils via Simultaneous Stimulation of Anaerobic Oxidation and Reduction Processes

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The Elimination of PCB Congener Interference in Organochlorine Pesticide Analysis Using Mass Spectrometry

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The analysis of organochlorine pesticides using traditional EPA methodologies that employ electron capture detectors (ECD) are often affected by PCB congener contamination causing the overestimation of some compounds. High biased results for oganochlorine pesticides can lead to an overall lack of data confidence and unnecessary environmental actions. To eliminate the congener interference two separate GC/MS methods were developed and evaluated. A method using Large Volume Injection (LVI) with GC/MS in the Selected Ion Monitoring (SIM) mode was compared with an LVI Ion Trap MS/MS method. Using standard extraction procedures combined with large volume injection, both methods were able to achieve detection levels equivalent to levels typically observed by ECD detection. The GC/MS methods were applied to water, soil/sediment and tissue matrices. Ion trap GC/MS/MS provided an additional level of selectivity over GC/MS SIM and showed advantages in complex matrices by further reducing co-extractable interferences. The use of ion trap GC/MS/MS for chlorinated pesticide analysis provides superior analyte selectivity resulting in increased data defensibility.

Degradation of Chlorinated Pesticides Using Stabilized Nanoscale Zero-Valent Iron Nanoparticles under Aerobic and Anaerobic Conditions

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Contamination of soils and groundwater by chlorinated pesticides such as lindane and atrazine has been a worldwide environmental challenge, and cost effective remediation technologies have been sought for decades. We have investigated the treatability of these chlorinated pesticides and herbicides in water using stabilized nanoscale zero-valent iron particles (nZVI) and the reduction-oxidation kinetics. While both lindane and atrazine were degraded by the monometallic nZVI particles, the degradation effectiveness was greatly enhanced by adding a small fraction (0.1% of Fe) of Pd to the iron nanoparticles. Complete degradation of lindane (1000-μg/L) using nZVI (0.5g/L) was observed over 3-hours with the Fe-Pd bimetallic nanoparticles under anaerobic condition. While 60% degradation was observed with the same amount of Fe-Pd nanoparticles in the same reaction time under aerobic condition. Complete removal of atrazine (1000-μg/L) was also observed using a low dosage of iron (0.05g/L) and Pd (0.1% of Fe) under anaerobic condition. Again, the degradation of atrazine was more effective under anaerobic condition than when the reactor was exposed to air (a 20 difference at an iron dose of 0.02g/L) in the presence of the stabilizer. Interestingly, the degradation efficiency of atrazine (5000-μg/L) was enhanced to 40% in the absence of the stabilizer under aerobic condition at the same dose of iron (0.1g/L). For both lindane and atrazine, the aerobic degradation kinetics was slower than that under anaerobic condition, which suggests that radical release from nZVI surface under aerobic condition is hindered by the stabilizer (NaCMC). Research is ongoing to further elucidate these observed phenomena.

Anaerobic Bioremediation of DDT and Toxaphene in Soils via Simultaneous Stimulation of Anaerobic Oxidation and Reduction Processes

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The organochlorine pesticides DDT and toxaphene are among the most recalcitrant man-made chemicals in the environment. Whereas there is a substantial body of literature on the partial biodegradation of chlorinated pesticides via the creation of anaerobic and reducing conditions that dates back to the 1960s (e.g., Guenzi and Beard, *Science*, 1967), more recent research suggests that certain metabolites of these "parent" compounds are resistant to further reductive dechlorination even under highly reducing conditions. For example, DDMu, a metabolite of the DDT-breakdown product DDE, is known to be persistent in marine sediments where anaerobic and reducing conditions prevail. Additional work has suggested that the reductive dechlorination of toxaphene "stalls" at congeners that contain from six to eight chlorine atoms. Accordingly, a major objective of this project was to overcome the shortcomings of prior approaches to anaerobic bioremediation of pesticides that have focused primarily on reductive dechlorination with a more comprehensive treatment process that involved the simultaneous stimulation of both anaerobic oxidation and reduction processes.

Previously, a case study describing a large-scale containment and anaerobic bioremediation project for 29,000 tons of DDT and toxaphene contaminated soils was reported (Hince et al., U.Mass Soils 2005). Subsequently, post-treatment data were collected from the soils in the most highly contaminated layer within the anaerobic biocell. Briefly, soils were pre-treated with a patented solid-chemical composition, BioGeoCheMix® ("BGC") that contains abundant plant materials, high-surface-area native iron and manganese (IV) minerals among other amendments. The manganese (IV) minerals in the BGC serve as both a sacrificial oxidative catalyst to minimize biofouling of the iron particles and as a relatively high-energy electron acceptor for anaerobic oxidation processes. The BGC also contained targeted co-substrates designed to help stimulate the anaerobic oxidation of less chlorinated toxaphene congeners and metabolites of DDT. After "BGC" treatment and placement of the soils in the biocell, the soils were subjected to a brief but intensive period of repeated applications of a patented liquid-chemical composition "N-Blend" to provide nitrates as an additional source of high-energy anaerobic electron acceptors along with complex phosphate nutrients and a suite of micronutrients.

Post-treatment soil sampling data collected within three months of treatment documented, on average, 95.4% reductions in toxaphene levels and 96.9% reductions in DDT concentrations. DDE levels changed only slightly whereas DDD reductions were significant (56.9% on average) but lower than for DDT. As DDD is produced by the first step in the reductive dechlorination of DDT, it follows that the decrease in DDD levels is less than that of DDT as "new" DDD was being formed by the removal of one chlorine from DDT. The proportions of DDT daughters (DDD + DDE) increased from less than 30% before treatment to greater than 87% after three months.

Phytoremediation

Phytoremediation of TPH-Contaminated Groundwater
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Assessment of Arsenic Phytoextraction Performance in the Spring Valley Area of Washington, DC Using High Intensity Composite Soil Sampling
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Does Metal Chelation Mobilize Aged PAHs in Vegetated and Non-Vegetated Contaminated Soils?
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Engineering Transgenic Plants for *in situ* Treatment of Explosives
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Application of Endophytic Bacteria to Improve the Performances of Poplar for Phytoremediation and Biomass Production
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Seaweed Uptake, Concentration and Detoxification of Organic Pollutants in Marine Waters: TNT and PAHs
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Phytoremediation of TPH-Contaminated Groundwater

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Groundwater phytoremediation systems were installed in 2003 near two adjacent retail outlets in Raleigh, North Carolina. Groundwater at the site contains dissolved-phase petroleum hydrocarbons, and a contaminant plume is migrating toward a near-by creek. The phytoremediation systems are comprised of poplar and willow trees planted in rows that are roughly perpendicular to the direction of groundwater flow, and the objective of the systems is to hydraulically control the rate of contaminant plume migration. The tree stands are planted in two different areas of the site: Area A is more highly contaminated than Area B. The water table is approximately 20 ft below ground surface, and therefore, special cultural practices were used to encourage the development of trees with very deep roots. For example, at each planting location deep boreholes were drilled, the boreholes backfilled with a sand/compost mixture, and the trees planted in the backfill. The young trees were irrigated using vertically installed subsurface drip lines, and the roots tend to follow the zone of moisture downward. When the trees are sufficiently mature, the irrigation will be discontinued and the plants will use groundwater as a source of moisture. An analysis of water balance parameters (*e.g.* groundwater flux, plant transpiration, precipitation) suggested that the mature stand will be effective for plume control. As a method of assessing rooting depth during the period of stand development, soil moisture probes were installed in the backfill at various depths at the time of installation. During the 2005 growing season, individual trees within the stands in Areas A and B were monitored for rooting depth as well as for transpiration rates using thermal dissipation probes. The main conclusion was that the cultural practices used to obtain deep rooted trees appeared to be effective in both Areas: Roots had extended deeply in the backfill to within a few feet of the saturated zone; some trees appeared no longer to be dependent upon subsurface irrigation and apparently were able to use water from the saturated zone. Rates of water use (seasonal averages) were higher in Area B (100 L/d) than in Area A (65 L/d), suggesting that the groundwater contaminants may be somewhat inhibitory. During the 2006 growing season, studies will be carried out to further assess the extent of groundwater uptake. Specifically, the ratio of stable isotopes of hydrogen will be analyzed in xylem sap, groundwater and vadose zone water.

Assessment of Arsenic Phytoextraction Performance in the Spring Valley Area of Washington, DC Using High Intensity Composite Soil Sampling

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The residential area of Spring Valley encompasses approximately six hundred sixty-one (661) acres in the northwest section of Washington, D.C. During World War I, at the American University Experiment Station (AUES), the Department of Defense produced the arsenic-based chemical warfare agents, Lewisite and Adamsite. Chemists and engineers tested these agents in the areas surrounding the AUES, which is now known as the Spring Valley residential neighborhood. Investigative soil sampling indicated the presence of arsenic at levels above background and risk-based concentrations (RBCs). In 2001, the Corps of Engineers initiated a removal action to address these areas of concern. The main remediation technology to be applied at residences with elevated arsenic is excavation followed by backfilling with clean soil. This technology can be environmentally disruptive and expensive. Phytoremediation activities were initiated in 2004 as an alternative for specific areas to minimize destruction of existing trees and reduce restoration costs. An initial field verification study was conducted to evaluate the potential of phytoremediation to address the elevated arsenic soil concentrations. Based on these results, the field activities were expanded in 2005 to include additional sites and continued in 2006. Resuls obtained in 2005 demonstrated continued improvement in soil arsenic concentrations. However, variability in the measured soil arsenic concentrations hindered the ability to assess performance in some test plots. Therefore, an alternative soil sampling approach was developed to obtain samples more representative of the actual soil concentration. The approach utilizes a high number of individual soil cores collected from each sampling grid for compositing, homogenization and subsequent analysis. This paper will present the results obtained using this sampling approach and evaluate its ability adequately assess phytoremediation performance.

Does Metal Chelation Mobilize Aged PAHs in Vegetated and Non-Vegetated Contaminated Soils?

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The bioavailability of Polycyclic Aromatic Hydrocarbons (PAHs) in contaminated media is a major concern when assessing the impact of phytoremediation. Evidence indicates that natural re-vegetation of sites with historical high levels of PAH contamination does attenuate these highly persistent contaminants. There is great interest in the ability of vegetation to remove available PAHs from soil, but the processes of sequestration and rhizo-degradation by which this occurs are generally poorly understood. Plant derived organic carbon moving into soils in the plant rhizosphere may enhance rhizo-degradation of PAHs by providing a ready source of labile carbon for microbial metabolism forcing PAH biodegradation, or plant derived organic matter can create an organic rich substrate for PAH sorption and sequestration. Humin structures are a major recipient of this new plant derived organic carbon. Disruption of humin complexes by chelation of polyvalent metal ions should release PAHs further sequestered by plant derived organic carbon, and thereby provide information about the extent of sequestration.

To determine the effects of plant organic matter on PAH sequestration in whole soil and humin fractions, soil fractions were disrupted with sodium citrate and PAH desorption was determined. Two types of soil samples, vegetated and non-vegetated, were analyzed from a fresh water canal contaminated with diesel fuel. In both cases, the chelation was carried out on native soils and soils in which available PAHs had been removed. All extracted/desorbed solutions were analyzed by GC/MS for total PAH concentrations. Less available PAH residues in vegetated sediments, even after chelation and humin disruption, appear to desorb at slower rates than sediments in which natural revegetation has not occurred.

Engineering Transgenic Plants for *in situ* Treatment of Explosives

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The contamination of the environment with toxic organic pollutants such as explosives presents a serious and widespread problem at sites across the world. Plants have a remarkable ability to extract compounds from the surrounding environment and have emerged as an affordable and effective clean-up strategy; however, the innate biodegradative abilities of plants are limited and often rates of uptake and metabolism can be slow. We asked whether plants could be engineered to yield an optimal system for *in situ* bioremediation of toxic explosives residues in soil. Progress has been made towards this goal and we have successfully combined the biodegradative capabilities of soil bacteria with the high biomass and stability inherent to plants. Explosives can be broadly classified into three groups: nitroaromatics (e.g. trinitrotoluene, TNT), nitramines (e.g. hexahydro-1,3,5-trinitro-1,3,5-triazine, RDX) and nitrate esters (e.g. nitroglyerin). We have isolated bacteria that degrade all the major classes of explosives. In order to achieve the removal of TNT and RDX from contaminated soil we have engineered plants expressing bacterial enzymes capable of TNT transformation and RDX degradation. Importantly, we have demonstrated that these transgenic plants are capable of restoring and maintaining the metabolic and genetic diversity of the rhizosphere soil.

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Application of Endophytic Bacteria to Improve the Performances of Poplar for Phytoremediation and Biomass Production

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Phytotechnologies are offering efficient tools and environmentally friendly solutions for cleanup of contaminated sites and water, improvement of food safety, carbon sequestration as a tool to reduce global warming, and the development of renewable energy sources, all of which are contributing to sustainable land use management. However, a profound knowledge is required of the complex interactions between plants and their associated microorganisms in order to exploit these interactions for the improvement of phytotechnologies for sustainable land use.

We demonstrated that endophytic bacteria can be efficiently used to improve phytoremediation of volatile organic contaminants: endophytic bacteria equipped with the appropriate degradation pathway significantly improved the *in planta* degradation of toluene and TCE in yellow lupine, resulting in its reduced phytotoxicity and release. We extended this concept to poplar, a plant species frequently used for the phytoremediation of groundwater contaminated with organic solvents. Inoculation of poplar with the endophyte *Burkholderia cepacia* VM1468 (pTOM-Bu61), which is able to efficiently degrade toluene, resulted in reduced environmental release and phytotoxicity of toluene, thus confirming our earlier results obtained with the yellow lupine model system. A major difference between the yellow lupine and poplar experiments is the use of non-sterile plants for the inoculation of the poplar. Analysis of the microbial communities associated with non-inoculated control plants and poplar inoculated with VM1468 showed that the strain had failed to establish itself within the endogenous endophytic community. However, horizontal gene transfer of the toluene degradation plasmid pTOM-Bu61 had occurred to different species of poplar's endogenous endophytic community.

During the course of this work we also noticed that certain endophytic bacteria affected the growth of their host plant, either in a positive or negative way. This observation is further exploited to improve the biomass production of poplar for carbon sequestration and biomass production.

Seaweed Uptake, Concentration and Detoxification of Organic Pollutants in Marine Waters: TNT and PAHs

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According to a recent report by the EPA on the condition of our nation's coastline, 27% of the Northeast's estuaries have sediments contaminated with PCBs and PAHs. Currently, the most common method for eliminating PAHs and PCBs from contaminated marine waters and sediments is to excavate and dispose of the sediment. We are investigating the feasibility of a new approach for the removal of such compounds - growing "phycoremediating" seaweeds on contaminated sediments. In our initial work for the ONR, we were able to show that seaweeds are capable of quickly taking up and metabolizing the explosive compound 2,4,6-triitrotoluene (TNT). The most promising seaweed we examined was the one cell thick, sheet-like alga *Porphyra yezoensis*, which at a biomass density of 1.2 g/L and an initial TNT conc. of 10 mg/L, removed 100% of the TNT in just 72 hrs and produced the TNT byproducts 2-amino-4,6-dinitrotoluene (2-ADNT) and 4-amino-2,6-dinitrotoluene (4-ADNT). Currently, we are investigating the ability of seaweeds to take up and concentrate or metabolize PAHs, using the three-ringed phenanthrene as a model compound. As a first step, we are screening seaweed samples from polluted and unpolluted sites for their ability to metabolize 10 ppm phenanthrene. So far, the green seaweed *Ulva* (*Enteromorpha) intestinalis* looks most promising. At a density of 1g/30mL, *Ulva* plants removed over 90% of a 10 ppm phenanthene seawater solution in less than 24 hrs. Preliminary GC-MS analyses have detected one as yet unidentified possible breakdown product. This research was supported by grants from the Office of Naval Research Environmental Research Program and the USDA Aquaculture Program.

Remediation

How Low do you Want to Go? In-Situ Thermal Desorption Consistently Achieves Low Cleanup Standards

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Design and Performance Evaluation of Air Sparging Trench for the Treatment of VOCs and Arsenic

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Electrochemical Generated Alkaline Barrier for In-situ Treatment of Hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX) Contaminated Groundwater

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Chlorinated Soils Remediation Using Steam Injection Into Fractured Bedrock

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Treatment of Trichloroethene with Reactive Nanoscale Iron Particles

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Use of High Concentration Magnesium Sulfate Solution to Remediate Petroleum Impacted Groundwater

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Completion of In-Situ Thermal Remediation of PAHs, PCP and Dioxins at a Former Wood Treatment Facility

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How Low do you Want to Go? In-Situ Thermal Desorption Consistently Achieves Low Cleanup Standards

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Establishing cleanup standards for contaminated source areas has long been a balance between what is considered technically feasible and what is mandated. With respect to dense non-aqueous phase liquid (DNAPL) source zones in soil and groundwater, a school of thought has become prevalent that assumes that volatile and semivolatile organic compounds (VOCs and SVOCs) of concern cannot feasibly be treated *in situ* to concentrations low enough to be consistent with meeting Maximum Concentration Limits (MCLs) in groundwater. This position has been most strongly held when it comes to DNAPL in challenging subsurface settings such as heterogeneous and fractured media.

Now, as a result of over fifteen completed source area remediation projects using In-Situ Thermal Desorption (ISTD), which combines Thermal Conduction Heating (TCH) and vacuum extraction, a new paradigm for source treatment is emerging. Because TCH takes advantage of the invariance of thermal conductivity across a wide range of soil types, no targeted area is left unheated. ISTD therefore is able to accomplish complete and rapid treatment of DNAPL in lower-permeability and heterogeneous formations. This presentation will review results from TCH projects treating both VOCs such as chlorinated solvents and SVOCs including PCBs, PAHs and dioxins, which have consistently met the very low cleanup standards that have been set. These projects have often been implemented under performance guarantee type contracts, reducing the site owners' risk. Recent examples include seven chlorinated solvent DNAPL source areas treated to mean concentrations <50 ug/kg of TCE and PCE, and eight SVOC source areas treated to similarly low concentrations of PAHs and PCBs. At a recent Brownfield site treated by ISTD, the enhanced property value that the owner derived through meeting residential cleanup standards was far greater than their remediation cost.

Design and Performance Evaluation of Air Sparging Trench for the Treatment of VOCs and Arsenic

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An air sparging trench alternative was compared to a capping/pump and treat remedy for groundwater impacted with volatile organic compounds (VOCs) and arsenic constituents of concern (COCs), as specified in a Record of Decision (ROD) at a United States Environmental Protection Agency (USEPA) Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) landfill site. The air sparging trench with an engineered backfill material was designed to intercept and treat COCs migrating with groundwater from beneath the landfill. The design and performance evaluation of the trench are presented.

The trench was designed to provide in-situ flow-through treatment of VOCs by a combination of volatilization and aerobic biodegradation, and arsenic by precipitation and sorption. Various laboratory and field-scale tests were performed to evaluate the effectiveness of the trench in removing COCs. The results of laboratory, field-scale testing, and a stripping analysis indicated that the trench could remove the majority of VOCs that are present at the site by air sparging. Organic compounds that are not expected to be completely volatilized were projected to degrade by aerobic microorganisms in the oxygenated groundwater within and down-gradient of the trench.

Geochemical modeling was performed to evaluate the ability of oxidizing conditions within trench to remove dissolved arsenic from groundwater through co-precipitation and sorption onto iron oxides. The modeling results indicated that oxidizing conditions created in the trench will result in precipitation of dissolved arsenic and other reduced minerals into the void spaces of the trench backfill material, significantly reducing the dissolved arsenic levels down-gradient of the trench.

Long-term performance issues (i.e., mineral precipitation and biofouling) observed at other air sparging trenches were evaluated and solutions for such potential issues were incorporated in the design. The air sparging trench alternative evaluation resulted in an amendment of the original ROD with a substantial cost saving to the client.

Electrochemical Generated Alkaline Barrier for In-situ Treatment of Hexahydro-1,3,5-trinitro-1,3,5 triazine (RDX) Contaminated Groundwater

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The use, manufacturing, and storage of nitroaromatic and nitramine explosive compounds resulted in contamination of soil and groundwater. The U.S. EPA lists hexahydro,1-3-5-trinitro-1,3,5-triazine (RDX) under the Unregulated Contaminant Monitoring Regulation for the Public in List 2. RDX groundwater contamination causes disruptions in the use of military training areas and impacts local drinking water supplies resulting in additional costs in long term groundwater monitoring and remediation.

Sand packed columns in a horizontal flow arrangement were used in laboratory experiments to simulate an in-situ electrochemical barrier. The simulated barrier was used to destroy the RDX at the cathode and eliminate its downstream migration. Mixed metal oxide coated titanium electrodes (anode and cathode) were installed in slotted PVC wells within the column to facilitate the direct and indirect destruction of RDX contaminated water by electrolysis and alkaline hydrolysis, respectively. Over the range of inlet concentrations (0.5 to 25 mg/L), RDX removal was approximately 95% with 75% RDX destruction near the cathode, presumably by electrolysis and 13% RDX destruction downstream of the cathode by alkaline hydrolysis with applied current densities of 8 to16 A/m^2. Nitroso-substituted products (MNX, DNX, and TNX) were below detection limits in the column effluent. The effluent end products of RDX ring cleavage detected were formate, nitrite, and nitrate. This study highlights the destructive potential of electrochemical processes for in-situ remediation of RDX contaminated water. The significance of this 3rd generation remediation technology is that the contaminant can be removed from the groundwater without chemical additions to the subsurface.

Chlorinated Soils Remediation Using Steam Injection Into Fractured Bedrock

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The former PR-58 Nike Missile battery Site was constructed in 1955/1956. It included a missile assembly and test building with an underground storage tank (UST), a generator building with a 4000-gal UST and personnel quarters, and was equipped with short range, conventionally-armed Nike Ajaz missiles. The facility was deactivated in 1962. The Army drilled holes in the bottom of the silos, backfilled them with clean sand and demolished the concrete structures surrounding the silos. There is no site-specific documentation regarding use, storage or disposal of hazardous materials, however, a variety of chlorinated organic solvents (CVOCs) such as carbon tetrachloride (CT), tetrachloro- ethane/ethenes (PCA/PCE)and trichloro-ethane/ethenes (TCE/TCE) were typically used for parts cleaning, degreasing and preparation cleaning for painting. Typical quantities used ranged from 30 to 120 liters/month of TCE and 190 to 380 liters/month for other solvents. The site geological units have been classified into three hydrogeological zones, an upper shallow overburden (typically glacio-fluvial sand), a deep overburden groundwater zone (sandy silty gravel to sandy gravelly silt – possibly till and a weathered bedrock zone), and a competent bedrock groundwater zone (upper 60 feet of competent bedrock). The deep and rock units are considered as a single heterogeneous groundwater zone and all three are in hydraulic communication. Contamination in these units is sporadic with the deep zone being the most contaminated. Total CVOCs range from 383,700 ug/L in MW03-14D and 118,148 ug/l 80 feet west at EA-102, and non detect to the west, southwest and north. The highest total CVOC concentration of 20,911 ug/L in the shallow competent bedrock was found in MW-03-14R. A steam enhanced remediation (SER) pilot test was undertaken to determine whether the CVOCs could be remediated by injection of steam and air and utilizing a dual phase vacuum extraction system. Steam (about 1550 lbs/hr) was injected in 4 well locations with a central extraction and 6 surrounding (pneumatic control) triple well clusters screened across the 3 zones. This injection/extraction system was centered inside a ring of perimeter wells to allow monitoring of potential impacts from thermal mobilization of the CVOCs. The project was delayed until the unusually high water table fell to the mid screen of the upper shallow zone and the injection system was then operated for 8 weeks. Several hundred pounds of CVOCs were extracted despite difficulties introducing steam into the series of micro fractures in the weathered and competent bedrock. Subsurface temperatures were monitored throughout the project.

Treatment of Trichloroethene with Reactive Nanoscale Iron Particles

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The treatment of trichloroethene (TCE) impacted groundwater with laboratory grade metallic and bimetallic nanoscale materials has received considerable attention. In this work, reactive nanoscale iron particles (RNIP) that are produced in bulk (200 to 400 metric tons per year) were used for the degradation of dissolved phase TCE. The 25 % nanoiron slurry used in this study was produced by Toda Kogyo Corporation, Japan. RNIP consist of an elemental iron core (α-Fe) and a magnetite shell (Fe_3O_4). RNIP also contained unidentified sulfur compounds determined as sulfur in concentrations of about 4,000 mg/kg. The average particle size was about 70 nm, and the average surface area was about 29 m^2/g. TCE degradation was studied as a function of RNIP and TCE concentration, and for different solution alkalinities and ionic strengths. The investigated initial TCE concentrations were representative of ground water source area contamination and ranged from 34 to 340 mg/L. The three different solutions used in this study consisted of deionized water, a solution with about 100 mg/L alkalinity and total ionic strength of 0.05 M, and a solution with about 400 mg/l alkalinity and total ionic strength of 0.1 M. The resulting total dissolved solids (TDS) concentrations of the batch tests were calculated to be about 2,440 to 5,027 mg/L. The investigated RNIP concentrations ranged from 1 to 8.3 g/L (total surface area of 0.86 to 7.17 m^2). For static tests, overall TCE mass reductions (sum of gaseous and aqueous phase) of more than 99 % for 1 g/L RNIP and more than 99.8 % for 4.2 g/L RNIP were observed. The production of degradation products was not proportional to the TCE dechlorination. Ionic strength did not affect the degradation rate. However, the acidity resulting from the dechlorination consumed the alkalinity and diminished degradation rates.

Use of High Concentration 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. 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 The use 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. The case studies presented will demonstrate the benefits of using high concentrations of Magnesium Sulfate solution (>10,000 mg/l) to stimulate the biodegradation of petroleum contaminants in groundwater under field conditions at various sites. Many of these sites have had other technologies applied prior to applications. Graphics depicting the historical concentrations and reduction trends will be provided. In addition to the relatively rapid degradation of petroleum compounds such as BTEX, this technology is quite cost effective in comparison to other currently available remediation techniques. A description of the technology, site selection criteria, dosage determination, and field scale performance results demonstrating contaminant concentration reductions in groundwater of more than 90% within a few months at some sites will be presented. Magnesium Sulfate was selected for use due to availability, low cost, high solubility and the relative safety associated with handling. This technology has advantages over others for many sites where physical limitations (buildings, utilities, etc.) preclude other technologies.

Completion of In-Situ Thermal Remediation of PAHs, PCP and Dioxins at a Former Wood Treatment Facility

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The largest in situ thermal conduction heating project ever undertaken at a wood treatment site was completed in March 2006. The site was a former utility pole treatment facility that Southern California Edison (SCE) operated from 1921 to 1957.

The subsurface soils were contaminated primarily with polyaromatic hydrocarbons (PAHs), pentachlorophenol (PCP), dioxins and furans, with soil treatment standards of 0.065 mg/kg benzo(a)pyrene Toxic Equivalents, 25 mg/kg PCP, and 1.0 µg/kg dioxin, expressed as 2,3,7,8-tetrachlorodibenzodioxin (TCDD) Toxic Equivalents (TEQ). A feasibility study led to the selection of TerraTherm's patented In-Situ Thermal Destruction (ISTD) technology, which utilizes simultaneous application of thermal conduction heating and vacuum to treat contaminated soil without excavation. The applied heat volatilizes organic contaminants within the soil, enabling them to be carried in the vapor stream toward heater-vacuum wells. Subsurface temperature monitoring tracked the progress of heating. A heating goal for inter-well temperatures of 325°C (620°F) was achieved, as were all the soil treatment standards and air emission standards.

Approx. 16,500 CY of predominantly silty soil was treated to a maximum depth of 105 ft. TerraTherm installed 785 thermal wells, including 654 heater-only and 131 heater-vacuum wells, in a hexagonal pattern at 7.0-foot spacing.

Final data results will be presented, including a comparison of pre- and post-treatment soil sampling, quantity of contaminants treated, and energy and material balances. Treatment mechanisms will be discussed, along with specific lessons learned and project costs.

Risk Assessment

Impact of Aging Time on the Risk from Dermal Exposure to Soil Contaminated with Phenanthrene
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What's The Matter With RBCA?
Roger C. Brewer, Hawai'i Department of Health, Honolulu, HI

Reducing Uncertainty in Ecological Risk Assessment: Measured Tissue Residues in Fish and Aquatic and Terrestrial Insects and Derivation of Bioaccumulation Factors
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Streamlining Ecological Risk Assessment Reporting With Interactive CD Technology
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Environmental Effects of Hurricane Katrina
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Impact of Aging Time on the Risk from Dermal Exposure to Soil Contaminated with Phenanthrene

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The health risk from exposure to contaminated soil is related to the fraction of chemical absorbed by the body (bioavailability), rather than to the total concentration of chemical in soil. Chemical bioavailability data are necessary to improve the accuracy of risk assessment following exposure to contaminated soil and to allow more realistic soil remediation goals. One of the factors that may influence chemical bioavailability and ultimately health risk from exposure is the residence time or "aging" of chemical in soil. Skin is a primary route of exposure to phenanthrene, a polycyclic aromatic hydrocarbon found in soil at former manufactured gas plant sites. This study was conducted to determine the extent to which soil alters the dermal bioavailability of phenanthrene with respect to soil aging and soil type. Bioavailabilty was assessed by measuring the penetration of phenanthrene through dermatomed male pig skin via an *in vitro* approach consisting of radiotracer and flow-through diffusion cell methodology. After 3 months aging, dermal penetration was significantly decreased by 83% in Atsion soil (high sand and high organic matter content) and by 69% in Keyport soil (high clay but low organic matter content) versus pure phenanthrene (without soil). Extending the aging time to 6 months, reduced penetration through skin by 94% in Atsion soil and 86% in Keyport soil. The results indicate that because human risk from exposure to soil contaminated with phenanthrene would be reduced by aging, less soil cleanup would be needed.

What's The Matter With RBCA?

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"Safe" buildings floating on lakes of highly flammable liquids. "Risk-free" sites with explosive levels of gasoline vapors lurking below. "Nonpotable" but highly contaminated groundwater discharging into sensitive aquatic habitats. "Nontoxic" backfill dripping with diesel fuel approved for reuse in residential areas. Healthy kids but dying landscaping. "Clean" backyards that could be mined for metals. Does no "exposure" mean no environmental concern? Fortunately, while often approved in "site-specific" risk assessments, the conditions noted above are rarely allowed to actually take place in the field, even if RBCA said it was OK.

State "Risk-Based Corrective Action" or "RBCA" programs implemented in the 90s provided a good starting point for the investigation, assessment and cleanup of contaminated sites. It's time, however, to take a fresh look at what's gone right and what's still missing in these programs. A wealth of good ideas and experience is ripe for harvest. For groundwater, potential environmental concerns that should at least be initially assessed at all sites include impacts to drinking water resources, emissions of subsurface vapors to building interiors, impacts to aquatic habitats (i.e., discharges to surface water) and assessment of gross contamination concerns (odors, sheens, general resource degradation, etc.). For soil, potential environmental concerns include direct exposure of residents and workers, emission of subsurface vapors to building interiors, leaching and impacts to groundwater, toxicity to ecological receptors and assessment of gross contamination concerns. The development and use of Environmental Screening Levels plays an important role in expediting the assessment of potential environmental concerns at contaminated sites. Not to be forgotten is the important role of professional judgment in assessing the need for remedial actions at contaminated sites. If RBCA is telling you something that just doesn't seem to make sense, it might be time to ask "What's the matter?".

Reducing Uncertainty in Ecological Risk Assessment: Measured Tissue Residues in Fish and Aquatic and Terrestrial Insects and Derivation of Bioaccumulation Factors

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It is becoming more common for the protection of ecological receptors, rather than human receptors, to drive the extent of remediation at environmental sites. At some sites and for some chemicals, food chain pathways can be a relevant source of potential exposure for ecological receptors. Default media-to-receptor bioaccumulation factors used in food web modeling are typically derived from literature studies or are calculated using algorithms based on chemical/physical properties and may not represent actual site conditions. For example, most of the available soil-to-insect accumulation factors are based on earthworm data. Unlike most insects, soil in the gut of an earthworm composes a large fraction of an earthworm's mass. Therefore, chemical concentrations in whole body earthworms mirror concentrations in gut soil and do not represent what is actually accumulated into tissues. Because most insects (e.g. flying insects) do not store soil in the gut, bioaccumulation factors for earthworms are not representative of bioaccumulation factors for insects. The potential exposure of certain insectivorous feeding guilds, such as birds and mammals that feed on flying insects, could be misrepresented when earthworm data are used to estimate uptake into flying insects.

This paper characterizes biota-sediment and biota-soil relationships for PAH and dioxins in forage fish and flying insects in two freshwater stream systems. Fish were collected using typical active and passive sampling techniques (deployment of minnow traps and seining). An innovative sampling program was designed to passively collect flying insects using a Universal Blacklight Trap. The data from these two stream systems illustrate the extent to which commonly used default bioaccumulation factors overestimate actual concentrations of PAH and dioxins in prey species. Site-specific bioaccumulation factors (expressed on a carbon- and lipid-adjusted basis) are derived for each of the two stream systems and are compared to default bioaccumulation factors.

Streamlining Ecological Risk Assessment Reporting With Interactive CD Technology

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Consistent with current regulatory guidance, Ecological Risks Assessments are required to provide an evaluation that is robust and scientifically defensible, while at the same time, remaining accessible to a broad-based and often non-technical audience. These potentially conflicting objectives frequently result in Ecological Risk Assessments that are cumbersome, redundant, and difficult to interpret. This presentation discusses an approach for using interactive CD technology with a tiered presentation to create a streamlined Ecological Risk Assessment that is consistent with regulatory guidance, eliminates redundancy, can be understood by a broader audience, and presents supporting data and background information in a detailed, but intuitive and user-friendly format. The presentation focuses on a case study application of this technology to an Ecological Risk Assessment which was recently completed for a tidal creek system at the U.S. Navy St. Juliens Creek Annex, located in Chesapeake, Virginia.

Environmental Effects of Hurricane Katrina

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When Hurricane Katrina made landfall in the New Orleans area of Louisiana, strong winds and flood waters destroyed many homes and businesses resulting in discharges of hazardous materials. Oil was released from cars, auto garages, and large bulk oil storage facilities, etc. Chemicals including metals and pesticides were released from homes, hardware stores, agricultural shops, and other facilities. These materials mixed with flood waters and were transported across a wide area potentially contaminating major portions of New Orleans.

To determine if contaminants were present in the New Orleans environment that might pose a risk to residents or the biota, the US Environmental Protection Agency (EPA) and Louisiana Department of Environmental Quality (LDEQ) have collected thousands of soil, sediment, water and air samples within the flooded area and analyzed them for metals, petroleum hydrocarbons, and pesticides. To date, the testing results show little to no health risk from Hurricane Katrina related impacts. This paper provides an overview of the methods and results used to assess the potential impact to human health and the environment.

Sediments

Sampling Methods and Techniques for Quantifying AVS/SEM and Metals Bioavailability in Estuarine Sediments

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Application of the USEPA's Equilibrium Partitioning Sediment Benchmark (ESB) Methods for Evaluating Metal Bioavailability and Toxicity in Lower Hudson River Sediments

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Performance Comparisons of Geostatistical Approaches for Delineating Sediment Contamination

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The Influence of Carbonaceous Organics on the Sampling, Analysis, and Remediation of PAH Contaminated Harbor Sediments

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Sediment Equilibrium Partitioning Benchmarks for Energetic Compounds: A Cautionary Note and Alternate Approaches

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Technical Challenges on the Marine Hydraulic Dredging Activities, New Bedford Harbor Superfund Site

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Subaqueous Capping Considerations for Coal Tar Contaminated Sediments

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Sampling Methods and Techniques for Quantifying AVS/SEM and Metals Bioavailability in Estuarine Sediments

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Recent (2005) USEPA guidance provides procedures for assessing metals bioavailability and toxicity based on concentrations of acid volatile sulfides (AVS) and total organic carbon (TOC). Studies have shown that sediments throughout the Hudson-Raritan Estuary, including the Lower Hudson contain sufficient AVS to limit bioavailability and toxicity. Sediment sample collection and laboratory analysis methods were developed to evaluate metal bioavailability/toxicity in sediments adjacent to a former cable manufacturing facility on the Lower Hudson River.

Accurate evaluation of the actual in situ concentrations of AVS and simultaneously extracted metals (SEM) required sampling, handling, analysis techniques that would maintain the in situ redox conditions. Guidance for collecting and handling of samples for AVS/SEM analyses is limited. Therefore, techniques were developed for collecting and processing representative sediment samples while minimizing changes to in situ redox conditions. The sampling procedures permitted the measurement of redox potential in the field and allowed for a relatively large representative volume of sample to be collected for analysis so that low analytical detection limits could be achieved. The sampling procedure made use of readily available sediment sampling tools and handling/management techniques that could be executed immediately upon sample collection. These techniques minimized handling and also allowed for visual examination of the surficial sample to note color changes in the sediment profile and/or the production of gas bubbles in the core. Following sample collection, special care was taken during transport and in the lab to ensure that the sample was carried through analysis without exposure to oxidizing conditions, thus emulating conditions as close to those existing in the subsurface as possible and producing representative concentrations of AVS/SEM and metals in porewater. These methods are discussed and compared with recent USEPA guidance. The results from this study are presented in more detail in a separate presentation.

Keywords: AVS, SEM, porewater metals

Application of the USEPA's Equilibrium Partitioning Sediment Benchmark (ESB) Methods for Evaluating Metal Bioavailability and Toxicity in Lower Hudson River Sediments

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The U.S. Environmental Protection Agency (USEPA) recently published its final guidance for evaluating the bioavailability and toxicity of metals in sediments using equilibrium partitioning sediment benchmarks (ESBs). The ESB methodology accounts for the sequestering of metals by acid volatile sulfides (AVS), organic carbon (OC), and other solid-phase and dissolved-phase ligands naturally present in sediments thus limiting their bioavailability and toxicity to benthic organisms. Specifically, the ESB guidance provides quantitative methods for evaluating the binding capacity of AVS and OC relative to the sum of the simultaneously extracted metal ($\sum$SEM) concentrations for six metals (cadmium, copper, lead, nickel, silver, and zinc), whereby when $\sum$SEM-AVS < 0 µmoles/g or when $\sum \text{SEM-AVS}/f_{oc} < 130$ µmoles/g_{oc} then these metals are fully bound and not bioavailable to benthic organisms and toxicity is not observed. To evaluate potential metals toxicity in Lower Hudson River sediments near a former copper cable manufacturing facility, 50 near-surface sediment samples were collected in November 2004 and November 2005 and analyzed for bulk sediment metals, AVS, SEM, total organic carbon (TOC), oxidation/reduction (redox) potential, and grain size. Application of the ESB methodology showed that the concentrations of AVS and TOC were sufficient to sequester these metals at $\sum \text{SEM-AVS}/f_{oc}$ values well below 3,000 µmoles/g_{oc} where toxicity would be predicted if exceeded. Although these data indicate substantial metals binding capacity, variability in AVS concentrations was observed both spatially and with depth. Based on mechanistic considerations, the most likely factors influencing AVS variability include sediment depth, redox potential, and grain size. The effects of these variables on the $\sum \text{SEM-AVS}/f_{oc}$ were further evaluated as was the applicability of the ESB method in establishing site-specific remedial goals for metals.

Performance Comparisons of Geostatistical Approaches for Delineating Sediment Contamination

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The relative performance of alternate interpolation methods for delineating sediment remediation areas, volumes, and dredge cuts was evaluated as part of the remedial design effort on a major Superfund remediation site. The methods evaluated included Thiessen polygons, a hybrid of ordinary kriging and indicator kriging, and full indicator kriging, with and without channel straightening. Full indicator kriging methods provide estimates of depth of contamination at varying levels of significance, defined as the risk of leaving contaminated sediment behind (false negative error). This type of error is balanced against the risk of unnecessarily dredging clean material (false positive error), to inform risk management decisions. Performance of alternative methods, as well as performance of the full indicator kriging method at a range of significance levels, was compared using cross-validation metrics. These metrics included sensitivity, specificity, false positives, false negatives, bias, mean absolute error, and root mean squared error. The hybrid ordinary/indicator kriging method and the full indicator kriging method showed excellent agreement and very comparable performance metrics; however, full indicator kriging showed less attenuation of extreme values (i.e., overestimation of shallowest areas, and underestimation of deepest areas. River straightening further improved performance. The use of the interpolations as the basis for dredging design, and applications of similar techniques to other contaminated sediment sites, will also be discussed.

The Influence of Carbonaceous Organics on the Sampling, Analysis, and Remediation of PAH Contaminated Harbor Sediments

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Studies by Means (1980), Talley et al (2002), and Ghosh et al (2004) have shown that particulate organic matter can play a prominent role in the adsorption and bioavailability of soil and sediment contaminants like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). An ongoing evaluation of a pilot-scale harbor sediment remediation project conducted in Duluth, Minnesota, since 2002 has highlighted the technical challenge of treating a heterogeneous sediment matrix that contains significant amounts of such particulate matter, i.e., carbonaceous organics like coal tar, coal, and vegetation. The pilot project has tested and evaluated an electrochemical remediation technology developed by Electro-Petroleum, Inc. of Wayne, PA, and electrochemical processes, llc Stuttgart, Germany. The technology, called Electro Chemical Geo-Oxidation (ECGO), has been applied to dredged harbor sediments contaminated with moderate levels, e.g., 150ppm to 200ppm, of PAHs in both a simulated submerged and heaped application.

Analytical results from the Duluth project illustrate two major findings related to the influence of particulate organics. First, the results appear to suggest that previously non-extractable PAHs, i.e., those strongly adsorbed to coal or other organic/carbonaceous particles (and therefore non-detectable by typical PAH analytical techniques), can be converted to an extractable (and therefore detectable) form via a desorption mechanism imparted by the ECGO process. Second, particles of coal tar present within the sediment contribute to a significant PAH "nugget effect" especially when the PAH concentration in the nugget is grater than 7.5 % of the nugget mass. If one follows EPA sampling protocols the larger "nuggets" may be removed from the sample prior to send to the laboratory for analysis. This nugget effect impacts sampling strategies, complicates the interpretation of analytical results, and even calls into question how meaningful those analytical results are from a remediation evaluation and regulatory perspective.

We discuss these analytical findings and our overall Duluth experience in greater detail, and offer strategies for how similar sediments and soils should be sampled, analyzed, and treated in future remediation projects.

Sediment Equilibrium Partitioning Benchmarks for Energetic Compounds: A Cautionary Note and Alternate Approaches

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The ecological risk assessment process uses ecological screening values (benchmarks) to identify constituents of potential ecological concern (COPECs). The relative lack of sediment screening values for energetics and other polar non-ionic compounds has led to the use of the equilibrium partitioning (EqP) method for the derivation of benchmarks. That method is intended for use with organic compounds for which hydrophobicity dominates the pore water-to-particle partitioning relationship. However, other intermolecular forces may increase the partitioning to sediment particulates for compounds with a low octanol-water partition coefficient (log Kow), such that the EqP model may substantially overestimate the potential for exposure (and therefore risks). A recent EPA procedure for deriving EqP benchmarks states that this method should be applicable to nonionic organic chemicals with a Kow above 3.0. Yet some published sediment screening values include EqP benchmarks for nitroaromatic explosives and other chemicals with log Kow values less than 3. The resulting benchmarks are on the order of 10 to 100 parts-per-billion in whole sediment. The unrestricted use of such conservative benchmarks may lead to limited resources being wasted on detailed evaluations or remediation of spurious COPECs. Alternative approaches for evaluating sediment concentrations of energetic compounds include using literature-derived Kd values for similar systems, measuring site-specific pore water concentrations, and performing site-specific biological tests. Understanding the factors that influence partitioning of these compounds will help the risk assessor evaluate the uncertainties associated with the available benchmarks and alternative methods of evaluation.

Technical Challenges on the Marine Hydraulic Dredging Activities, New Bedford Harbor Superfund Site

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Jacobs Engineering Group, Inc. (Jacobs) and Sevenson Environmental Services, Inc. (Sevenson) are conducting remedial activities at the New Bedford Harbor Superfund Site (Site) under contract with the US Army Corps of Engineers (USACE). Funding and oversight for this project is provided by the US Environmental Protection Agency (EPA) through the national Superfund Program. The Site is located in Bristol County, Massachusetts, approximately 55 miles south of Boston. Contamination at the Site consists of marine sediments impacted by polychlorinated biphenyls (PCBs) and heavy metals from industrial activities adjacent to the shoreline.

The selected remedial alternative for the Site involves hydraulic dredging for removal of the PCB-impacted sediment. Following removal, the remedy includes sand separation, sediment dewatering, wastewater treatment, and sediment transportation to an offsite disposal facility. In 2004 and 2005, the Team (Jacobs, Sevenson, USACE and EPA) solved a number of technical challenges related to dredging in this unique marine setting. Hydrogen sulfide (H_2S) gas at concentrations exceeding current permissible exposure levels was immediately released from the marine sediments upon initiation of dredging and processing. The elevated H_2S concentrations were mitigated through engineering controls consisting of chemical treatment and local exhaust ventilation. Ferric sulfate ($Fe_2(SO_4)_3$) was injected into the dredge slurry to reduce or eliminate H_2S by precipitating ferric sulfide (FeS). Slotted hoods were installed to capture any un-reacted H_2S. A second challenge involved maintaining the required dredge production despite the presence of urban debris embedded in the sediment. To overcome this challenge unique equipment was designed to remove the debris while maintaining the low water column turbidity thresholds established for environmental protection. A third challenge presented to the Team was the accurate monitoring of the vertical and horizontal progress of the dredging in the shallow tidal marine setting. This was accomplished by using a combination of tools, including a Global Positioning System (GPS), laser level soundings, and acoustic bathymetric surveys.

Resolving these technical challenges allowed the Team to reduce the risk of personal injury and increase overall productivity. The lessons learned on the New Bedford dredging program can be applied to other freshwater and marine dredging environments where success is measured not only in sediment removal rates per day, but in worker safety metrics and process quality control.

Subaqueous Capping Considerations for Coal Tar Contaminated Sediments

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Subaqueous capping of contaminated sediments is highlighted in the EPA Sediment Remediation Guidance (EPA, 2005) and often offers a cost effective alternative to dredging that addresses risk. Subaqueous caps require knowledge of a prescribed set of key design variables to predict performance, including; groundwater seepage rate, pore water concentration of dissolved constituents, existence of indigenous microbes and their degradation rates, and physical migration of NAPL due to cap construction. This is especially important where coal tar in the form of NAPL is the contaminant driving a remediation. This paper explains how these variables can be determined, illustrates the links between them, and shows how they impact cap design at coal tar sites. Insight into these and other variables has been the subject of on-going research efforts by Purdue University, and this paper presents a summary of those findings. A new type of flux meter, developed and field tested, in cooperation with the USEPA Office of Research and Development is described. This simple flux meter; produces virtually no resistance to flow; addresses gas generation, NAPL migration, and isolation from river flow; and develops high quality repeatable field data. The equilibrium distributions, between the water, and MAH and PAH fractions of coal-tar contaminated sediment have been measured and evaluated for consistency with a Raoult's Law-based quantitative relationship, which allows for the calculation of pore water concentration based on the solubility and mole fraction concentration of the compound within the liquid coal tar. The presence of indigenous microbes capable of degrading coal tar constituents and their ability to be revived to colonize a cap are demonstrated. Lastly, a series of experiments to assess NAPL migration into the cap were performed to increase confidence in determining cap thickness.

Site Assessment

Characterization of a Nitrate and Technetium Plume with Environmental Geophysics

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Investigating Coal Tar NAPL in Primary and Secondary Fractures in Bedrock

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Estimating UXO Spatial Density Using a Composite Index Technique

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Concentrations of 170 Analytes in Rural New York State Surface Soils

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Vertical Delineation of BTEX Using Soil, Soil Gas, and Tree Core Sampling

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Characterization of a Nitrate and Technetium Plume with Environmental Geophysics

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Fissile material production generates an enormous quantity of liquid inorganic and radioactive waste. During the Cold War, Hanford, a production facility located in eastern Washington, generated billions of gallons of nitrate waste laden with transuranics and other radionuclides, heavy metals, and organics. The waste was disposed in either large sealed tanks or disposed directly to the ground in unlined trenches, cribs, reverse wells, and ditches. With a thick vadose zone, it was originally anticipated that the contaminants disposed directly to the ground would not likely reach the water table in any measurable time period. To demonstrate waste migration beneath a former disposal site, a geophysical study was conducted on the Hanford complex at a site that contained 22 trenches and 6 cribs. The site, called the BC Cribs and Trenches Site, received approximately 30 million gallons of sodium nitrate waste, with upwards of 400 Ci of Tc-99 during the period of 1956-1958. The geophysical study mainly included electrical resistivity to map the distribution of electrical properties to a depth of 60 meters. The results of the survey showed that most of the waste is tied up in the vadose zone. However, one area near the cribs may have had a breakthrough and nitrate waste could be reaching the water table located 120 meters below ground surface. A correlative analysis was used to convert electrical properties to nitrate concentrations, with a calculated mass balance that agreed well with the disposed mass. Although not *directly* imaged with electrical resistivity method, a strong correlative relation also exists between the electrical properties and the Tc-99 concentration, which has similar transport properties as the nitrate.

Investigating Coal Tar NAPL in Primary and Secondary Fractures in Bedrock

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The investigation of coal tar in bedrock at manufactured gas plant (MGP) sites can sometimes prove to be a daunting, costly, and a physically difficult task. Investigations led by blindly installing wells in the supposed upgradient and downgradient locations at a site may be case limiting to gathering an optimal set of data. Approaching a site investigation with the intention of collecting bedrock specific information on fractured networks lays a foundation for the better placement of secondary or tertiary well sets. A fracture-specific investigation approach to a well installation project may improve future site conceptual models. Using an assortment of down-hole tools helps provide qualitative data sets and also can improve the interpretation of groundwater flow in fractured networks. The sorptive capacity of certain rocks varies considerably and influences the flux of coal tar movement in fracture networks. Investigating both the matrix and secondary porosity of bedrock during continuous coring operations provides insight into the storage capacity of a fractured network. Contaminants can either sorb to rock or diffuse through fractures depending on the rock type. Differentiating the ratio between sorption and diffusion partially becomes a function of the ability to isolate discrete fracture networks during down-hole investigations. New promising down-hole bedrock investigation techniques can provide a site investigator with the opportunity to install less intrusive bore holes at a site and yield the same amount of information from many holes drilled. More characterization from one or two wells rather than from many is also more cost effective and reduces the risk of interconnecting fractures at a site which can potentially cause widespread NAPL dispersion in bedrock aquifer fracture networks.

Estimating UXO Spatial Density Using a Composite Index Technique

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Mapping spatial density of Unexploded Ordnance (UXO) at a military training range using conventional methods is costly and dangerous. The presented methodology predicts UXO density by overlaying multiple independent datasets to compute a composite index. At the 21,000-acre Massachusetts Military Reservation (MMR), a 1,600-acre area was divided into one-acre grid cells. Three metrics representing *historical evidence, process knowledge, and present signature* were used to build a relative spatial-density ranking for each cell.

Historical evidence includes records that directly map site conditions or activities related to UXO deposition. These data may include mapped cratered or burned areas or records of training activities, if geographically specific. For MMR, historic air photos revealing temporary vegetation clearance caused by ordnance impact were used to map a time-weighted clearance value for each grid cell. *Process knowledge* leverages the understanding of how the spatial UXO distribution was created. At MMR, because artillery shells were fired at specific targets, we were able to construct a curve of declining UXO density with distance from a known target, based on limited site-specific data. This relation was used to compute a target proximity value for each grid cell. *Present signature* includes data that directly reflect UXO presence in soil. At MMR, aeromagnetic data are available, and median signal intensity correlates with known UXO density. During analysis it was discovered that using the median-intensity statistic reduces the effect of the large metallic target objects. Data sets in this category that may exist at other sites include spectral/remote sensing, and mapped geochemical and geobotanical data.

By compositing the three metrics, a relative index value was created for each grid cell that was then scaled by comparison to areas of known UXO density. A field program designed to validate this methodology through intrusive investigation is planned for summer 2006.

Concentrations of 170 Analytes in Rural New York State Surface Soils

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Few published data describe typical concentrations of chemicals in the shallow surface soils of rural New York State. We conducted a statewide survey that determined concentrations of 170 analytes in 269 discrete surface soil samples collected from randomly selected rural parcels. Rural properties (*n*=125) were selected for sampling using a digitized grid map and a random number generator. Target analytes included volatile and semi-volatile organic compounds (VOCs/SVOCs), organochlorine pesticides (OCPs), Aroclor mixtures of polychlorinated biphenyls (Aroclors), metals, amenable cyanide and total cyanide. Field staff collected at least two types of surface soil samples at each property: a "source-distant" sample and a "remote" sample. Source-distant samples (0-5 centimeters depth) were obtained from areas that were reasonable points of human contact with soil but at least 5 meters distant from potential sources of the target analytes (*e.g.*, trash, roadways, driveways or structures). Remote samples (0-15 centimeters depth) were collected from areas that were not foci of regular human activity. At a subset of properties, staff also collected a "near source" soil sample (0-5 centimeters depth) near a roadway or driveway (*n*=28). After completion of sampling, field documentation and aerial photographs were reviewed to identify a subset of 96 remote samples that were collected from habitat, defined as areas potentially providing food and shelter for wildlife, that appeared only marginally influenced by human activity. Several metals were frequently detected in all sample types, and several SVOCs were frequently detected in near source samples. Most other analytes were rarely, if ever, detected. For example, Aroclors and OCPs were rarely detected, and neither total cyanide nor amenable cyanide was detected in any sample. These data contribute substantially to our understanding of current analyte levels in rural soils, especially with regard to differences among the rural environments surveyed.

Vertical Delineation of BTEX Using Soil, Soil Gas, and Tree Core Sampling

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At a gas station site in Raleigh, North Carolina, free product is encountered 20 ft bgs at the station grade and 10 ft bgs down slope from the station, adjacent to a creek. Mature trees are present on the slope, and, at the station grade, trees were planted to aid in hydraulic containment and phytoremediation. A prior investigation at the site detected low levels of benzene in two tree trunk cores collected down slope. To confirm these results and investigate the concentration gradient from the free phase product up to the rhizosphere, soil gas samples were collected using GORE^{TM} Modules, passive, sorbent-based samplers, placed at three different depths in co-located boreholes. Discrete soil samples were collected at corresponding depths under the mature trees, beneath the phytoremediation stand, and in a treeless area down slope. Modules were also inserted into tree core holes to determine BTEX presence within the tree systems.

Soil gas and tree cores were analyzed for volatile and semivolatile organic chemicals and soil samples were analyzed for VOCs only. The soil gas results showed a two to three order -of - magnitude decrease in BTEX mass within five feet of the free phase gasoline interface; BTEX was trace to undetectable in shallow (2.5 bgs) soil gas and core samples. BTEX was observed in GORE^{TM} Modules inserted into tree core holes. In this field investigation, the GORE^{TM} Modules were effective in delineating the vertical extent of BTEX in soil gas; this ability may prove useful in vapor intrusion investigations. The module placement inside the tree is in effect an in-tree extraction, and reflects the uptake of these compounds by the tree. When compared to repetitive tree trunk coring with an increment borer, sampling with GORE^{TM} Modules is minimally invasive, sensitive to low concentrations, and may allow for repetitive sampling.

Vapor Intrusion

Near-Building and Structure Sampling Results from Vapor Intrusion Sites in New York, Implications for Site Screening Approaches

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Using a Weight of Evidence Approach to Show no Indoor Air Impacts at Homes Located at a Site Impacted with Chlorinated VOCs

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Vapor Intrusion Attenuation Factors Based on Long-term Data

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The Use of Tracer Gas in Soil Vapor Intrusion Studies

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Emerging Approaches for Weighing the Significance of the Vapor Intrusion Pathway at Petroleum Hydrocarbon Sites

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A Practical Guideline to Vapor Intrusion: ITRC's Perspective

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Near-Building and Structure Sampling Results from Vapor Intrusion Sites in New York, Implications for Site Screening Approaches

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Over the past several years, the New York State Department of Environmental Conservation, in partnership with the New York State Department of Health, have undertaken a comprehensive evaluation of the vapor intrusion pathway at remedial sites throughout the state. Investigations have taken place or are underway at more than 250 sites, and more than 70 sites have required installation of mitigation systems to address exposures associated with vapor intrusion. Based on the information obtained from these sites, it is clear that spatial, and to a lesser degree temporal, variability in soil gas contaminant concentrations are significant factors that must be addressed in the site screening process. At many sites, there are significant differences between the soil gas concentrations of samples obtained from probes near (< 100 feet) structures and from the neighboring sub-slab probes. Near-structure soil gas probe data often under-represent the concentrations of soil gas obtained from sub-slab structures at nearby structures. Accordingly, New York State routinely includes structure sampling programs into almost all vapor intrusion investigations where even low-level (5 Fg/m^3) concentrations of chlorinated VOCs are observed in soil gas samples.

Using a Weight of Evidence Approach to Show no Indoor Air Impacts at Homes Located at a Site Impacted with Chlorinated VOCs

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Although the risk assessment for the site showed there is no significant risk posed by chemicals from the site, a residential indoor air-testing program was completed at the request of local officials and residents. The objectives of the sampling program were to determine if the site groundwater plume is a source of VOCs detected in indoor air samples, and if so, to (1) assess if the levels of VOCs present in indoor air were above published background concentrations and, (2) assess whether those VOCs pose a potential significant risk of harm to human health.

Shaw sampled indoor air in approximately 30 homes during the summer and again during the winter. Using a weight of evidence approach, Shaw was able to show that the VOCs in indoor air had not come from the site, nor is there any significant risk to residents from the site. Sampling and data evaluation in this indoor residential air assessment was completed in accordance with recently published state guidance.

Vapor Intrusion Attenuation Factors Based on Long-term Data

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Screening for vapor intrusion potential is likely to be required at a large number of sites in the future, due to federal or state requirements, real estate transactions, or voluntary cleanups. At many sites, only groundwater data will be available in sufficient quantity to conduct initial screening. Therefore, groundwater data will tend to drive the need for additional vapor intrusion investigations. The current EPA subsurface vapor intrusion screening guidance (EPA 2002) assumes that soil vapor concentrations immediately above the water table are at equilibrium with groundwater concentrations and that indoor air concentrations in overlying buildings are 1000 times lower (an attenuation factor of 10-3), due to attenuation through the soil column and building shell. According to EPA (2002), attenuation factors based on groundwater and indoor air measurements are less than 10-3 approximately 95% of the time. Unfortunately, the resultant groundwater screening levels are often at or below federal drinking water standards (MCLs). In most cases however, the data used to develop this attenuation factor were based on measurements of groundwater and indoor air at one point in time. Groundwater and indoor air monitoring at a number of houses in Colorado over the past eight years has allowed comparison of attenuation factors based on 1,1-DCE at single points in time and on long-term averages. These data indicate that single point measurements can significantly differ from long term average attenuation factors. The upper bound attenuation factor based on short-term tests at several hundred homes was about 10-3, similar to the findings of the EPA studies. However, short-term attenuation factors were observed to vary by one-half to one order of magnitude over time in homes where long-term monitoring was conducted. Long-term attenuation factors were in the 10-5 to 10-7 range, with a 95 percentile of approximately 10-5. Vapor intrusion screening levels based on long term average attenuation factors and groundwater concentrations may provide a more realistic approach to vapor intrusion screening in the future.

The Use of Tracer Gas in Soil Vapor Intrusion Studies

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There has been a rapid rise in the need for soil vapor intrusion (SVI) assessments to meet environmental compliance requirements regarding brownfields development and asset improvement.

Our approach to SVI sub-slab testing for existing structure interiors incorporates a tracer gas monitoring technique that has proven to be very cost effective. This method allows for verification that the sample collected from beneath an impervious surface is truly isolated from the ambient air inside the building. Implementation of this method has met with the approval of New York regulators and is consistent with their Soil Vapor Intrusion Guidance, which was published in 2005.

An inert tracer gas is used to first blanket the surface of the slab and a gas tight seal is formed between atmosphere and the sub-slab sample targeting point, sometimes just inches below the ambient space. The sample point is isolated with a small enclosure that is then charged with the tracer gas until the concentration exceeds 90%. The isolated sampling point below grade is then purged and tested for the same tracer gas to measure the potential for sampling influence (or bias) from the overlying ambient space. Once it has been determined that the target sample is relatively free from bias (by a measured tracer gas concentration of 10% or less), sampling proceeds. The tracer gas blanket and sampling space are monitored throughout the sampling period to ensure that the potential for ambient air to migrate into the sampling zone is minimized.

For sample collection, the events targeted VOCs by Method EPA TO-15. However, other data collection efforts using calibrated pumps and sampling media, such as EPA TO-11A for the measurement of Formaldehyde, also were used.

The reduced time and effort associated with these sampling techniques allow for expedited assessment of analytical data and early recognition of potential environmental risks associated with the purchase and improvement of real property.

Emerging Approaches for Weighing the Significance of the Vapor Intrusion Pathway at Petroleum Hydrocarbon Sites

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While it is increasingly recognized that the potential for subsurface petroleum vapors to migrate inside buildings is less for than chlorinated solvents, developing reliable site screening approaches remains a challenge. The complexity arises from the difficulty in quantifying the significance of biodegradation and background sources of petroleum-derived compounds in indoor air. Improving our understanding of which combinations of site characteristics are significant for petroleum vapor intrusion (e.g., foundation type, source strength, vertical and horizontal source location relative to a building, and petroleum type), may lead to a more useful screening approach. Our goal is to identify the types of sites that truly need additional site-specific data collection before a decision can be made about the significance of the pathway. Several promising approaches are emerging that should improve our ability to screen petroleum sites including: 3D vapor and oxygen transport modeling, vertical profiling of unsaturated zone hydrocarbon and oxygen soil gas concentrations, and the use of tracers and pressure measurements for assessing transport and attenuation across the foundation.

A Practical Guideline to Vapor Intrusion: ITRC's Perspective

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The Interstate Technology & Regulatory Council (ITRC) formed a Vapor Intrusion Team in January 2004 to prepare guidance that would present a comprehensive national approach to the evaluation, investigation and remediation of VI sites. Once completed, the goal of the team is to reach concurrence with all 50 state environmental agencies and provide Internet and classroom training to state regulators, consultants and interested parties.

Working with a diverse group of state and federal regulators, environmental consultants, Department of Defense personnel, industry representatives, and community stakeholders, ITRC's VI Team has conducted two regulatory surveys and prepared a series of guidance documents to meet that goal.

The ITRC approach is outlined in the companion documents, Vapor Intrusion Pathway: A Practical Guide and Vapor Intrusion Pathway: Investigative Approaches for Typical Scenarios. Both guidance documents have recently completed external review and should be released by December 2006.

An overview of the vapor transport mechanisms involved in the VI pathway, as well as the complicating factors that influence the collection and interpretation of analytical data are discussed in the documents. A basic framework for the preliminary assessment, investigation and mitigation of the VI pathway at a contaminated site is provided. The investigation of six typical scenarios (e.g., gas station, dry cleaners, Brownfields) are presented with detailed discussions on workplan development, sampling, data interpretation, and technical rationale.

Since various states express a wide range of comfort about the data types that are acceptable for assessing a site, the ITRC approach is not prescriptive as to the specific investigative tools or technical methodology appropriate. Rather, it is intended to assist the investigator in understanding the factors and techniques that may be used to assess the vapor intrusion pathway. A comprehensive directory of mitigation methods is included with detailed information on passive and active building control remedies, institutional controls, ongoing monitoring and maintenance, sitewide approaches and closure.

Tuesday, October 17, 2006

Poster Session- Acid Mine Drainage

Short-term and Long-term Passive Treatment of Acid Mine Drainage in Bioreactors

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An Overview of Occurrence and Evolution of Acid Mine Drainage in the Slovak Republic

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Short-term and Long-term Passive Treatment of Acid Mine Drainage in Bioreactors

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Passive biological treatment of acid mine drainage (AMD) relies on sulfate-reducing bacteria (SRB) supported by a biodegradable organic carbon source. Treatment long-term performances can be limited by degradation rates of organic carbon available to SRB, and low metal stability in spent reactive mixtures.

The first part of this study focused on characterization of six natural organic materials and their short-term effectiveness in sulfate-reduction and metal removal from synthetic AMD. In the second part, long-term performance and metal forms in the reactive mixtures were assessed. Maple wood chips, sphagnum peat moss, leaf compost, conifer compost, poultry manure and conifer sawdust were analyzed in terms of their carbon and nitrogen content, as well as their easily available substances content (EAS). Single substrates and a mixture of them were tested in a 70-day batch experiment (2-L reactors) and in an extended study for up to 350 days. Geochemical modeling and scanning electron microscopy (SEM) was used to assess the minerals present in the solid phase.

The highest EAS content and the lowest C/N ratio suggested poultry manure as the best substrate. Nevertheless, the lowest efficiency was found in the poultry manure reactor, whereas the mixture of three organic materials was the most effective. After 350 days, the mixture of organic carbon sources was still efficient for AMD treatment. SEM analysis of the solid phase indicated the presence of iron sulfides.

Substrates' characterization provided insight on organic carbon availability but did not inform of their ability to promote sulphate-reduction and metal removal. Further research is needed to accurately predict long-term carbon availability and to assess the metal forms in spent reactive mixtures.

An Overview of Occurrence and Evolution of Acid Mine Drainage in the Slovak Republic

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The mining activity which markedly affecting the water quality has in the Slovak Republic (the Middle Europe) the hundreds of years old tradition. The attenuation of mining activity mainly at the beginning and in the middle of twentieth century gave rise to extensive flooding of sulphide ores with the contents of Cu, Fe, Au, Ag, Zn, Pb, Sb, and Hg. Thereby were formed the suitable conditions for generation of acid, high mineralized mine waters, known as Acid Mine Drainage – AMD, which negatively affects the surrounding environment.

The article presents the results of monitoring of acid mine drainage at the flooded sulphide ores realized at the Institute of Geotechnics of the Slovak Academy of Sciences in Kosice. The monitoring was realized at 24 localities in the area of West Slovakia, Middle Slovakia and in the area of East Slovakia.

On the basis of quantitative chemical analysis of metals, sulphates, pH, and Eh we evaluated the situation at the localities and their assumed evolution into the future. The locality Slovinky was flooded lately and the locality Rudnany is flooded only partly. At these localities will be interesting to observe the process of generation and evolution of AMD, which activity begins influencing. The localities Sobov and Smolnik were the preferred localities of the research and they are the classical example in term of generation and occurrence of AMD. AMD at these localities very markedly and negatively affects the surrounding environment.

Poster Session- Analysis

Sampling and Chemical Analysis of Cranberries Potentially Affected by the Localized Discharge of Groundwater Containing Ethylene Dibromide

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Sampling and Chemical Analysis of Cranberries Potentially Affected by the Localized Discharge of Groundwater Containing Ethylene Dibromide

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Groundwater contaminated with ethylene dibromide (EDB), referred to as the Fuel Spill-28 (FS-28) plume, is currently migrating beneath a series of commercial cranberry bogs within the Town of Falmouth, Massachusetts. The FS-28 plume is detached from its source, which is inactive and located on the Massachusetts Military Reservation (MMR). Although most of the FS-28 plume is being captured by an extraction-treatment-discharge system operated by the Air Force Center for Environmental Excellence (AFCEE), EDB was detected at very low concentrations (0.012 micrograms per liter) in the summer of 2005 in ditches adjacent to the Augusta Bog for the first time in 6 years. These ditches represent areas of groundwater discharge. To determine if the discharge of groundwater containing EDB actually affected the cranberry fruit in the Augusta Bog, the Air Force Center for Environmental Excellence sampled and analyzed cranberries for EDB. Samples were analyzed using gas chromatography mass spectrometry with Selected Ion Monitoring. Advantages in using this method included low method detection limit (MDL) and the ability to target a specific compound. A critical component was the performance of a MDL study for this non-traditional environmental medium (i.e., homogenized cranberry fruit). The results of the study established a MDL sufficiently low to meet the project data quality objectives. EDB was not detected above the MDL in any of the cranberry samples.

Poster Session- Environmental Fate

Determining the Influence of Cranberry Bog Flooding on Plume Migration

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Contamination of Soil and Groundwater by Leaking Sewers

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Determining the Influence of Cranberry Bog Flooding on Plume Migration

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A study was performed to determine the influence of cranberry bog flooding on groundwater plume migration at the Massachusetts Military Reservation. These cranberry bogs are flooded to facilitate the harvesting of the berries in the fall and for frost protection in the winter. This flooding changes the bog water levels by up to three feet, either continuously or intermittently, from October through March. Hydrologic changes of this magnitude can produce changes in the groundwater flow field near the bogs. Since the annual flooding lasts for five or six months, these changes have the potential to modify plume migration and contaminant discharge near the bogs. The purpose of this study was to identify the effects of bog flooding on plume migration and discharge, and evaluate the differences between model-simulated plume migration under transient flow conditions and migration simulated under traditional steady-state flow.

The data collection effort focused on two areas; understanding the bog flooding practices, and measuring the hydraulic response in the aquifer due to the flooding. A yearly record of bog flooding practices was divided into multiple characteristic periods that mimic the actual sequence of water-level variations. To record the hydraulic response in the aquifer, continuous water level measurements were collected at numerous multi-screen wells and staff gauges in and around the bogs.

The field data were used in concert with the model to evaluate the magnitude and extent of the hydraulic differences between the flooded and non-flooded conditions. The need for focused adjustments to the model aquifer parameters was evaluated. The model was then used to evaluate the differences in simulated plume migration between runs using the average steady-state flow fields and the transient flow fields that reflect the effects of seasonal bog flooding.

Contamination of Soil and Groundwater by Leaking Sewers

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At least half of the sewers in Germany or most European countries are more than 50 years old. Leaks lead to losses of sewage as high as 20 % of the total amount. However, the German soil protection law, based on EU regulations, does not allow to pollute soil and the underground with any anthropogenic substances, including sewage. We investigated the fate of sewage, that trickles from leaky sewers into the unsaturated soil and from there into the groundwater.

Normally, sewers are layed in more than 3 m depth below the surface and there is not much oxygen available for aerobic respiration of sewage compounds. Under mainly anaerobic conditions, between 75 and 85 % of the COD of sewage is degraded during passage of sewage through the unsaturated underground (dry weather conditions, low groundwater level) or the saturated underground (rain weather conditions, high groundwater level). Even if enough oxygen would be available all the time, degradation of COD would not excede the 92 – 94 % COD-removal, that are obtained in sewage treatment plants, although most of the biodegradable compounds are degraded in the first 25 cm trickling stretch of sewage already. In soil columns in the laboratory nitrogen compounds are leaving the columns after 1.25 cm trickling stretch as ammonia and little nitrate, most of the nitrate being denitrified in the columns after biofilm development. Heavy metal ions are precipitated mainly as sulfides in the first 25 cm (which provide anaerobic conditions) after the sewage left the sewers. If oxygen would be available, re-oxidation and solubilization of metal sulfides would be possible. In a sandy/silty soil the grains themselves would adsorb most of the metal ions presumably by ion exchange reactions.

A biofilm is formed with time on the sand particles of the soil, which influences the trickling rates to some extend and which stabilizes the purification effect of the soil. More than 99 % of the microbial flora of the sewage are filtered off or attached to the biolfilm during trickling of sewage. Never-the-less, more micororganisms leave the sandy soil after 125 cm trickling stretch than allowed e.g. by the European Bath Water Directive. Most of the bacteria have an increased multiple antibiotic resistance spectrum against therapeutically applied antibiotics and antibiotics produced from the indigeneous soil flora, such as pseudomonads or Streptomycetes sp..

The residual organic compounds in the effluent of the soil columns resemble humic compounds (humification), have a higher proportion of non readily degradable organic matter such as aromatic compounds, in comparison to the non-aromatic residues and are distributed with the groundwater.

The above mentioned investigations were part of a multi-discipline research project on “Risk assessment of sewage from leaky sewers for soil and groundwater” at the University of Karlsruhe, funded by Deutsche Forschungsgemeinschaft and coordinated by J. Winter.

Poster Session- Heavy Metals

Effect of pH on Partitioning and Leaching of Heavy Metals from Bottom Ash
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New Approach to Inactive Landfill Containing Wastes of Mercury and other Heavy Metals
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Effect of Microwave Processing on the Leaching Characters of Sediment Sludge with Heavy Metals
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Investigation of the Use of Mine Tailings for Unpaved Road Base Construction
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Reference Values for Heavy Metals Concentrations in Sediments of River Tietê Basin, Southeast of Brazil
Marcos R. L. Nascimento, Comissão Nacional de Energia Nuclear, Poços de Caldas, Brazil
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Sites in the Republic of Slovenia Polluted by Heavy Metals and their Remediation
Branko Druzina, University of Ljubljana, Ljubljana, Slovenia
Andrej Perc, E-NET Environment, Ljubljana, Slovenia

Mathematical Modeling and Experimental Studies on Biochemical Conversion of Cr^{+6} of Tannery Effluent to Cr^{+3} in a Chemostat
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Absorption of Antimony in River Water by Weathered and Altered Rock
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Etsuko Chiba, Ehime University, Matsuyama, Japan
Rie S. Hori, Ehime University, Matsuyama, Japan

On Site Quantitative Evaluation of Heavy Metal in the Soil by New Micro Cartridge Type Heavy Metal Measuring System, Geo-REX™
Ryuji Takeda, Kinki University, Nara, Japan
Kazuaki Nakagawa, Kinki University, Nara, Japan
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Poster Session- Heavy Metals

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Effect of pH on Partitioning and Leaching of Heavy Metals from Bottom Ash

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Texas 7-days leaching tests were conducted on three different types of bottom ashes at four different pHs (3, 6, 9, 12) to understand the leaching pattern of heavy metals, such as Cr, Cu, Ni, Se, Zn, and Al. The leaching of Cr, Cu, Ni, Zn, and Al increased with decreasing pH, where as, the leaching of Se decreased with decreasing pH. Total amounts of metals in bottom ashes were determined from total elemental analysis and the partition coefficients of metals in solid and liquid phase were estimated for each different pHs. Partition coefficients of metals in bottom ashes were compared with that of similar types of materials, such as fly ashes and soil at similar pHs and the partition coefficients in metals in bottom ashes are generally much lower than the other two materials.

New Approach to Inactive Landfill Containing Wastes of Mercury and other Heavy Metals

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The article presents analysis of some complex problems connected with old closed landfills in Poland, illustrated by some examples of municipal and industrial sites. These landfills have been usually protected without any assessment of filtrating abilities of the layers below the bottom and the layers directly surrounding wastes, or with no analysis of the soil physical and chemical properties, microstructure, and so on. Control of the inactive waste disposal sites includes only tests of composition of leachate (randomly drawn), time of sampling is not related to remediation intensity, sampling frequency is usually not established. In general, waste composition is not analysed, percentage of the deposited waste coming from local industry remains unknown. Technical solutions tending to maximum possible stoppage of impurities in the inactive landfills are proposed. Such solutions allow to reduce influence of impurities on geological environment, namely they must be separated from the environment by special walls (screens against filtration) made as cavity walls. In the case of permeable soils below the landfill bottom, and the impermeable layer is very deeply under the bottom, it is possible to stop vertical filtration owing to formation of an impermeable horizontal layer below the bottom. These protections are expensive, but the costs should be compared with the costs resulting from the protection lack, i.e. invaluable loses for environment and local community. The known methods should be improved all the time, and waste materials should remain in the disposal sites to the moment of application of new remediation techniques. Co-disposal of hazardous and municipal wastes need a special analysis. Very important is monitoring of changes in chemical composition of wastes mass during bioremediation.

Effect of Microwave Processing on the Leaching Characters of Sediment Sludge with Heavy Metals

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The large quantity of industrial wastewater contains a high level of heavy metal ions. During the bio-treatment the heavy metals are removed into the sediment sludge which may cause serious soil and underground water pollution through a metal ions leaching process in the direct disposal at landfill sites. The objective of present study was to investigate the heavy metals (Cu^{2+}, Cr^{6+}, Zn^{2+} and Pb^{2+}) behavior during leaching procedure of sediment sludge which was dried by microwave radiation and blast heating respectively. And the immobilization mechanism of heavy metals in microwave drying sludge was discussed further. The sediment sludge could be dried quickly in the 900W microwave and the energy consumption was much lower than the blast heating. The stabilization of drying sludge was evaluated from different metal leaching tests. The results showed that the concentration of heavy metal in the supernatant liquid from the microwave drying sludge in the aclinic shake leaching test was declined by 70%~63% compared with the sludge dried by blast heating. And the heavy metals concentrations of microwave drying sludge in the leaching test of simulated natural waters conditions were much less than the blast heating one. The immobilizing effect of heavy metals in microwave drying sludge was determined in descending order as Pb^{2+}, Zn^{2+}, Cr^{6+}, Cu^{2+}. The chemical composition and pore structure were explored by scanning electron microscopy and X-ray diffraction. And it was determined that the heavy metals were fixed into the 0.075 um ~0.75 um pores of stabilized matrices by following procedures, crack and pile up the cell wall of sediment sludge, package up the metals in the fragments, and fusing to fix the heavy metals. This investigation gives a better understanding of immobilization of heavy metals into sediment sludge.

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Investigation of the Use of Mine Tailings for Unpaved Road Base Construction

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Tailings have been traditionally stored in ponds surrounded by tailings dams for many years but since many accidents, including fatal ones, took place that involved tailings dams, a new approach has become necessary for their storage. An approach devised by Robinsky in the early seventies for the storage and disposal of mine tailings suggests that it is more advantageous environmentally to strengthen the tailings before disposal. This work attempts to emphasize this point by seeking to explore the possibility of using these hardened tailings as base materials for the construction of unpaved (temporary access) roads. Six different types of tailings that represent a cross section from several mines in eastern Canada are used and preliminary physical characteristics tests were performed followed by unconfined compressive testing. Initial results indicate that the tailings sustained more than the minimum amount of stress normally required for filling stopes and the layer coefficients determined for five of the tailings used match reasonably well with values from ten United States state departments of transportation.

Key words: tailings, Portland cement, heavy metals, unconfined compression.

Reference Values for Heavy Metals Concentrations in Sediments of River Tietê Basin, Southeast of Brazil

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This paper represents the first effort in Brazil towards the proposition and establishment of reference concentrations values for metals and metalloids in bottom sediments of freshwater. The selected study site is the Tietê River basin (São Paulo State, southeast region), a watershed which is under significative environmental impact and degradation since the onset of the Brazilian revolution at early-midd 50's. In order to consolidate the analytical values, metal and metalloids determinations were performed encompassing 84 sampling points in 27 municipalities, from the upper stream parts of the river down to its mouth at the Paraná River. Sediment samples were collected in small streams and rivers as closest as possible to their upper reaches, as well as in rivers and reservoirs in locations minimally affected by human contamination. Samples were initially sieved for separation of the particles <63 µm, dryed at 50 °C, submitted to extraction with a mixture of HNO_3 and H_2SO_4 acids for mercury determination, or with a strong acid attack (HNO_3, HF, $HClO_4$ and HCl) for solubilization of others elements. Chemical analyses were performed by inductively coupled plasma atomic emission spectrometry for Co, Cr, Cu, Ni, Pb, Ti, Zn and V, and by atomic absorption spectrometry using graphite furnace for Cd and Ag, hydride generation for As and Se, and cold vapor for Hg. Molecular absorption spectrophotometry, using Arsenazo III as colorimetric reagent, was used for U and Th determinations. The reference concentrations determined by this study showed significant differences regarding the assumed global geological reference for some elements; differences were also detected among the concentrations of the same element from different basin regions, and they can be attributed to differences in regional geochemical characteristics. Four different sets of reference concentrations values are being proposed to different regions of the studied basin as a consequence of these lithological variations.

Sites in the Republic of Slovenia Polluted by Heavy Metals and their Remediation

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In the Republic of Slovenia there are five larger sites polluted wit heavy metals. The largest is the waste disposal site of the lead and zinc mine in north part of the country, the second is the waste and tailing disposal site of the world second largest mercury mine. Both mines are now closed.

The other three sites are smaller as above described and they are: the tailings disposal site of the uranium mine, the waste disposal site of the ironworks and the waste disposal site of the aluminium processing plant. The article will present up to date data on the quantities of disposed wastes as well as measurements of some parameters connected with harmful effects on the environment and on the human health.

Hazardous heavy metals from mines are monitoring in the soil, flowing waters, groundwater and in the air. In some cases they are monitoring also in some vegetables and in tissues and organs of humans. The results of blood analysis for the content of heavy metals for mine workers and the general population will be presented for two mining towns.

On the largest sites, the waste disposal site of lead and zinc mine and the waste disposal site of mercury mine, some remediation activities are in progress.

The results will be presented in graphs and tables.

Mathematical Modeling and Experimental Studies on Biochemical Conversion of Cr^{+6} of Tannery Effluent to Cr^{+3} in a Chemostat

STUDENT PRESENTER

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Biodegradation of hexavalent chromium present in tannery waste has been studied using *Pseudomonas* sp. (JUBTCr1) and *Bacillus* sp. (JUBTCr3) isolated from their native source. A 5L double-jacketed chemostat with 4L working volume has been used as contacting device for the kinetic investigation of the biodegradation process. Varying the feed volumetric rate from 118-133 ml/h for different inlet hexavalent chromium concentrations (30 to 90 mg/dm^3), an attempt has been made to study the reaction engineering behavior of the system. It is observed that Haldane type substrate inhibited model can satisfactorily be used to predict the extent of bioconversion for different dilution rate. Using the kinetic parameters of proposed Haldane equation, a CSTR model was developed. Model prediction agreed well with experimental data.

Absorption of Antimony in River Water by Weathered and Altered Rock

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We report the ionic migration of antimony during the chemical weathering, with some particular cases. Ichinokawa abandoned mine, Japan, is famous to produce stibnite. The antimony deposits are mainly in Sambagawa metamorphic rocks and the brecciated rocks (Ichinokawa breccia) formed through a hydrofracturing process associated with hydrothermal fluid related to Tertiary igneous activity around the area.

Antimony content in river water around the mine is extremely high (over 200 ng/mL), which means antimony dissolves into the water from the country rocks by the chemical weathering. We examined the antimony contents in variously weathered and altered country rocks forming the streambed, to understand the transfer of the element. Consequently, antimony content in brown-colored, strongly weathered and altered part of the rocks is higher than that in the weakly weathered part. The antimony content in strongly weathered part is several tens to hundreds ppm, although the content in weakly weathered part show significantly low, sometimes under the detection of XRF. They probably indicate that the antimony in the river water is adsorbed selectively to the strongly weathered and altered part of the streambed rock. The strongly weathered and altered rocks contain many clay minerals and iron hydroxides, which the minerals may trap antimony ion from the water.

The similar phenomenon is recognized from the other area. This probably means that a high distribution of antimony ion into the strongly weathered and altered rocks including clay minerals and iron hydroxides against the water is ubiquitous.

On Site Quantitative Evaluation of Heavy Metal in the Soil by New Micro Cartridge Type Heavy Metal Measuring System, Geo-REX™

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Since the Soil Contamination Countermeasure Law was enforced in Japan on February 2003, interest in land pollution and its remediation have been increasing. This law requires land owners or polluters to remove land pollution, thus restoration of polluted land has become an important issue. In particular, land pollution investigation must be conducted more rapidly. In the official methods, a dissolution test is used. Quantitative analysis of heavy metals is performed by Atomic Absorption Spectrophotometry (AAS) or Inductively Coupled Plasma spectoroscopy (ICP). However, it takes several days until preliminary treatment and the measurement results are available. In addition, the investigational running cost is high and the exhaustive survey of large site requires much labor. In this study, we compared the official method using AAS or with our new quick heavy metal measuring system based on voltammetry method. Then we considered whether on-site screening investigation as possible.
In comparison with the official method, we were able to largely shorten the measurement time. Correlations of measurement with our new instrument and AAS or ICP were good. Our new micro cartridge type heavy metal measuring system, Geo-REX proved to be a highly useful screening apparatus for on-site land pollution assessment.

Poster Session- Innovative Technologies

The Versatility of Organoclays for Permeable Barriers

George Alther, Biomin, Inc., Ferndale, MI

Remediation of a Clay Contaminated with Petroleum Hydrocarbons using Soil Reagent Mixing

Vito Schifano, Arcadis Geraghty and Miller International Ltd, Newmarket, UK
Billie-Jo Thibault, Arcadis BBL, Boston, MA

The Versatility of Organoclays for Permeable Barriers

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Permeable barriers at creosote and PNAH containing sediments, require a barrier, which is permeable, and, at the same time, traps creosote and PNAH plumes. Such plumes can also include such organic hydrocarbons as PCP and other chlorinated phenolic compounds, PCB's and BTEX's. Lab tests and actual field applications have shown that organically modified clays are an excellent medium to trap such compounds in groundwater and in sediments at old MPG sites.

The PNAH compounds include naphthalene, pyrene, fluorine, anthrazene and others. Organoclays are very well suited to trap these compounds efficiently. Since pesticides are also a serious problem for groundwater and sediments, a brief literature review is included.

This article reports on various laboratory tests and actual field results, which have been obtained over the years, showing the suitability of organoclays as a component of permeable barriers.

Remediation of a Clay Contaminated with Petroleum Hydrocarbons using Soil Reagent Mixing

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Soil reagent mixing (SRM) is an in-situ remediation technique whereby powder or slurried reagents are delivered and mixed to contaminated soils or sediments by augers or other types of soil mixers. This paper summarises the work carried out for a laboratory treatability study of SRM on soil samples contaminated with petroleum hydrocarbon compounds from a petrol filling station site in Kent, UK. The studies examined the effects of mixing several binder reagents on the concentrations and leachability of the hydrocarbons. Quicklime, Hydrated Lime, Ordinary Portland Cement in a number of different formulations were used in the study. Furthermore, the addition of Gypsum to some reagent formulations was evaluated in an attempt to improve the strength of the binder/soil mix. After mixing the soils with the reagents, pH, temperature, moisture content, Atterberg limits, Total Organic Carbon (TOC) and concentrations of petroleum hydrocarbon compounds were determined on soil and leachate samples extracted from the treated soils. Significant decreases in concentrations of petroleum hydrocarbon compounds were measured in soils and leachates upon mixing of the reagents. The mechanisms responsible for these decreases were examined. The effects of the addition of binders on the Atterberg limits and unconfined compressive strength of the samples were determined. Significant increases in the remolded strength of the clay were observed upon addition of certain binders.

Poster Session- Legal/Regulatory

Will You Be Covered? – Professional Liability Insurance for Environmental Professionals
John G. Nevius, Anderson Kill & Olick, P.C., New York, NY

Pollution Exclusions Not Really Absolute
John G. Nevius, Anderson Kill & Olick, P.C., New York, NY

Wetlands: Federal Programs, Federal Policies, and Innovative Uses
William Schaal, TN & Associates, Vacaville, CA
Daniel Servetas, Shaw Environmental & Infrastructure, Latham, NY
Heide-Marie Dudek, New York State Department of Environmental Conservation, Albany, NY

Will You Be Covered? – Professional Liability Insurance for Environmental Professionals

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For environmental professionals, the uncertainty and variability associated with work involving the natural environment – especially the subsurface – is replete with the risk of litigation and potential liability. You need to understand the legal risks you may face in order to avoid them. You also need to understand the insurance you have in case you or your company gets sued. Implementation of even the best, most well thought-out plans can lead to unintended consequences. For instance, suppose that in performing an environmental site review prior to a commercial real estate transaction, the contaminated property is erroneously given a clean bill of health. Similarly, imagine that the remedial design does not work, there is a collapse, or the perils of chlorinated solvents, hydrocarbons, or indoor air quality are not properly addressed. These kinds of mistakes can carry with them an infinite set of potential risks, including litigation liability. Professional liability insurance, commonly known as errors and omissions ("E&O") insurance, can potentially insulate the environmental professional from this risk of litigation liability. Scientists, engineers, and other environmental professionals not only need to grasp the legal implications of their work, but also to comprehend that ignoring insurance likely will exacerbate future liability. This presentation will provide a basic primer on professional liability insurance designed for environmental professionals.

The first issue is whether there has been a "loss." Insurance policies generally define "loss" to include all damages and judgments rendered against, or settlements entered into by, the policyholder. Not only must there be a "loss" to trigger coverage under an E&O insurance policy, there must also be a "negligent act, error, or omission" committed by the policyholder during the policy period and in the performance of "professional services." A lot depends on the allegations o any lawsuit or other claim. Other issues to be addressed include the timing of notice and what it means to have "claims made and reported" coverage. Common exclusions on coverage will also be discussed, including those relating specifically to "pollution" and to what you knew and when.

Environmental professionals need to understand insurance coverage for their own purposes as well as for those of their clients. Matching the activities conducted to the coverage sold is crucial. Proper disclosure on insurance applications, during the underwriting process and in the event of an actual or potential claim can be the determining factor in whether or not coverage is ultimately obtained. Insurance, just like a chlorinated solvent, can be volatile and may break down when you do not expect it. Don't let this happen to you!

Pollution Exclusions Not Really Absolute

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Soil or other contamination can render real estate undesirable for sale or development. The first order of business then is to address the contamination concerns whether or not the site is on the regulators' radar screen. Whether the necessary investigation and/or remediation will be accomplished depends on the availability of funds. Phase I, Phase II and other investigative reports prepared by environmental professionals often represent the baseline description of environmental conditions. How you present information in such reports has many implications, but may determine whether insurance funds will be available for cleanup. In fact, environmental reports are often used against policyholders seeking insurance for problems they thought were covered. There are a number of exclusions on insurance coverage potentially relevant to soil contamination and other forms of pollution. Insurance companies often push the envelope in citing these exclusions to avoid coverage.

This presentation will cover the history, development, rise, use, abuse and recent legal decisions regarding so-called pollution exclusions. The latest generation of exclusions, i.e., the "absolute" or "total" pollution exclusions use language right out of CERCLA, but have been cited in all kinds of circumstances from ambient background soil concentrations to application of fertilizer, wastewater discharges, paint fumes, chlorinated drinking water, vapor intrusions – even exhaust from the Zamboni at your local ice rink. Earlier generations of exclusions were designed to discourage intentional pollution, but have been used to deny coverage for any releases that could be characterized as gradual.

It is important that environmental professionals do not unwittingly provide ammunition that could be used to deny "environmental" claims and, thereby, prejudice potential funding sources. Many people only think about insurance when they write premium checks. You need to know about environmental coverage in order to properly advise clients facing costly cleanups or liabilities. Whether the issue is tapping historic coverage to off-set present liabilities and fund Brownfield redevelopment or risk management going forward in real estate transactions, this presentation will assist in avoiding common pitfalls.

Wetlands: Federal Programs, Federal Policies, and Innovative Uses

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Wetlands have long been recognized for providing benefits that include recreation and aesthetics; shoreline erosion protection; flood storage; and fish and wildlife habitat. This paper examines wetlands from three related perspectives: 1) federal regulatory programs, 2) federal policy; and 3) innovative technology. In doing so, it aims to strengthen engineering, scientific, and planning practices by highlighting new programs, selected policies, and innovative uses for wetlands. The federal Environmental Protection Agency (EPA) develops programs that actively pursue improvement and protection of wetlands in order to perpetuate the benefits associated with them. For example, the EPA administers the Five Star Restoration Program to promote environmental education through grants to support projects that restore wetlands. Additionally, in early 2006 EPA Region 9 awarded $1.5M for programs that protect wetlands and EPA Region 3 awarded nearly $2.6M for projects that focus on linking state and Tribal program activities to measurable environmental outcomes; particularly no net loss of wetlands, net gain of wetlands and the protection of vulnerable wetlands.

Federal agencies craft and enforce policy to protect wetlands. For example, EPA has prepared guidance documents for national management measures to protect and restore wetlands and riparian areas through the abatement of nonpoint source pollution and to use best management practices (BMP) to control nonpoint source pollution in urban areas. As a result of the 1995 document, “Federal Guidance on the Establishment, Use, and Operation of Mitigation Banks,” released by a consortium of federal agencies, the number of estimated banks exceeded 450 in recent years and nearly 200 more are proposed for future development.

There is a growing international interest in employing wetlands for improving and contributing to environmental quality. Environmental engineers and scientists are constructing wetlands for successful storm water control; treating municipal, industrial, and agricultural waste water; and mitigating mine drainage and landfill leachate.

Poster Session- Miscellaneous

Applied Environmental Forensics For Defining A Nutrient-Based TMDL Target And Reduction Goal

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Communications with the Community: Picking the Right Strategy

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Qualitative and Quantitative Analysis of Water Quality Trends in a Sub-Watershed of the Wachusett Reservoir

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Soy-derived Biofuels as Replacements for Petroleum-derived Fuels

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Applied Environmental Forensics For Defining A Nutrient-Based TMDL Target And Reduction Goal

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This paper describes a unique approach for incorporating environmental forensics as tools for developing a TMDL for nutrients for a small northern Idaho lake (Black Lake), listed on USEPA's §303(d) impaired water body list for total phosphorus (TP). Recent data have shown that Black Lake, which is partially located on the Coeur d'Alene Tribal reservation, is currently eutrophic due to elevated levels of TP. A dispute has continued between the State and the Tribe regarding whether the lake is naturally eutrophic, thus warranting delisting, or whether anthropogenic TP discharges have caused the nutrient impairment, thus requiring TMDL development. Part of the purpose of the study is to determine whether Black Lake is naturally a mesotrophic or eutrophic water body, and whether observed eutrophication represents an historical condition or whether logging, mining, ranching, or other activities could have contributed to its current eutrophic status. To assist in making this determination, paleolimnologic techniques, which integrate data from remains of phytoplankton and zooplankton to infer past lake conditions, have been integrated into the study as an environmental forensics tool. Paleolimnology is known to be a useful tool for helping to set realistic load reduction goals based on lake conditions prior to "impact". These techniques were instrumental in establishing the TMDL target to be used as a basis in calculating the TMDL as well as any necessary load and waste load allocations, and specific load reductions required. This paper will summarize the forensics-based approach used to calculate the TMDL target, explain how the data has been used to infer limnologic characteristics and yield quantitative estimates of key limiting nutrients, and show how numerical modeling techniques (specifically, the Generalized Watershed Loading Function and the BATHTUB models) were also incorporated to generate a practical nutrient reduction goal for this watershed.

Communications with the Community: Picking the Right Strategy

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Perceived health or environmental risks can generate fear, particularly if people feel they are not being heard or that risks are beyond their control. Ineffective response or miscommunication can lead to misperceptions of environmental information about your site or the potential risks imposed. Thus, selecting the appropriate public communications strategy for a site, including the right level of communication, can be an important factor to consider in the overall project management of a site. This paper will discuss the steps involved in evaluating the necessity of a public communications program for a site, developing a communication strategy, and implementing a communication program in the context of several case studies. Example strategy plans and implementation materials for sites will be shared – ranging from low/high concern sites to low/high trust communities.

Qualitative and Quantitative Analysis of Water Quality Trends in a Sub-Watershed of the Wachusett Reservoir

STUDENT PRESENTER

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To help control impacts from development, a sewer system was constructed for the town of West Boylston and the surrounding areas between Worcester, Massachusetts and the Wachusett Reservoir. Assessing whether the sewer has positively impacted the water quality in this area is necessary for future sewer projects as well as the continuation of research in this area. In the West Boylston Brook sub-watershed, there continues to be periodic high concentrations of fecal coliforms, indicating possible source contamination. Connecting to the sewer system is optional, and consequently some residents have chosen to continue using their septic systems often because of financial constraints. This study analyzes data from both before and after the sewer was constructed and begins to confirm trends in the water quality data. The study concentrates on fecal coliform concentrations in the areas of interest, but also explores how other microorganisms and water quality parameters vary. These include such indicators as sorbitol-fermenting *Bifidobacteria E. coli*, and *R. coprophilus*, and water quality parameters such as flow, temperature, pH, turbidity, and total phosphorus. The analysis completed in this study includes statistical analysis, graphical analysis, and qualitative analysis of topographical maps of the area, as well as age and types of the septic systems. For the results, fecal coliform counts of over 200 CU/100mL were found in the system within a day of a major rain event. Summer was found to have the most cases of fecal coliform concentrations above the yearly median, total phosphorus correlated positively with fecal coliform concentrations (Spearman's Rank of 0.592), Fecal Coliform had the highest mean concentration and 75th percentile at Site C, and R. coprophilus had the largest 75th Percentile and 90th percentile concentrations at Site A and largest mean value at Site B.

Soy-derived Biofuels as Replacements for Petroleum-derived Fuels

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It is environmentally enticing to consider replacing or blending petroleum derived middle distillate fuels with biofuels for many reasons. Major considerations include the soaring world-wide price of petroleum products, especially diesel fuel and home heating oil, the toxicity of the petroleum-derived fuels and the environmental damage that leaking petroleum tanks can cause. For these reasons, it has been suggested that domestic agricultural renewable energy sources be considered as replacements, or at the least, as blending stocks for middle distillate fuels. If recycled soy restaurant cooking oils could be employed for this purpose, this would represent a further environmental advantage. Renewable plant sources of energy tend to be less toxic than their petroleum counterparts. This is an important consideration when tank leakage occurs. In proposing such a replacement, considerations must be given to the many problems that could arise. Problems to be studied include fuel storage stability, fuel solubility, oxidative stability, and seawater stability. Unlike air environments, water environments can also have a pH factor that has to be considered. Biodiesel have been shown to be an excellent replacement choice for ground transportation fuels. However, shipboard fuel tanks that compensate for diminishing fuel by the addition of seawater to the fuel tank for buoyancy considerations cannot use biodiesel fuels. It was found that this would lead to fuel instability problems such as filter plugging and other serious engine damage. The question was what in the soybean derived biodiesel led to the observed fuel degradation.

Poster Session- Modeling

Modeling of Pollutant Migration and its Immobilization in Porous Reactive Barrier

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Delineation of Three-Dimensional Zones of Contribution for Production Wells

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Extending the Utility of the Three-Dimensional Sediment Model

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Modeling of Pollutant Migration and its Immobilization in Porous Reactive Barrier

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The wastewater effluents may origin from different point sources, e.g. propagation of toxins from radioactive point disposals, solid wastes sites etc and they negative impact to the environment can exist for a very long time.

The implementation of reactive barriers is a well-known *in situ* remediation technique [1]. The reactive barriers are permeable zones (single-layer or of a composite structure), characterized by the appropriate physico-chemical and hydrological properties and when located on the groundwater "route" can effectively immobilize the toxins. Modeling of pollutant migration and its immobilisation within the barrier (verified by the experiments) would give the obvious advantages: the overview on the undergoing processes, the decisive mass transfer resistances and could be a good tool for the evaluating barrier effectiveness, design as well as its utilization time.

The mathematical general model of the substance migration in the porous media, formed in the earlier works [2]-[3] has been modified according to the problem of pollutants propagation and immobilization in the barrier. In the proposed model it seems reasonable to divide the whole barrier (and the ground) into 2 horizontal layers: the "upper layer", extending from the ground level to that of the groundwater with the partial saturation, infiltrated by the rainfall water (liquid flow only in the vertical direction), and the "lower layer", extending from the groundwater level to the surface of the impermeable layer, where the groundwater flow takes place (that zone is fully saturated).

Following the presented suggestions, in the system where the groundwater flow takes place under hydraulic gradient, assuming the appropriate boundary conditions, the model equations were formulated, taking into account both convective and diffusive mechanism of mass transfer as well as possible processes of substance immobilization: sorption on the grains of the barrier and chemical reaction of pollutant decay.

The aim of the present model is to simulate the hydrological and mass transfer processes that take place within the reactive barrier under the conditions of the contaminated groundwater flow.

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Delineation of Three-Dimensional Zones of Contribution for Production Wells

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Understanding the spatial relationship between groundwater contamination and the capture zone of a production well often requires a three-dimensional perspective of the hydraulic conditions that affect both subsurface contaminant transport and the flow of groundwater to a production well. During an investigation of a chlorinated solvent plume at the Massachusetts Military Reservation (MMR), contamination was detected near the two-dimensional wellhead protection area for a production well. To understand better the spatial relationship between the contaminant plume and the capture zone of the production well, groundwater modeling was used to: (1) delineate the zone of contribution for the well in three dimensions, and (2) determine if the migration of the plume is either affected by pumping or if it would affect the water quality at the production well in the future. Because of the seasonal variation in groundwater use on Cape Cod, both the long-term average pumping rate and the maximum permitted pumping rate of the production well were evaluated. Model output was combined with GIS data to produce three-dimensional representations of the hydraulic capture zone, the contaminant plume, and the surrounding region. Interactive models, animations, and figures produced from these results were highly effective in conveying the relationship between the contaminant plume and the portion of the aquifer affected by the pumping of the production well to regulatory agencies and the public.

Extending the Utility of the Three-Dimensional Sediment Model

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A three-dimensional contaminant distribution model has been developed for a contaminated river sediment site located in the Northeast to aid in the assessment and evaluation of collected analytical data. The model was developed using the Mining Visualization System (MVS) software package. The model and associated output was composed of individual grid cells modeled on a 10 ft by 10 ft horizontal grid dimension and a 2 ft vertical dimension. The resulting model consisted of approximately one million cells.

Modeling results for the constituents of concern were graphically displayed as three-dimensional sampling locations, three-dimensional sediment volumes, and three-dimensional Kriged geological surfaces. Modeling algorithms included use of the Kriging geostatistical interpolation method based on a weighted moving average for chemical distribution prediction. Sediment constituents modeled included organic compounds and metals.

Predicted contaminant volume and mass calculations from each cell were used to develop sediment volume and contaminant mass removal estimates for various remedial action scenarios. The modeling technique allowed for minimum, nominal, and maximum sediment volume and mass removal estimates to be undertaken within a very fine grid. A unique and innovative approach was taken in analyzing sediment volumes, contaminant mass, and locations based on this detailed three-dimensional data.

The innovative approach taken to model the contaminated sediments at the site in an unusually precise manner and the impact this precision had on the project team decision making process during development and presentation of remedial scenarios to regulators will be discussed. In addition, the influence various sampling, modeling, and analysis systems had when developing the model will also be examined.

Poster Session- Phytoremediation

Phytoremediation of Arsenic and other Heavy Metals

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Brownfield Phytoremediation Using Salix Species and Herbaceous Plants

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Metal Mobilization and Secretion of Short-chain Organic Acids by Rhizosphere Bacteria Associated with a Cd/Zn Hyperaccumulating Plant, *Sedum alfredii*

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Use of Conventional Crop Plants for the Removal of Heavy Metals from a Severely Contaminated Industrial Site

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Phytoextraction and Phytovolatilization of Arsenic From As-contaminated Soils by *Pteris Vittata*

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A Full-Scale Phytoremediation Approach at a Former MGP: Objectives, Concept, Design and Implementation

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Enhancing the Phytoremediation of RDX with Mycorrhizal Fungi

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Phytoremediation of Arsenic and other Heavy Metals

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Heavy metals have accumulated in the soils of many industrial sites as a result of various industrial and commercial processes and waste disposal activities. Heavy metals have also accumulated in agricultural fields in the United States and elsewhere as a result of the evaporation of irrigation waters and precipitation of metal salts or the use of herbicides containing arsenic. The heavy metals of most concern in industrial sites include what are known in the U.S. as the RCRA heavy metals. In agricultural sites, arsenic, selenium and boron are the primary metals of concern.

Phytoremediation (bioremediation using plants) to remove heavy metals has been an area of increased research for the past five years. This paper presents a summary of the research and compares the effectiveness of various plant species with Malvaceae. Native North American Malvaceae species grow in brackish settings where heavy metals naturally accumulate. Georgia Bost recognized their potential application for phytoremediation and sought funding to assess their potential. Malvaceae species native to the United States were tested with the support of funding from the U.S. Department of Agriculture, resulting in the issuance of a U.S. patent (international patenting is in progress). The initial research found that Malvaceae species were particularly effective at removing selenium and boron from soils and irrigation water. The species were effective in reducing other heavy metals in soils at a test site. Subsequently, additional funding from the U.S. Department of Agriculture was obtained to assess the dosage-uptake relationship in order to have a better basis for assessing the relative effectiveness of Malvaceae phytoremediation versus other options for addressing heavy metals in soils or irrigation water. Replicate testing with controls was conducted using irrigation water of differing concentrations of RCRA heavy metals with different species and patented hybrids. The research was designed to assess the dosage-uptake relationship and to identify in what parts of the plants the metals tended to accumulate. Soil concentrations were tested periodically through the studies and compared with controls. The results provide a basis for estimating the potential effectiveness of phytoremediation in larger scale applications.

Brownfield Phytoremediation Using Salix Species and Herbaceous Plants

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Phytoremediation can be a viable option to reduce soil pollutants and rehabilitate brownfield sites. Field trials were established in a heavy metal contaminated area of the City of Montreal where soil analyses showed that Cu (416.8 mg/kg^{-1}), Pb (857 mg/kg^{-1}), and Zn (899.4 mg/kg^{-1}) exceeded Canadians limits. In spring 2000, seeds of one herbaceous species *Brassica juncea* L. were sowed and the cuttings of two tree species *Salix miyabeana,* Seem. and *S. viminalis* L. were planted using a split plots design. Two treatments were applied: EDTA (ethylenediaminetetraacetic acid) treated plots (T1) and untreated plots (T0). The study compared metal concentration and content in aerial parts (leaves, fruits, stems) and roots of each species at the end of the first growing season and assessed the effect of EDTA in metal transfer from soil to plants. During this trial, no symptoms of phytotoxicity were observed in the plants. The results showed that *B. juncea* transferred more Cu and Pb and less Zn from soil to their tissues when compared with the two species of willows. In the herbaceous species, the EDTA treatment resulted in a positive effect on metal transfer. Generally, *S. viminalis* transferred more metals than *S. miyabeana*. The metal concentration in leaves was more important compared to the total aerial parts concentration (considered 100 %). For *B. juncea* these proportions were: Cu=58.5 %, Pb=73.5 %, Zn=51.5 % and for willows: 58.5 %, 82 % and 85.5 % respectively. The distribution of metals between aerial parts and roots was different for each species. *B. juncea* accumulated more metals (Cu, Pb and Zn) in its aerial parts than in the roots whereas in the willows, Cu and Pb, principally accumulated in the roots and Zn in the aerial parts (mostly in the leaves). At the end of the first growing season, the total biomass yield of *B. juncea* (annual plant) was higher than that of the willows (perennial plants) and consequently total metal plant accumulation was also more important. However, previous studies suggest that over a long term period the willows will be much more productive than *B. juncea*. As biomass production is a determinant factor of plant metal accumulation (beside metal concentration), the willows can be successfully utilised in brownfield phytoremediation.

Metal Mobilization and Secretion of Short-chain Organic Acids by Rhizosphere Bacteria Associated with a Cd/Zn Hyperaccumulating Plant, *Sedum alfredii*

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Sedum alfredii (Family: Crassulaceae), a newly reported cadmium (Cd) and zinc (Zn) hyperaccumulator native to China, can accumulate Cd and Zn exceeding 1 000 and 10 000 mg kg^{-1} respectively in its shoot (dry weight) when growing under metal contaminated habitats. Several strains of bacteria were isolated from the rhizosphere of *S. alfredii* from different Pb/Zn mines in Hunan Province and Zhejiang Province, China, which can resist high levels of heavy metals. Among these strains, *Burkholderia cepacia* showed the highest ability in mobilizing Cd and Zn as well as resisting high concentrations of soluble Zn (500 mg L^{-1}). The soluble Zn concentration in the medium increased from 13 to 72 and 99% ($p<0.01$) after bacterial inoculation on the MS medium supplemented with zinc oxide and zinc carbonate respectively and pH was decreased from 7.00 to 2.93. The Cd concentration was also increased from 8 to 96% ($p<0.01$) and pH was decreased to 2.65. Short chain organic acids were also analyzed and the results indicated that oxalic acid, tartaric acid and formic acid had a significant correlation ($p<0.01$) with the concentrations of metals (Cd and Zn) mobilized during the assay,

The effects of inoculation of bacteria on the metal bioavailability, mobility and leaching potential were also investigated in the soil column experiment through single chemical extraction, sequential extraction and *in situ* soil solution extraction technique. Bacteria inoculation significantly increased the water-soluble and HOAc-soluble Zn and Cd, possibly by dissolution and desorption from the secretion of proton and various ligands. It is suggested that the role of bacteria in increasing the bioavailability of Zn and Cd would be a great significance for a successful phytoextraction of metals from metal contaminated sites.

Use of Conventional Crop Plants for the Removal of Heavy Metals from a Severely Contaminated Industrial Site

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The ability of commercial crop plants to extract lead (Pb), cadmium (Cd), and zinc (Zn) from a metalliferous waste disposal site in Western Europe was studied in the greenhouse and in the field. In the greenhouse, spinach (*Spinacea oleracea*); cabbage (*Brassica oleracea*); broad bean (*Vicia faba*); and a grass mixture (red fescue, *Festuca rubra*; ryegrass, *Lolium perenne*; and spreading bluegrass, *Poa pratensis*); were grown on blast furnace slag or baghouse dust amended with composted peat. Soil Pb ranged from 12 to 5120 mg/kg, Cd from 1.0 to 275.2 mg/kg and Zn from 550 to169,900 mg/kg. In most cases the majority of soil Pb, Cd and Zn occurred in the organic-bound, carbonate-bound, and sulfide/residual forms; relatively low percentages occurred in soluble and exchangeable forms. Several species were capable of accumulating and distributing soil metals to upper plant parts. No plants were capable of growth on non-amended soil material. Metal uptake was partly a function of the chemical forms occurring in soil. For example, tissue metals correlated with soluble and exchangeable soil metal concentrations. Field plots established at the waste site were treated with composted peat or cattle manure, or a mixed NPK fertilizer. Plots were seeded with spinach, cabbage, and a grass mixture. Soil Pb, Cd and Zn tended to accumulate in roots with variable translocation to upper plant parts. Dry matter production was greatest for the composted peat treatment and lowest for the control (no soil amendments) treatment. Ground cover was most extensive on the peat treatment, followed by the cattle manure and NPK fertilizer. No significant leaching of Pb, Cd, or Zn occurred in any treatment.

Phytoextraction and Phytovolatilization of Arsenic From As-contaminated Soils by *Pteris Vittata*

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Phytoremediation of metal contaminated soil and water offers a lower cost method for remediation and some extracted metals may be recycled for value. Both use of the phytoextraction and phytovolatilization of metals by plants offer realistic remediation on commercial project. Arsenic is of great environmental concern due to its extensive contamination and toxicity. Ma *et al*. (2001) has recently discovered the first known and extremely efficient, arsenic hyperaccumulating plant, *Pteris vittata*. If we can use phytovolatilization for As-contaminated soils, it minimizes the production of As-laden plant material and the duration of remediation.
Material balance of As between uptake by *Pteris vittata* and reduction from As-polluted soils has not been kept based on our results of many greenhouse experiments. Vapor sample were collected to determine volatilization of arsenic compounds from leaves of *Pteris vittata* grew in As-polluted soil to the atmosphere. A low-density polyethylene bottle was completely placed over each stem and sealed on the open bottleneck with sealant and tape to produce a tight seal around the stem and chambers during 2-7days. The bottles were fixed in the same location during sample collection. Concentration of arsenic in trap samples was measured by ICP-MS and speciation of arsenic was analyzed HPLC/ICP-MS system.

Concentrations in collected water samples (ca. 3-10ml) reached 10.68–30.8 μg-As/L (2-7 days). Percentages of arsenic components in one sample are 37 % for arsenite and 63 % for arsenate. The results of our experiments suggest that *Pteris vittata* is a plant species that has shown to be particularly effective at volatilizing As; it removed about 90% of the total uptake of As from As-contaminated soils in greenhouse, like the subtoropics. However, the problem of whether volatile arsenic from *Pteris vittata* is still toxic or not still remains unknown.

A Full-Scale Phytoremediation Approach at a Former MGP: Objectives, Concept, Design and Implementation

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ENSR developed an innovative Phytoremediation approach for a former MGP Site in New Hampshire with the objectives to a) provide hydraulic control to slow and reduce groundwater migration off-site, b) provide the potential for passive aerobic microbial rhizospheric degradation of residual BTEX in groundwater, and c) provide an attractive greenspace at the site in the form of a robust, mixed deciduous and coniferous forest. A concept was developed to promote the establishment of deeply rooted phreatophytic live cuttings to tap the capillary fringe of the groundwater table to promote the natural "pump and treat" process of evapotranspiration, thereby reducing the hydraulic gradient on-site, and slowing the migration of residual MGP by-products in the groundwater. Groundwater Flux simulations were modeled for existing and proposed conditions with assumptions for the successful interception of the groundwater table to establish some baseline goals and to support the rationale. Integral to the concept is getting the trees to send their roots deep into the soil (capillary fringe 3-10 ft bgs) to use this water and not just water infiltrating from precipitation. ENSR's design approach integrated the installation of densely planted live cuttings of trees deep into the soil (2-3 ft bgs) along with traditional bare root installations (1-2 ft bgs), all over 1 acre in a sandy loam upland adjacent to two streams. Over 1,000 trees were installed. To further promote the roots to penetrate the capillary fringe, a low-tech irrigation system consisting of 3-4 ft (2 inch diameter PVC) irrigation tubes were placed with each tree and set below the bottom of the planting. ENSR designed and constructed the system in 2005 and continued irrigation in 2006. To date the system has experienced 92% survival of the plantings and early indications are that roots are extending downward toward the capillary fringe. This poster presents the concepts, objectives, design and construction.

Enhancing the Phytoremediation of RDX with Mycorrhizal Fungi

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Previous studies have shown that the phytoremediation of RDX can lead to its bioaccumulation in leaf tissues. Bioaccumulation has many undesirable ecological effects, such as the potential for food-chain contamination or increased transport via leaf litter. The principle objective of this research was to decrease the bioaccumulation of RDX in hybrid poplar trees (*Populus deltoides* × *nigra*, DN34) and switchgrass (*Panicum virgatum)* by exploiting the naturally occurring symbiotic relationship between these plants and mycorrhizal fungi. Mycorrhizal fungi usually perform the function of providing nutrients to the plant that may be scarce within the soil such as phosphorus or nutritional metals such as zinc. To date, the vast majority of phytoremediation research has neglected the potential benefits of these fungi. This is especially surprising given the fact that other basidiomycetes such as the white rot fungus (*Phanerochaete chrysosporium*) have been proven to mineralize RDX. Prior to dosing with [U-^{14}C]RDX, plants were grown in a greenhouse for periods ranging from one to four months in order to establish the plant-fungi symbiosis. The results from this research have indicated that the presence of mycorrhizal fungi does not significantly ($p < 0.05$) decrease the concentration of RDX in leaf tissues relative to controls for experimental periods ranging from 7 to 30 days. Results also indicated that a volatile organic compound was emitted by both plant species. This is the first evidence that a plant can facilitate the transformation of a non-volatile anthropogenic chemical to a volatile organic chemical.

Poster Session- Radionuclides

Indoor Radon: Short- and Long-Term Influence of Prolonged Precipitation

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Indoor Radon: Short- and Long-Term Influence of Prolonged Precipitation

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For long-term radon measurements, home occupants are allowed by USEPA recommendations to open windows. Although the partial vacuum caused by rising warm air in a home is diminished when windows are open, rainfall still increases indoor radon concentrations. Our studies have shown that a significant rainfall (more than 1/4" in one event) increases radon until the rain stops and evaporation begins. More importantly, we found that a season of above-average rainfall produces above-average radon concentrations, even if a measurement is taken during a non-rainfall interval. This seasonal effect can result in measurements that are atypical for a home.

Poster Session- Risk Assessment

A Comparison of EPA's Current and Proposed Toxicological Approach to Evaluating Risk from Asbestos

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Evaluation of Ecological Risks to Amphibians Exposed to Metals-Contaminated Sediment and Soils

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Risk-Based Investigation and Assessment of Very Large Agricultural Areas- Strategies From Hawai'i

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Creative Solutions During Construction to Eliminate Hazard Exposures and Reduce Risk

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The Distribution of Fish Advisories for Mercury in Massachusetts

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Alice Doyle, Massachusetts Department of Environmental Protection, Boston, MA

Angler Survey at an Eastern Massachusetts Lake

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A Comparison of EPA's Current and Proposed Toxicological Approach to Evaluating Risk from Asbestos

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EPA is in the process of updating their approach for estimating health risks from asbestos to better reflect studies on the carcinogenic and non-carcinogenic effects of asbestos. Despite the fact that considerable advancements have been made in the last 18 years in our understanding of how asbestos exposure contributes to adverse health effects, EPA's current cancer toxicity value for asbestos has not been updated since 1988. For example, studies demonstrate the significance of asbestos fiber type, fiber size, and smoking status on the toxicity of asbestos. Toxicity studies indicate that certain types of asbestos fibers are significantly more toxic than others, particularly toward induction of mesothelioma. Studies also indicate that fibers longer than 10 µm and thinner than 0.4 µm contribute most to asbestos-related disease, and that asbestos-induced lung cancer is higher among smokers than non-smokers. The current approach for evaluating risk from asbestos, however, is applied equally to all asbestos fiber types and lengths. This poster will discuss EPA's 2003 document, which provides an overview and evaluation of the toxicity studies on asbestos and proposes an updated asbestos toxicity model that incorporates asbestos fiber type and size into cancer risk calculations for asbestos, and provides a model for accounting for smoking status. Although the proposed approach will likely provide a better estimate of asbestos risk, this poster will discuss remaining uncertainties associated with the proposed approach. This poster will compare estimates of asbestos risk from real site data using the current approach and the proposed approach, and discuss the implications of the proposed approach.

Evaluation of Ecological Risks to Amphibians Exposed to Metals-Contaminated Sediment and Soils

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Amphibians are a front-line indicator of possible adverse impacts to wetland ecosystems; however, no standardized procedure exists to evaluate the potential toxicity of sediments and hydric soils to amphibians. A multi-phase project was initiated to develop a standardized approach for assessing potential risks to amphibians at Department of Defense facilities. The first phase of work included a literature review, development of standardized laboratory testing techniques, limited validation of toxicity testing procedures, quantification of amphibian screening values, and preparation of a guidance manual for assessing potential risks to amphibians. The ongoing work includes additional analysis and validation of laboratory standard operating procedures, lab and field assessment using two constituents (lead and copper) commonly co-located at military sites and ranges, and evaluation of a variety of bioavailability scenarios designed to quantify the effects of site-specific physico/chemical characteristics on environmental toxicity and risk. Recently completed test refinement activities have included dilution series toxicity testing with terrestrial adult salamanders (*Plethodon cinereus*) and tadpoles (*Rana pipiens*) exposed to lead, copper, and lead/copper mixtures in sediments and hydric soils. These tests have included evaluation of lethal and sub-lethal effects, as well as tissue residue analysis, and histopathological evaluations. The refinement phase of work has been designed to consider site-specific conditions that influence exposure (e.g., bioavailability), yield results that are protective of various life stages of amphibians, and develop amphibian risk-based screening values that consider such factors as cation exchange capacity and organic carbon. In addition to refining the laboratory portion of the protocol, the project team recently demonstrated and field-validated the protocol at two DoD sites (east and west coast) contaminated with lead and/or copper. The results of this field validation using amphibians as

sentinel organisms are contrasted with the results obtained through the use of more traditional risk assessment technologies.

Risk-Based Investigation and Assessment of Very Large Agricultural Areas - Strategies From Hawai'i

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Investigating large, former agricultural areas for residential and commercial redevelopment can be a daunting task. For example, the proposed Wai'awa Ridge project in Hawai'i calls for the construction of several thousand homes and numerous commercial complexes, schools and golf courses over a 3,000-acre area. The primary contaminant of concern is arsenic, assumed to be related to the past use of arsenite-based pesticides.

Existing guidance that calls for the collection of a small number of discrete soil samples per acre was deemed inadequate from both a statistical and risk perspective. Testing of each individual lot is not feasible, however. Consolidation of lots into larger and more manageable "decision units" for testing is appropriate but including too many lots in a single sample could cause lot-size hot spots to go undetected.

A better alternative is to combine "multi-increment sampling" and "risk-based screening level" methods to equate decision unit size and sampling strategies with maximum acceptable health risk. The approach developed for the Wai'awa Ridge project and similar sites can be summarized as follows: 1) Compile list of target contaminants, 2) Develop primary and maximum-acceptable, risk-based screening levels for specific land uses; 3) Subdivide the area into "decision units" based on land use, topographic features, soil type, anticipated lot size and target risks; 4) Collect a multi-increment sample from each unit; and 5) Compare data to primary screening levels and determine the need for additional actions. The maximum number of lots that can be grouped into a single decision unit is equal to the maximum-acceptable screening level divided by the primary screening level. For arsenic, this equates to approximately five lots per decision unit. Statistical methods can be used to limit the number of decision units actually sampled. Bioaccessible arsenic data are collected for decision units that significantly exceed anticipated background arsenic concentrations.

Creative Solutions During Construction to Eliminate Hazard Exposures and Reduce Risk

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Encountering contamination during a construction project, albeit unwelcome, does not always need to be the costly problem that it first appears to be. When contamination is encountered during a construction project it is critical to think fast, rapidly evaluate options and communicate with client and regulators to address the problem with minimal disruption to the original project. We present two examples where creative remediation strategies were employed to eliminate hazard exposure and manage risk at the sites. One example employed a creative solution to address asbestos impacted soil encountered during construction of a municipal building. Secondly, we present an innovative solution where the construction of an abutting development was extended and utilized to remediate a lead impacted municipally owned facility. The easiest solutions were to excavate and remove the impacted soil; however, both projects resulted in significant cost savings to the clients when compared to the more traditional "dig and haul" approach.

The Distribution of Fish Advisories for Mercury in Massachusetts

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The Massachusetts Departments of Environment Protection, Public Health, and Fish and Wildlife have tested fish for mercury since the 1980's. So far, 234 waterbodies have been tested, resulting in 97 fish advisories, where fish had mercury levels above 0.5 mg/kg. Fish from 135 waterbodies did not contain unhealthful levels of mercury.

The range of advisories in a watershed and the exact percentage of advisories in the watersheds where three or more waterbodies have been tested are portrayed using GIS mapping techniques. More specific information on lakes that have been tested can be found at the MassDEP website at http://mass.gov/dep/toxics/stypes/hgres.htm. More detailed information on fish advisories, including which species to avoid consuming in lakes with fish advisories, is available at the Massachusetts DPH website: http://db.state.ma.us/dph/fishadvisory/.

Emissions controls for incinerators were imposed in 2000. Twenty-six lakes have been retested since emissions controls took effect. Twenty-four had previous advisories for mercury. Tests in 11 lakes (~46%) showed that mean mercury levels had fallen below 0.5 mg/kg. Many of the lakes that were retested are in the northeastern part of the state, where four incinerators were located, and industrialization occurred early in the 20th century. Patterns and trends of fish mercury distribution are discussed in relation to meteorological phenomena and regulatory management of mercury emissions.

Angler Survey at an Eastern Massachusetts Lake

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An angler survey was conducted on a recreational lake in Natick, Massachusetts because of potential health concerns associated with polychlorinated biphenyl (PCB)-contaminated sediments at the shoreline adjacent to an active army research facility. Fish consumption practices for anglers harvesting fish from the lake during the open water season were evaluated using an on-site roving creel and recall surveys that included questions about fishing habits, meal size and frequency, fish species caught and whether the species were native or stocked, fish preparation and cooking methods, household members sharing fish, and home town. The survey was conducted between August 13 and October 30, 2005 and a total of 163 different individuals were interviewed. Of those individuals, approximately 67% stated that they were "catch and release" anglers only (sport anglers) that predominantly targeted largemouth bass. Approximately 19% stated that they took the fish home to eat or were observed taking fish home to eat. Another 14% stated that they would catch and release some fish species and take other fish home to eat, some only consuming stocked species of fish (trout and salmon). Fish observed in the creel were measured and weighed. This study provided data on fishing practices for a variety of ethnic groups fishing at a suburban lake near urban centers. Average daily fish ingestion rates were calculated for anglers that took home fish to eat, with the ingestion rates for native and stocked species calculated separately. Statistics were also calculated for demographics, ethnic group, fish preparation/cooking method, frequency of fishing, and other study parameters.

Poster Session- Site Assessment

Environmental vs. Forensic Investigations of Soil Contamination

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Apparent versus Actual NAPL Thickness: How Much is Really There? Case Studies and Site Closure

Frank Ricciardi, Weston & Sampson Engineers, Inc, Peabody, MA
Kelley Race, Weston & Sampson Engineers, Inc, Peabody, MA

Difficult Site Characterization Due to Topographic Site Conditions and Historic Site Use

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Perfluorooctane Sulfonate and Perfluorooctanoate Concentrations in Yamato River Water System in Japan

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Trace Metal Speciation by the Sequential Extraction Method in Sediments from Lis River (Portugal)

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Environmental vs. Forensic Investigations of Soil Contamination

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Environmental professionals are frequented called upon to design investigations to determine the nature and extent of contamination at sites. There are several models that can be used to develop these investigations including the ASTM E1903-97 Standard Guide for Environmental Site Assessments: Phase II Environmental Site Assessment Process as well as a number of EPA and state environmental agency guidelines.

The objective of a classic Phase II investigation is generally to “confirm the presence of hazardous substances or petroleum products” at a site or provide the environmental professional with “sufficient information to render a professional opinion that there is no reasonable basis to suspect the presence of hazardous substances or petroleum products” at a site. However, in an environmental forensic investigation, the goals also include identifying the source(s) (both current and historic) of contamination found at a site and its probable transport with a certainty acceptable in a court of law.

To design an effective environmental forensic site investigation, the environmental professional must know:

1. Historic and current operations on the subject and surrounding sites.
2. Raw materials, intermediate products, by products, final products, and wastes from historic and current operations.
3. Chemical and physical characteristics of each of these materials.
4. Transport pathways and fate for each of these materials.
5. Site geologic, hydraulic, and/or hydrogeologic conditions at and surrounding the site.

While the goals of a Phase II investigation may be met by determining the presence of hazardous substances or petroleum products, the environmental professional when conducting an environmental forensic investigation will usually need to determine the chemical form of each of these substances. This paper will provide two case comparisons of Phase II and environmental forensic investigations of soil contamination and compare the usefulness of each in achieving forensic goals.

Apparent versus Actual NAPL Thickness: How Much is Really There? Case Studies and Site Closure

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In a 1995 Ground Water Issue, The USEPA reports that "proven field methods for accurate and reliable estimation of mobile LNAPL volume using well thickness information are not currently available. Further research and development of methods for directly assessing subsurface LNAPL distribution are warranted." So what has been done in the last decade to assess the actual versus apparent LNAPL thickness in the subsurface? This paper will seek to address current estimation methods for correlating the actual versus apparent LNAPL thickness and what field methods are most reliable for generating useful data. We will also assess the role of the following conditions on LNAPL thickness as observed in actual LNAPL sites:

- Site stratigraphy and hydrogeologic characteristics
- Temporal changes in apparent LNAPL thickness
- Water table fluctuations
- Petroleum type, age, and physical/chemical parameters
- Vertical and horizontal migration of LNAPL in heterogeneous aquifers
- LNAPL bail-down test results
- Volume released versus estimated in-situ volume observed
- Monitoring well diameter, construction methods, and materials of well construction

This paper will also present an analysis of the different field methods used to estimate product thickness including geophysics, direct-read field instruments, boring programs, the TRIAD Approach, Rapid Optical Screening Technology (ROST), cone penetrometer, and other screening technologies. The Massachusetts Licensed Site Professional Association (LSPA) has struggled with this issue and has published a white paper on achieving site closure via a Class A RAO (Permanent Solution) at LNAPL sites. We will focus on methods to demonstrate that site closure has been attained even though the apparent LNAPL thickness as measured in monitoring wells may exceed regulatory cleanup standards.

Difficult Site Characterization Due to Topographic Site Conditions and Historic Site Use

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Many Brownfield sites contain areas where intrusive investigations cannot be readily conducted due to unstable ground conditions. Described in this paper are the means used at the Former Oxford Paper Mill Site in Lawrence Massachusetts to assess and remediate an unstable area containing asbestos and elevated levels of PCBs. An area totaling approximately 35 feet wide by 200 feet long contained many voids created by partial demolition of basements and subsequent backfilling in the early 1980's. It was known that PCB and asbestos contamination was present in this area but the nature and extent was unknown. The paper describes the use of remote intrusive investigations combined with assumptions regarding site characterization leading to a final assessment of soils in place that was utilized to successfully address the problem.

Perfluorooctane Sulfonate and Perfluorooctanoate Concentrations in Yamato River Water System in Japan

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In recent years influence of human body by an internal secretion disturbance chemical compound (environmental endocrine disrupter) becomes a terrible problem. It is mainly concerned about a cause of hypospadias, thyroid gland aberration and sperm count decrease.
Perfluorooctane sulfonate (PFOS) is special class of chemical used in variety of applications that include lubricants, paints, cosmetics and fire-fighting foams. PFOS has been reported to be globally distributed in variety of living organisms and humans. Perrfluorooctanoate (PFOA) is also formed through the degradation or metabolism of certain other manmade fluorochemical products. PFOA has been reported to cause diverse toxic effects in laboratory animals including primates. An epidemiological study of workers exposed to PFOA revealed a significant increase in prostate cancer mortality. A cross-sectional study of PFOA perturbs sex hormone homeostasis, but recent long-term follow-up studies on the workers could not confirm the earlier adverse effects. In this study, we evaluated the PFOA and PFOS concentrations in Yamato River water system in Japan.

Quantitative analyses of PFOS and PFOA are performed by LC/MS with a solid phase extraction method. In Yamato River water system, PFOS and PFOA were present in the surface water which we obtained from a place and confluence spot with much domestic wasted water.

Trace Metal Speciation by the Sequential Extraction Method in Sediments from Lis River (Portugal)

STUDENT PRESENTER

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The determination of extractable trace metals in sediments is often used to gain an insight into chemical speciation. The mobility of metals, as well as their bioavailability and related eco-toxicity, depends strongly of their specific chemical forms or ways of binding. Consequently, these have to be determined rather than the total element content in order to assess the toxic effects and study geochemical pathways. However, the determination of specific chemical species or binding forms is difficult and often hardly possible. Therefore, determinations of extractable forms can be a good compromise to give information on environmental contamination risk.

In this case study, Lis River sediments have been studied to determine their environmental pollution levels. The Lis River is an urban river located in the centre of Portugal and is extremely polluted due to waste discharges and incorrect water uses. Since this river constitutes the main inland water resource for domestic, industrial and irrigation purposes, it is imperative to prevent and control the river pollution and to have reliable information on mechanisms about trace metals transportation and their complexes both in water and sediments. The BCR sequential extraction procedure was used to determine the distribution of trace metals (Cu, Zn, Pb, Ni, Cr, Fe, Mn and Al) as exchangeable, water and acid soluble, reducible, oxidisable and residual fractions. The river sediments were monitored at different sites located in relatively low, moderate and high pollution regions, between 2003 and 2005. The dried sediment samples were sieved through a 63 μm screen and metal concentrations were analysed by AAS in the fraction <63 μm. The accuracy, assessed by comparing total metal concentrations with the sum of the amounts given by the three sequential extractions, proved to be satisfactory.
The enrichment of Zn, Cu, Cr and Mn in the river, associated with a high organic matter content, is indicative of the influence of cattle-farm wastes, sewage and agricultural runoff on the detected situation.
BCR – Community Bureau Reference (European Commission)
AAS – atomic absorption spectroscopy

Wednesday, October 18, 2006

Poster Session- Arsenic

Treating Arsenic - Contaminated Soil at a Former Herbicide Blending Facility

Ajit K. Chowdhury, RMT Inc., Madison, WI
Robert Stanforth, RMT Inc., Madison, WI
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An Investigation of Arsenic Contamination from CCA-Treated Wood in a Local Playground in Bridgewater, Massachusetts

Cielito DeRamos King, Bridgewater State College, Bridgewater, MA
Michael Grima, Bridgewater State College, Bridgewater, MA
Eric D. Curry, Bridgewater State College, Bridgewater, MA

Use of Native Organic-Rich Soil for Passive Removal of Arsenic from Groundwater

P. James Linton, Blasland Bouck and Lee, Inc., Tampa, FL
Susan Tobin, Task Remediation, Inc., Tampa, FL

Arsenic and Fluoride in Drinking Water in Some Parts of Eastern India: a Serious Threat to the Community

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Sorption and Desorption Behavior of Arsenite, Arsenate and Diphenylarsinic Acid (DPAA) in Soils

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Treating Arsenic - Contaminated Soil at a Former Herbicide Blending Facility

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Arsenic-contaminated soil at a Superfund site in Missouri was treated during 2005 using a ferric sulfate-based additive. Initial testing indicated that 20% Portland cement was needed to treat the soil, in contrast only around 2% of the ferric sulfate additive was required. The exact dosage depended on the arsenic content of the soil. Arsenic screening using X-Ray Fluorescence (XRF) was used for in-field determination of the dose required for each batch of soil. Varying levels of available iron in the soil was an additional factor in selecting the dose of treatment chemical. More than 70,000 tons were successfully treated and disposed, at an average chemical dose of 2%. The correlation of XRF arsenic data with wet compositional analysis, relationship of available iron to arsenic ratio with TCLP-arsenic analysis, and dosage-response for chemical treatment of soil comparing the bench-scale and full-scale treatment data will be presented.

An Investigation of Arsenic Contamination from CCA-Treated Wood in a Local Playground in Bridgewater, Massachusetts

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The EPA banned the use of pressure-treated wood containing chromated copper arsenic (CCA) for residential applications on December 31, 2003. However, existing pressure treated wood may contain up to 22 % arsenic, a carcinogen that can seep into the surrounding soil. The Rainbow's End playground in Bridgewater, Massachusetts consists of CCA-treated wooden structures such as fences, decks and picnic tables. It was chosen for this study because it is the largest playground in the town of Bridgewater. The goal of this study is to quantify the levels of arsenic in the soil at the Rainbow's End playground and determine if significant leaching of arsenic from the CCA-treated wood is taking place, thus exposing children who use the playground to arsenic in the soil. A total of 101 playground soil and control samples were collected manually or with a core sampler on two separate dates: fall 2004 and fall 2005. The test samples were collected at random approximately 5-30 ft from the center of the playground. The control samples, taken 20 to 30 feet beyond the boundary of the playground, will be used to establish the background level of arsenic in the area. The samples were analyzed for arsenic levels using a graphite furnace atomic absorption spectrometer following EPA standard method. Of the 51 test samples analyzed to date, 33 % have arsenic levels above the Massachusetts DEP's action level of 30 mg/Kg. In comparison, the 11 control samples have significantly lower levels of arsenic compared to the test samples. The results of this study will be disseminated to Bridgewater town officials.

Use of Native Organic-Rich Soil for Passive Removal of Arsenic from Groundwater

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In 1996, the State of Florida enacted the Lake Apopka Restoration Act to accelerate the restoration of the Lake Apopka Basin through acquisition of agricultural lands impacting the Lake. One 120-acre parcel in this acquisition was historically used for horticultural purposes that included a muck mining area, structures and disposal areas. Groundwater in an area associated with historic burn disposal was found to contain dissolved arsenic above State of Florida guidelines; however, sandy soil in this area, both above and below the water table, did not contain significant concentrations of arsenic.

Studies conducted by the University of Florida (Ma, et al., 1997, 1998 and 1999) have suggested that arsenic has an affinity for soil with a high organic content and reduced pH. A bench-scale test was conducted to determine if the native organic-rich soil (muck) could be used to passively remove arsenic from the groundwater. Results for this test were presented to the Florida Department of Environmental Protection, application of the method as the selected remedial alternative was approved, and the remedial action has been implemented at the time of preparation of this abstract.

The groundwater plume was delineated, the sandy soil within the plume area was excavated, and the excavation was backfilled with native muck soil. Subsequent groundwater sampling has show a significant reduction in arsenic concentrations in the groundwater with time since treatment.

This poster presents the methodology and results of the bench-scale test, describes remedial implementation, and provides a discussion of effectiveness of the alternative under field conditions.

Arsenic and Fluoride in Drinking Water in Some Parts of Eastern India: a Serious Threat to the Community

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Arsenic is one of the abundant elements in the Earth's crust. It is released into the environment through a variety of natural and anthropogenic ways. Arsenic occurs in rocks ,soil , water and air. The principle source of arsenic in the natural environment is arsenic bearing minerals mostly ores containing ores containing sulphide along with Copper, Nickel, Lead, Cobalt and other metals. Similarly, Fluoride is also related to the natural ores present in different forms.

Arsenic contamination in groundwater occurs naturally and released from the soil under conditions conducive to dissociation of arsenic from a solid phase in sediment to liquid phase in water. At present, arsenic contamination is considered to be a dangerous environmental threat and a social health risk, which is well known.

The present paper deals with the analysis of arsenic and fluoride in drinking water in selected parts of Eastern India, which are facing multifaceted problem due to these contaminants affecting the health, social and economic status of the community, especially the poor. Mitigation measures have been discussed in detail.

Sorption and Desorption Behavior of Arsenite, Arsenate and Diphenylarsinic Acid (DPAA) in Soils

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Inorganic arsenic compounds have been frequently detected in contaminated sites as well as lead and chromium. Organoarsenic compounds such as diphenylarsinic acid (DPAA) have created new type of soil and groundwater contamination in Japan. Comparative studies were conducted on their sorption and desorption behavior in six different soils [pseudogleyed yellow-brown forest soil (PY), red-yellow soil (RY), yellow-brown forest soil (YB), Kuroboku soil (KS), Kanuma pumice (KP), and thionic gley soil (TG)]. A series of 25 mL of 0.02 mM arsenate [As(III)], 0.2 mM arsenate [As(V)] and 0.02 mM DPAA solutions of different initial pH were prepared and 0.25 g of a soil was added. Sorption of As(III) by every soils was appreciable in the wide pH range 3 to 11. High percentage sorption was obtained for As(V) in the weak acid pH range. Almost 100% As(V) sorption was obtained for soils PY, YB, KS, and TG. DPAA was sorbed by the soils in the acid pH range. The isotherms for sorption of As(III) and As(V) by the six soils were well described by both Freundlich and Langmuir equations. But the isotherms for DPAA sorption by some soils did not fit these models. Yellow-brown forest soil was artificially contaminated by As(III), As(V), or DPAA to prepare model contaminated soils for use in desorption study. The desorption characteristics of arsenic from soil was analyzed in a wide pH range.

Poster Session- Bioremediation

Enhanced Bioremediation of Chlorinated VOCs Using Sodium Lactate and Dibasic Ammonium Phosphate

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Bioremediation of VPH and EPH Contaminated Groundwater Using *in-situ* Submerged Oxygen Curtain (iSOC) Technology

Jacqueline Lees, ENSTRAT, Inc., Marlboro, MA
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Extracellular Electron Shuttling (EES) Compounds in Bioremediation

Caitlin Bell, University of Illinois, Urbana, IL
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The Effect of Aggregate and Initial Contaminant Concentration on the Biodegradation Rate of Total Petroleum Hydorcarbons

Ramona Boodoosingh, Tufts University, Medford, MA
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Isolation and 16S rDNA Characterization of Two Soil Bacteria Capable of Degrading Quinalphos and Organophosphorus Insecticide

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Degradation of Oil-Derived Hydrocarbons by Bacteria Isolated from Oil-Contaminated Soils

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Degradation of Dyes by Bacteria Isolated from the Activated Sludge of a Textile Industry

E. Dias-Franciscon, Universidade Estadual de Campinas (UNICAMP), Brazil
Lucia R. Durrant, Universidade Estadual de Campinas (UNICAMP), Brazil

Physiological Approaches to Increase Molar Hydrogen Yield in Anaerobic, Fermentative Bacterial Cultures

Jennifer L. Hatch, University of Illinois, Urbana, IL
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Enhancing Bioremediation of DNAPL TCE in Carbon-Poor, Slightly Oxidizing Groundwater within Glacial Soils

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The Biodegradation of Petroleum Hydrocarbons in Three Ecuadorian Crude Oils

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Natural Gene Transfer to Develop Resistance to Metal Toxicity in Microbial Communities at the Oak Ridge Reservation Field Research Center

Safiyh Taghavi, Brookhaven National Laboratory, Upton, NY
David Moreels, Brookhaven National Laboratory, Upton, NY
Craig Garafola, Brookhaven National Laboratory, Upton, NY
Garry Crosson, Brookhaven National Laboratory, Upton, NY
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The Effect of PCB Partitioning between Aqueous and Organic Phases on Rate and Extent of Biodegradation

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Behavior of Autotrophic Perchlorate Reducing Bacteria and Analysis of Royal Demolition Explosive [RDX] in Water by High Performance Liquid Chromatography, HPLC/UV

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Biodegradation of Weathered Oil in Soils with a Long History of TPH Contamination

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Enhanced Bioremediation of Chlorinated VOCs Using Sodium Lactate and Dibasic Ammonium Phosphate

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Historic discharges at a former industrial facility in New Jersey created a plume of chlorinated ethenes in groundwater, including trichloroethene (TCE), cis-1,2-dichloroethene (c-DCE) and vinyl chloride (VC). The presence of degradation products c-DCE and VC suggest that reductive dechlorination is occurring, but after several years of monitoring, concentrations of these compounds have not decreased significantly. Groundwater quality data indicated that a lack of total organic carbon (TOC) and nutrients such as phosphate and nitrogen may be limiting degradation processes. A field pilot test was conducted to enhance the on-going reductive dechlorination process. Amendments were manually injected into the plume weekly for a period of three months. The amendments consisted of sodium lactate (WilClear^{TM}) solution and dibasic ammonium phosphate (DAP). The sodium lactate was diluted to ease injection and the crystalline DAP was mixed into the sodium lactate solution. Amendments were injected via gravity feed through tubing into injection wells. After each injection, a submersible pump was used to circulate groundwater from contaminated monitoring wells into injection wells to distribute the amendments throughout the plume. Monitoring data collected during this pilot test indicates that the injections were effective at enhancing the reductive dechlorination of target contaminants. Concentrations of TCE decreased 86% to 96% while c-DCE concentrations remained constant and VC production was limited. Dissolved oxygen concentrations in all monitoring wells within the plume decreased to 0 mg/l and redox potential decreased from 64 mV and 209 mV to –155mV and –157 mV, respectively. Production of acetic and propionic acids and methane increased and peaked 3 months after the injections ceased. Within six months of the end of the injection program, however, contaminant and geochemical parameters had rebounded to pre-injection levels. Based on the results of the sodium lactate/DAP injections, a workplan is being prepared to inject a longer lasting lactate-based substrate.

Extracellular Electron Shuttling (EES) Compounds in Bioremediation

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Electron shuttling compounds are a class of molecules that accept electrons from microbial respiratory pathways and transfer electrons abiotically to more electronegative electron acceptors. Recent reports suggest that extracellular electron shuttling (EES) molecules may serve as "redox active" agents in bioremediation applications for organic and inorganic contaminants; humic substances, extracellular quinones, and reactive Fe(II) have been investigated in most detail. Our research has focused on humic substance mediated biodegradation of electronegative contaminants, catalyzed by prokaryotes and eukaryotes. Recent data suggest that white and brown rot fungi will reduce the synthetic humic analogue, anthraquinone-2,6-disulfonate (AQDS), in the presence of oxygen. *Gloeophyllum trabeum* reduced approximately 4mM AQDS in 12 days in aerobic, aqueous cultures, which is comparable to anaerobic cultures with AQDS. Fe(III) was also reduced in the presence of oxygen; Fe(II) re-oxidation kinetics were limited by fungal biomass. The reduced EES were stable in air, suggesting that electron transfer to contaminants such as the explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) may be possible in aerobic environments. To date reductive strategies are applied in anaerobic systems; these data indicate that fungal reductive processes may be possible despite aerobic geochemical conditions.

Chlorinated contaminants are also environmentally relevant electron acceptors. To date research has focused on direct dechlorination by specific microorganisms, which are not present in all environments. Preliminary data suggest that highly chlorinated compounds (tetrachloroethylene (PCE) and trichloroethane (TCA)) may accept electrons from the reduced EES AQDS. Bioremediation strategies for chlorinated compounds predicated on EES will be broadly applicable to all environments, as the microorganisms involved have been identified in all environmental media. Future studies will investigate EES mediated transformation of polychlorinated biphenyls, which are hydrophobic and inaccessible in aqueous media. EES may overcome the mass transfer limitations by cycling electrons from microbial respiration to adsorbed contaminant mass, without the need for direct cell-PCB contact.

The Effect of Aggregate and Initial Contaminant Concentration on the Biodegradation Rate of Total Petroleum Hydorcarbons

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Bioremediation is one of the most cost-effective, and environmentally friendly methods to remediate many different types of waste materials widely used by many private and public entities. Though the parameters that affect the rate of bioremediation differ for each project, some parameters can be more easily controlled in the field than others. For example, effective microbial action is crucial to the success of bioremediation. However, microbes can be detrimentally affected by an initial contaminant concentration that is too high. In addition, the type of bulking agent or aggregate used affects the ability of the mixture to retain moisture, the amount of drainage, aeration and ultimately the length of time for biodegradation.

A two-month field study was conducted in Trinidad and Tobago on crude oil contaminated waste. This paper will look at the effect of two parameters, initial concentration and type of bulking agent, on the rate of biodegradation of Total Petroleum Hydrocarbons (TPH) in the oily waste being treated in this tropical environment. A nutrient-supplying bioremediation agent was used to enhance the bioremediation process. The results of this study can assist in the design of effective bioremediation projects in tropical environments.

Isolation and 16S rDNA Characterization of two Soil Bacteria Capable of Degrading Quinalphos an Organophosphorus Insecticide

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Quinalphos is an organophosphorus insecticide and acaricide with contact and stomach actions. No enough studies has been done on biodegradation of quinalphos. Hence attempts were made in the present study to isolate and identify bacteria from insecticide contaminated soils, which are capable of degrading quinalphos by utilizing it as a sole source of carbon and energy. An enrichment culture technique was used to isolate bacteria responsible for the enhanced biodegradation of quinalphos from soil previously exposed with various pesticides. Microscopic examination and physiological tests were followed by 16S rDNA sequence analysis to characterize the two bacterial isolates. One of the isolated bacteria was identified as a *Pseudomonas sp*. and another as *Bacillus sp*. Both *Pseudomonas sp* and *Bacillus sp were* found to be very active in degrading quinalphos, upto 92% degradation at original concentration of 12mg L^{-1} of quinalphos within 15days was observed.Mix cultures study with *Pseudomonas* sp. and *Bacillus* sp. showed 83.71% degradation in10 days. The degradation of quinalphos was maximum in the range of pH 7.0 and pH 8.0. With glucose and in Nutrient broth, in 10days *Pseudomonas* sp. and *Bacillus sp.* showed complete degradation. This shows that slight addition of rich carbon source stimulate the degradation of quinalphos by both *Pseudomonas* sp. and *Bacillus* sp.. Our findings showed that indigenous microorganism are a better means for degradation studies since *Pseudomonas sp.* and *Bacillus sp.* which we had isolated form the natural habitats are a potential degrader of quinalphos. These isolates could be used to remediate quinalphos contaminated sites.

Degradation of Oil-Derived Hydrocarbons by Bacteria Isolated from Oil-Contaminated Soils

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Oil and its derivatives continue to be our main energy source. Constantly we receive information through the media of the ecological disasters and social problems caused by oil spills or by its derivatives. It is estimated that of the 3.2 billion tons of oil produced per year, 3.2 million tons enter the marine environment. This work had the objective to evaluate the capacity of *Bacillus circulans*, *Chromobacterium sp* and *Enterobacter aerogenes*, isolated from oil-contaminated soils, to grow and degrade oil-derived hydrocarbons. They were cultivated for 12 days at 30º C and 150 rpm, in a medium containing minerals and 0.05% (final concentration) of one of the following hydrocarbons: tridecane, tetradecane, pristine, hexadecane, phenyldecane, phenanthrene, naphthalene, pyrene and benzo[a]pyrene. The remaining hydrocarbons were extracted with hexane and analyzed by gas chromatography. *Bacillus circulans* degraded tetradecane (24%), tridecane (23%), hexadecane (24%), pristine (24%), phenyldecane (25%), naphthalene (100%), phenanthrene (25%), pyrene (100%) and benzo[a]pyrene (100%). A *Chromobacterium sp* degraded the same hydrocarbons in the ratios of 20%; 21%; 21%; 21%; 22%; 100%; 100%; 100%; 100% respectively. *Enterobacter aerogenes* degraded 37%; 33%; 35%; 37%; 34%; 100%; 23%; 100%; 100% of the hydrocarbons present in the culture media, respectively. Our results indicate that these three bacterial strains have potential to be used in future studies of oil-derivatives contaminated environments.

We acknowledge financial support from FAPESP-SP, BRAZIL.

Degradation of Dyes by Bacteria Isolated from the Activated Sludge of a Textile Industry

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Reactive azo dyes are widely used in the textile industries. They are characterized by the presence of one or more azo bond, -N=N-, which function as a chromophoric group. Under usual dyeing conditions these dyes do not bind completely to the fibers resulting in colored effluents. Dye removal is desired, not only by esthetic reasons, but also because many azo dyes and their derived products are toxics to aquatic life and mutagenic to humans. Although activated sludge process has been extensively used by the textile industries this treatment is not effective and these dyes are adsorbed by the biomass, being later disposed in landfills, causing contamination of these wide areas.

Trying to solve these problems, three bacterial strains were isolated from activated sludge of textile industries near Campinas (SP, Brazil). Isolates were cultivated with different dyes: Reactive azo-dye Remazol Red RR (C.I. RBN 198) and Remazol Reactive Blue (C.I. RB 220) and degradation of the dyes was determined by UV-visible spectrophotometry and confirmed by liquid chromatography and also COD reduction (Chemical Oxygen Demand). Complete degradation of RBN 198 and RB 220 was found after 24 hs and 168 hs, respectively, by *Trichococcus sp.* and COD reduction was 41 and 68%, respectively. In the case of *Enterobacter sp,* RBN 198 dye was 95 % and RB 220 completely degraded, while COD was found to be 76 and 63 % respectively. A *Bacillus sp* degraded 75% of RB 220 and 84% of the RBN used, with COD reductions of 85 and 88%, respectively.

The ability to decolorize these dyes and reduce of COD by these strains, suggest that they may have potential to be applied in the treatment of effluents and sites contaminated by dyes.

We acknowledge financial support from CNPQ - BRAZIL.

Physiological Approaches to Increase Molar Hydrogen Yield in Anaerobic, Fermentative Bacterial Cultures

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Most approaches to increase hydrogen production focus on reactors without regard to increasing the hydrogen yield per mol of substrate consumed. Optimized reactor designs are necessary; however, increasing the molar hydrogen yield is necessary before hydrogen-based fuel strategies can be commercially applied in a cost-effective manner. This research aims to circumvent organic acid synthesis and increase hydrogen production by altering the electron transfer pathway in fermentative bacteria. Carbon and hydrogen metabolisms of a fermentative pure culture (*Clostridium beijerinckii*) will be altered along with culture conditions to develop strains of microorganisms and co-cultures which will over-produce hydrogen.

This approach in the over-production of hydrogen is alteration of the redox potential of the proton/H_2 couple so that electron transfer to protons becomes favorable relative to organic acid synthesis. By utilizing electron transfer molecules such as quinones to increase the relative redox potential of the H^+/H_2 redox couple, it is possible to cycle electrons from glucose oxidation through the electron carriers to hydrogenase and protons; this circumvents the organic acid synthesis pathway and increases hydrogen yield.

C. beijerinckii was grown anaerobically in glucose-rich medium in order to perform resting cell suspensions under non-growth conditions in anaerobic bicarbonate buffer. 250 μM biologically reduced AQDS (AH_2QDS) increased hydrogen production by 50% above the expected stoichiometry for *C. beijerinckii*. Adding 5-100nM NAD^+ increased the rate of hydrogen production as well as the yield by 75% for *C. beijerinckii*. With increasing concentrations of AH_2QDS, hydrogen production was seen to increase, but with addition of NAD^+, decreased concentrations proved to increase hydrogen yield.

The extent of AQDS and acetate cycling between *Geobacter metallieducens* (GS-15) grown on AQDS media and *C. beijerinckii* will be evaluated on batch and reactor scales while monitoring hydrogen production. The effects of several different environmental samples such as agricultural waste and digester fluid for substrate will also be investigated in a reactor using pure and mixed cultures. Ultimately, hydrogen from this process will be recovered for use in fuel cells.

Enhancing Bioremediation of DNAPL TCE in Carbon-Poor, Slightly Oxidizing Groundwater within Glacial Soils

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This paper describes a field pilot study of enhanced bioremediation (reductive dechlorination) of trichloroethene (TCE) at a site located in western Connecticut. Geology at the test location consisted of glacial till overlying weathered gneissic bedrock. The estimated static groundwater velocity was 0.17 ft/day. The concentration of TCE in the study area varied spatially, but was up to 768 mg/L (~ 70% solubility of TCE), indicating the presence of DNAPL. Low levels of the degradation products *cis*-1,2-dichloroethene (*cis*-1,2-DCE) (330 μg/L), vinyl chloride (85 μg/L), and ethene (7.7 μg/L) were detected, suggesting the occurrence of microbially-mediated reductive dechlorination. Groundwater chemistry was characterized as follows: circum-neutral pH; slightly oxidizing (~ 2 mg/L dissolved oxygen); low total organic carbon (TOC) content (2.7 mg/L TOC); moderate sulfate (43 mg/L); and measureable methane (45 μg/L) and dissolved hydrogen (19 nM), indicating the potential for methanogenic activity. Methanogenic bacteria were detected at moderate levels. *Dehalococcoides spp*. bacteria, the only known bacteria capable of completely reducing TCE to ethene, were also detected, but at levels several orders of magnitude lower than the methanogens.

A dilute solution (10% – 15%) of EOS^{TM} emulsified soybean oil, amended with a bromide tracer, was injected into the subsurface, providing a source of carbon and reducing power for the naturally-occurring microbial populations. The injectate was chased with potable water to facilitate distribution in the saturated subsurface. Reducing conditions, characterized by negative oxidation-reduction potential and decreased DO levels, were achieved within several weeks of the injection event. The distribution of EOS^{TM} was evaluated using TOC and bromide concentrations, and indicated the presence of preferential flow paths in the subsurface. Aqueous TOC concentrations ranged from 22 mg/L to 17,000 mg/L within the test volume. Chlorinated ethenes, geochemical parameters, electron acceptors, and microbial populations were measured as a function of time. An evaluation of the efficacy of enhancing reductive dechlorination at the site was performed.

The Biodegradation of Petroleum Hydrocarbons in Three Ecuadorian Crude Oils

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When crude oil is released to the environment its hydrocarbon composition begins to change due to physical/chemical/biological process collectively known as weathering. Physical weathering such as evaporation and water washing may occur relatively rapidly, however the most important process related to the long term degradation and removal of the oil from the environment is biodegradation. A laboratory study has been performed to evaluate the compositional changes and biodegradation potential of three crude oils. Nutrients and naturally occurring bacteria were added to crude oil samples from Ecuador and incubated in the laboratory at 30°C for up to twenty weeks. The bacterial inocula, used in this study were developed with indigenous bacteria from soils in petroleum producing regions in Ecuador. These tests showed that volatile hydrocarbons, including gasoline range organics (GRO, C_5-C_{12} range TPH) such as benzene, toluene, ethylbenzene and xylenes (BTEX), in the crude oil were degraded by naturally occurring bacteria within 1-7 days. A second group of compounds, semi-volatile hydrocarbons, were also measured in the crude oil. This group of compounds includes petroleum hydrocarbons such as diesel range organics (DRO, C_{10}-C_{28} range TPH) and the USEPA 16 priority pollutant polycyclic aromatic hydrocarbons (PAH) such as naphthalene, fluorene, phenanthrene and chrysene. Laboratory tests showed that semi-volatile hydrocarbons were significantly degraded within 2 weeks. Approximately 84%-89% of the DRO and 97% of the total USEPA Priority Pollutant PAHs within the semivolatile range of crude oil were biodegraded after twenty weeks. Crude oil residues found in site soils from Ecuador appear to be degraded to a degree similar to that documented in this laboratory study. These similarities indicate that significant biodegradation has occurred—either naturally or as the result of remediation activities—at these sites.

Natural Gene Transfer to Develop Resistance to Metal Toxicity in Microbial Communities at the Oak Ridge Reservation Field Research Center

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The Field Research Center (FRC) at Oak Ridge National Lab is characterized by mixed pollution consisting of heavy metals, radionuclides and nitrate. The remediation of toxic metals depends on a method of *in situ* containment that decreases their mobility and bioavailability, which in the case of uranium is based on its reduction by dissimilatory sulfate and iron reducing organisms. However, the presence of high levels of heavy metals and nitrate can inhibit their activities: especially high levels of nitrate, used by anaerobic bacteria as an electron acceptor, will decrease the efficiency of U(VI) and metal reduction. Under these conditions a two-step approach is required. In a first step nitrate is removed via the activity of nitrate reducing bacteria, followed by a second step of U(VI) and metal reduction/precipitation. Unfortunately, the activity of nitrate reducing bacteria is inhibited under conditions of elevated heavy metals. It was therefore hypothesized that inoculation with nitrate reducing organisms, which were genetically engineered with heavy metal resistant genes, might improve nitrate reduction, either via establishment of the inoculum or via horizontal gene transfer of the heavy metal resistance determinant into the indigenous community of nitrate reducing bacteria.

In order to test our hypotheses, *in situ* simulating lab-scale column experiments were set-up with soil samples taken from the FRC site and percolated with a mineral medium contaminated with nickel. The columns were bio-augmented with *Pseudomonas* DM-Y2, which was engineered with *nre* isolated from heavy metal resistant *Cupriavidus metallidurans* 31A. The efficiency of nitrate reduction and U(VI) reduction by the established complex microbial community was evaluated by following the microbial community dynamics and by chemical analysis of the column effluents. In function of time the population was characterized by most probable counts of nitrate, sulfate and iron reducing organisms. The fraction of nickel resistant organisms was counted after spread plating on nickel containing selective media. Sequencing and cloning of the 16S rDNA genes of the eubacterial population was used to identify the predominant community members. Spectroscopic techniques were used to determine sulfate and nitrate concentrations, while iron, nickel and uranium concentrations and speciation were determined by ICP-MS and

EXAFS. Based on our data we concluded that under conditions of Ni selection a shift in community composition occurred from a population dominated by β and γ-proteobacteria to a community dominated by Ni-resistant, nitrate reducing *Arthrobacter*, *Pseudomonas* and *Sphingomonas* species. In addition to nitrate reduction we also observed the establishment of a second redox-zone in which increased sulfate and U(VI) reduction occurred, even in the presence of nickel.

The Effect of PCB Partitioning between Aqueous and Organic Phases on Rate and Extent of Biodegradation

STUDENT PRESENTER

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Octanol/water partitioning coefficients of environmentally significant compounds such as polychlorinated biphenyls (PCB) or polycyclic aromatic hydrocarbons (PAH) are in the order of 10^4 to 10^5. This might result in extremely low aqueous phase concentrations of these compounds if an organic phase is present at contaminated sites. It was the scope of this study to investigate whether or not the presence of an, otherwise non-toxic, organic phase can become the limiting factor in aerobic PCB degradation.

Burkholderia xenovorans LB400 is the most studied organism for aerobic PCB degradation, and its degradation kinetics for biphenyl were studied in a two-phase partitioning (TPPB). The use of a TPPB allowed it to operate a bioreactor at constantly low aqueous phase substrate concentrations near the half saturation concentration of the Monod model. The specific growth rate and the half saturation constant of the Monod model were estimated to be $\mu_{max} = 0.25\ h^{-1}$ and $K_S = 0.0001\ g\ L^{-1}$, with a yield coefficient of $Y_{X/S} = 0.48$ g biomass per g biphenyl. The estimated value of K_S is at the low end of the typical values for bacteria, which is expected for an organism utilizing a hydrophobic substrate. PCBs are degraded via the biphenyl pathway by the same enzymes as biphenyl, allowing the assumption that the half saturation constant for PCBs is in a similar range, most likely higher than the one for biphenyl. Hence, it was expected that low concentrations of PCBs could not be degraded in the presence of a large organic fraction. Experiments with a constant amount of PCBs and different amounts of two organic solvents showed that PCBs could only be degraded in the presence of a small organic fraction. The concentration in the aqueous phase became too low for successful biodegradation as soon as the organic fraction reached a certain level. It can therefore be concluded that reduced bioavailability of PCBs due to partitioning in an organic fraction can be the limiting factor during biodegradation of PCBs.

Behavior of Autotrophic Perchlorate Reducing Bacteria and Analysis of Royal Demolition Explosive [RDX] in Water by High Performance Liquid Chromatography, HPLC/UV

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Perchlorate, (ClO_4^-) contamination in ground and surface waters can cause serious human health effects, severe ecological and environmental consequences. Perchlorate can disrupt thyroid function and may impact fetal and newborn development, resulting in changes in behavior and learning capability. Many times ClO_4^- is a co-contaminant with RDX. This research investigated biological reduction of perchlorate and RDX by autotrophic sulfur oxidizing bacteria. ClO_4^- was analyzed with Ion Chromatography (IC). RDX can enter the water from disposal of waste water from Army ammunitions plants, and it can enter water or soil from spills or leaks from improper disposal at hazardous waste sites. RDX can cause seizures in humans and animals when large amounts are inhaled or ingested. The Environmental Protection Agency (EPA) has determined that RDX is a possible human carcinogen (Class C). The RDX was measured with High Performance Liquid Chromatography (HPLC) with a Photo Diode Array Detector (PDA). The experiment was conducted following the Method 8330 from EPA. The bacteria population change was determined with a Bicinchoninic Acid (BCA) Protein Assay. Regarding the bacteria population, we saw an increase from 190 µg/ml to 270 µg/ml protein in the solution over 20 days. Perchlorate was degraded from 9.2 ppm to 8.6 ppm. In the case of RDX alone with the bacteria, RDX degraded from an initially 475 ppb to below the MDL (about 5 ppb). Also the RDX, perchlorate and the bacteria, the concentration of RDX was decreased from 467 ppb to lower than the MDL. In conclusion the setup for the RDX analysis was accomplished and the bacteria can degrade both contaminants, ClO_4^- and RDX.

Biodegradation of Weathered Oil in Soils with a Long History of TPH Contamination

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Sites with a long history of exposure to petroleum hydrocarbons contain mainly long chain hydrocarbons or “weathered oil”. This is because petroleum is a complex mixture of many organic compounds and these compounds biodegrade at different rates. Under aerobic conditions the shorter hydrocarbon chains biodegrade first and the longer chains are more recalcitrant.

Long chain hydrocarbons are less soluble in water and more like tar in consistency than the shorter chain hydrocarbons, so a major problem with the degradation of these compounds is that bacteria that break down hydrocarbons do not come into contact with them. These compounds are not bioavailable and therefore do not biodegrade.

A petroleum refinery that has been active for many years has a large amount of weathered oil the surrounding soil and groundwater. A treatability study was performed on samples from the Site to determine whether conditions could be manipulated to stimulate the biodegradation of the weathered oils. Several sets of microcosms containing soil and groundwater were set up. Along with nutrients and an oxygen source, a biodegradable surfactant was added to some of the sets in order to determine whether increasing the bioavailability of the hydrocarbons would enhance their degradation.

After the microcosms were set up, there was an initial increase in hydrocarbons in the aqueous phase and a decrease in hydrocarbons in the soil phase in the microcosms that had received surfactant. This change was due the surfactant solubilizing hydrocarbons out of the soil and into the water. As the experiment progressed, however, a decline in hydrocarbon levels in both soil and groundwater was observed.

It was determined that by manipulating the conditions and solubilizing the hydrocarbons, biodegradation of weathered oils could be stimulated. Hydrocarbons could be removed from soils that had contained these weathered oils for many years without any appreciable degradation.

Poster Session- Brownfields

A Brownfields Success Story– Redevelopment of an Abandoned Contaminated Manufacturing Facility into a State-of-the-Art Warehouse in 12 months

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A Brownfields Success Story– Redevelopment of an Abandoned Contaminated Manufacturing Facility into a State-of-the-Art Warehouse in 12 months

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This paper describes a successful Brownfields project during which an abandoned manufacturing facility in Worcester, Massachusetts was remediated and transformed into a modern warehousing operation. The project involved comprehensively evaluating the environmental conditions at the former manufacturing facility, completing an environmental risk assessment, conducting limited remediation under the Massachusetts Contingency Plan (MCP) and cooperation with City and State officials to restore the property for productive reuse.

Shaw Environmental & Infrastructure, Inc. (Shaw E & I) assisted a manufacturing company expand their operations in Worcester, Massachusetts by conducting necessary environmental activities on an adjacent, contaminated parcel to support redevelopment of this Brownfields property. The project resulted in the following benefits to our customer and their community:

- Successfully redeveloped an abandoned adjacent former industrial building into an active warehouse facility
- Expanded operations of the manufacturing company *within* the city limits and increased corporate revenues without relocation
- Created additional permanent skilled jobs resulting from the new and expanded warehousing operations
- Comprehensively evaluated the environmental conditions present at the contaminated parcel and demonstrated that the chemical concentrations associated with former industrial activities conducted at the site did not pose a significant risk to the nearby neighbors or potential on-site workers
- Removed the environmental stigma that had been associated with the property for over twenty years and had previously prevented site redevelopment
- Assessed value of the property increased by 300 percent due to the elimination of the environmental stigma
- Increased tax revenues to the city as the parcel was returned to productive re-use after sitting abandoned for two decades.

Prior to purchase of the adjacent two-acre parcel, Shaw E & I conducted a MCP Phase I Initial Site Investigation on the property to evaluate existing site conditions on behalf of the prospective buyer. This information was used to identify potential assessment and remediation costs associated with future property redevelopment. Funds were placed in escrow to handle planned environmental activities and the property was purchased at a deep discount well below the assessed market value.

Within 12 months, the contaminated property with an abandoned industrial building present was converted into a state-of –the-art warehousing facility employing numerous workers. This project was made possible due to a well-defined environmental regulatory program in Massachusetts with specific risk-based end-points, the foresight of an innovative Worcester business and the cooperation of City and State officials who are dedicated to making Brownfields projects work to return impaired properties to productive reuse.

Poster Session- Chemical Oxidation

Evaluation of Various Technologies to Remediate a Complex Chlorinated Solvent Source Area

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Influence of Heterogeneity on Effectiveness of ISCO Treatment: Step 1

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Surfactant Enhanced In Situ Chemical Oxidation

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Principles and Practices with a Novel Chemical Oxidation System: RegenOx™

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Case Studies: Gasoline and Fuel Oil Remediation Using Biologically Enhanced Chemical Oxidation

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Evaluation of Various Technologies to Remediate a Complex Chlorinated Solvent Source Area

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One or more historical releases of 1,1,1-trichloroethane (TCA) and trichloroethene (TCE) occurred at a site underlain by heterogeneous glaciolacustrine sand and silt deposits. Hydraulic conductivities range from 5.5×10^{-5} cm/s to 1.6×10^{-3} cm/s. The vertical distribution of hydraulic conductivity, evaluated using a combination of cone penetrometer and Waterloo Profiler borings, indicates a layered system, consisting of silt over sand over silt. A series of remedial pilot studies were conducted, including air sparging and soil vapor extraction (AS/SVE), in situ chemical oxidation (ISCO) using permanganate, and in situ biological reductive dechlorination (BRD) using sodium lactate. Results of these pilot studies indicated that heterogeneous geologic conditions limited the efficacy of AS/SVE. ISCO was effective at treating TCE within the pilot area, but had little effect on TCA. A BRD pilot study indicated that this technology was effective at treating both TCA and TCE. Based on results of the BRD pilot study, a full-scale BRD recirculation system has been designed and installed, and will begin operation in 2006.

Influence of Heterogeneity on Effectiveness of ISCO Treatment: Step 1

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Insitu chemical oxidation (ISCO) treatment can effectively destroy chlorinated solvents, such as tetracholoroethylene (PCE). Treatment effectiveness depends on the distributions of nonaqueous and aqueous-phase masses, stratigraphy, groundwater velocity, geochemistry, and adequate reaction time.

ISCO treatment was initiated in September 2003 at the Operable Unit 1 (OU1) of the Savage Superfund site in Milford, NH. The site has a large (0.5 mi^2) volatile organic compound (VOC; primarily PCE) plume. Remediation of OU1 began in 1998 by installing a slurry wall through glaciofluvial deposits surrounding suspected source areas. Among these sources is a former drain and pit area, now targeted by a test well field (INEEL well field). The ISCO treatment injected 8,500 pounds of permanganate in an active flow scheme using two injection and two extraction wells in the INEEL well field. The ISCO test was tracked for reactants and reaction byproducts for over 1 year.

Estimated amounts of PCE destroyed ranged from 5 to 300 times preinjection aqueous-phase concentrations, indicating that the bulk of the oxidized VOCs were in nonaqueous phases prior to the injection. The higher rates were in areas of low preinjection concentrations, indicating that nonaqueous VOCs were probably more susceptible to oxidation than those in areas of greater concentration. Permanganate persisted more than 1 year in selected areas, which helped suppress aqueous phase concentrations of VOCs.

A primary factor affecting the persistence of permanganate was convective mass transport. Extraction well pumping induced transport along a northeasterly sloping basal stratigraphic contact between a permeable coarse sand layer and a less permeable basal till layer. This contact had the highest initial dissolved VOC concentrations suggesting a likely DNAPL source. Although, the DNAPL position is affected by the contrasts in vertical permeability between the coarse sand and basal till, the permanganate transport is affected by the lateral transport in the coarse sand layer.

Surfactant Enhanced In Situ Chemical Oxidation

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In situ chemical oxidation (ISCO) has been used for decades for the remediation of residual dissolved phase contamination, however, does not address adsorbed or non-aqueous phase (NAPL) source area which exists at many sites. Specialized surfactants have become increasingly popular for enhanced recovery of petroleum and chlorinated hydrocarbons. Successful, cost-effective application of ISCO requires solubilization of the contaminants, as ISCO takes place in the aqueous phase. The application of specialized surfactants can significantly enhance ISCO by solubilizing and increasing the bioavailability of adsorbed phase NAPL to allow the ISCO (and residual bioremediation) processes to proceed with optimal effectiveness. Several case studies will be presented which demonstrate how remediation costs and timeframes can be significantly reduced using surfactants and in situ chemical oxidation. The interaction of geology, contaminant fate and transport, surfactant and ISCO chemistry, and economics will be discussed.

Principles and Practices with a Novel Chemical Oxidation System: RegenOx™

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RegenOx™ is a proprietary (patent-applied-for) in *situ* chemical oxidation process using a solid oxidant complex (sodium percarbonate/catalytic formulation) and an activator complex (a composition of ferrous salt embedded in a micro-scale catalyst gel). With its highly active catalytic system, RegenOx is capable of treating a broad range of soil and groundwater contaminants including both petroleum hydrocarbons and chlorinated solvents. RegenOx uses a *basic oxidizer complex* and thus generates alkaline conditions (high pH) and does not rely on operating under the acidic conditions (low pH) that are required when using standard catalyzed hydrogen peroxide (Fenton's chemistry). RegenOx is safe and easy to apply to the contaminated subsurface without the health and safety concerns and lingering environmental issues that have become associated with other chemical oxidation technologies. RegenOx has been applied at over 50 sites for both chlorinated and petroleum-based contaminants. Several successful applications are now complete.

The case studies to be presented are from sites exhibiting varying lithologies, using different application methods (such as direct push injection, in-situ and ex-situ soil mixing) and within different regulatory environments. Treatment results from sites containing a variety of contaminants will be presented, including a site with a mixed chlorinated solvent and petroleum hydrocarbon plume. Initial contaminant concentrations ranged from 20-80 mg/L for the primary contaminants of concern. After the first injection round, BTEX concentrations decreased by 50-66% and chlorinated solvents decreased by 63-90%. The presentation will include a discussion on evaluating the principles of design, practical lessons learned, and life-cycle costs for chemical oxidation with RegenOx. The discussion will also evaluate various methods available to perform on-site feasibility tests and bench tests which can be utilized to evaluate the potential effectiveness of in-situ chemical oxidation.

Case Studies: Gasoline and Fuel Oil Remediation Using Biologically Enhanced Chemical Oxidation

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Chemical oxidation is transitioning from an innovative technology to a common remediation technique for cleanup of hydrocarbon impacted soils and groundwater. Concerns regarding the implementation of chemical oxidation include safety during application and disruption of natural contaminant attenuation. These concerns stem from the exothermic nature of the oxidation process and sterilizing effects of the oxidants on soil microorganisms. The extent of contamination can, in theory, increase substantially in the absence of natural attenuation. Close examination of the oxidation reactions has brought about modifications that increase safety and dramatically stimulate aerobic microbial activity resulting in integrated chemical oxidation and bioremediation and subsequent enhanced natural attenuation.

Lessard Environmental, Inc. has developed a process called Biologically Enhanced Chemical Oxidation (BECO, US Patent 6,923,596) which integrates chemical oxidation and bioremediation as a concurrent and co-located process. Implementation of BECO is both temporally flexible and spatially scaleable. The process integrates the oxidation and bioremediation by increasing subsurface temperature, available oxygen and nutrients and by modifying contaminant distribution during remedial additive applications.

Case studies demonstrating the effectiveness of BECO will be presented for gasoline and fuel oil treatment. Remediation progresses as an integrated couplet of remedial additive applications and biological activity. The stimulated microbial activity reduces the total quantity of oxidant and number of applications required for remediation with oxidant alone. Heterotrophic plate counts during the remediation projects typically increased from baseline concentrations of 10^2 to 10^3 CFU/mL to concentrations of 10^5 to 10^7 CFU/mL following BECO application events.

Biologically Enhanced Chemical Oxidation transitions to natural attenuation seamlessly. The close integration of the chemical oxidation and biological action precludes field efforts to establish the proportionate effects of each process separately. The presented case studies will demonstrate the effectiveness of BECO in reducing fuel oil and gasoline associated hydrocarbons in full scale applications.

Poster Session- Environmental Forensics

Comparison of Two Methods for Estimating Time of Release for Diesel Fuel NAPL

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Improved Chemical Fingerprinting of Heavy Petroleum Fuels, Residua, Lubricants, Asphalts, Waxes, and Acid Sludge Waste using Conventional and High Temperature Gas Chromatography

Edward Healey, NewFields, Rockland, MA
Scott A. Stout, NewFields, Rockland, MA
Dan C. Villalanti, Triton Analytics Corporation, Houston, TX

Distinguishing Fuel from Non-Fuel Contamination in Soils at a Former Petroleum Terminal and Rail Yard using Chemical Fingerprinting

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Vincent Maresco, Groundwater & Environmental Services, Inc., North Syracuse, NY

Environmental Stability of PAH Source Indices in Pyrogenic Tars

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Comparison of Two Methods for Estimating Time of Release for Diesel Fuel NAPL

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One of the most challenging tasks facing forensic chemists today is identifying when a petroleum product was released to the environment. This is an important issue because it has a direct impact on who is financially liable for the site cleanup, and what insurance policy was in place at the time of release. Several methods are currently used to estimate time of release. For example, in gasoline NAPL, specific additives such as MTBE or tetraethyllead may provide vital chemical data do determine ownership and liability for the NAPL contamination. Distilled and blended petroleum products such as diesel fuel however, do not have any time specific additives that can be used to reliably age date a diesel fuel release. Diesel fuel age dating methods rely on two technical approaches. The most common approach currently used to age date diesel fuel is the Christensen and Larsen method. This method relies on the disparity in the rate of biodegradation among hydrocarbon classes such as *n*-alkanes (e.g., *n*-C_{17}) and isoprenoid alkanes (e.g.,pristane). Christensen and Larsen calibrated the rate of *n*-C_{17}/pristane degradation at 12 sites in northern Europe soils where one-time release of diesel fuel/fuel oil #2 reportedly occurred at a known time. The degradation rates determined in this study have been used at multiple sites in the United States to estimate the time of release in soil and NAPL samples with a purported error of approximately 2 years. The second approach to diesel fuel age dating is to utilize the regulated reduction in sulfur content to constrain the age of the diesel NAPL. Two case studies involving diesel fuel NAPL will be examined where both methods will be used to estimate the time of release. The advantages and limitations of each method to age date diesel fuel NAPL will be discussed.

Improved Chemical Fingerprinting of Heavy Petroleum Fuels, Residua, Lubricants, Asphalts, Waxes, and Acid Sludge Waste using Conventional and High Temperature Gas Chromatography

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Chemical fingerprinting of hydrocarbon contamination, which is commonly used in forensic investigations involving the nature and source(s) of contamination, is generally conducted using conventional gas chromatography (GC) using fused-silica, capillary columns with a non-polar stationary phase, often with a flame ionization (FID) or mass spectrometry (MS) detection. Conventional GC can provide “fingerprints” of hydrocarbons boiling between about C_5-C_{44}, with the upper boiling limit constrained by the stability of the GC column’s stationary phase (e.g. EPA Methods 8015 or 8270 and ASTM D2887).

High temperature simulated distillation (HTSD) is an adaptation of conventional GC/FID that utilizes a non-polar, low bleed stationary phase column (0.05-0.15 μm film thickness and 0.53 mm internal diameter), which safely can withstand temperatures up to 430°C. The high phase ratio of the column permits the elution of hydrocarbons 260 to 316°C below their true boiling points, and thereby permits elution and quantification of the percent mass of hydrocarbons with boiling points up to 750°C – i.e., up to C_{120}. When combined with cryogenic initial GC conditions, HTSD can expand the carbon range “fingerprint” from C_5-C_{120}, and allows the forensic expert to evaluate hydrocarbon distributions that conventional GC cannot. Some loss of chromatographic resolution of hydrocarbons in the C_5-C_{44} range is experienced by HTSD, but this is overcome when conventional GC and HTSD fingerprinting are used in parallel. The combination of conventional and high temperature GC provides added information in forensic investigations involving high boiling contamination, such as heavy fuels and crude oils, petroleum asphalts, waxes, greases, and petroleum or tar residua. The HTSD method is amenable to soils, sediments, and products (including semi-solids and solids). The forensic application of the combination of conventional GC/FID and HTSD is demonstrated for various petroleum fuels, residua (flux), various specialty asphalts produced via oxidation of flux, petroleum waxes, and lube oil acid sludge.

Distinguishing Fuel from Non-Fuel Contamination in Soils at a Former Petroleum Terminal and Rail Yard using Chemical Fingerprinting

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A peninsula located at the confluence of two rivers in upstate New York has had a long anthropogenic history, which has included an Indian village and French (1749-1760), and later British (1760-1783) and American (1783-1812), fortification. By the late 1800's the site was developed as a commercial/industrial area which included use as a municipal dump and large rail yard, and by about 1920 there was a small petroleum fuel terminal (west) and a barge dock (east) connected by ~1500′ of underground piping that spanned the rail yard (central) site. Rail yard operations ceased in the 1970s and petroleum handling operations ceased in 1984.

Soils throughout the former rail yard and petroleum terminal were impacted with hydrocarbons, including PAHs, that required determination of the "nature and extent" prior to remediation. NYDEC prescribed analytical methods, viz., (1) NYDOH 310-13 TPH fingerprinting, (2) EPA Method 8260 full analytes and TICs, and (3) EPA Method 8270 full analytes and TICs, which were augmented using "advanced chemical fingerprinting" based upon modified EPA Method 8015B and 8270.

The regulatory-required data were unable to recognize the eight predominant hydrocarbon sources – four petroleum sources and four non-petroleum sources - identified by advanced chemical fingerprinting. The normalized distribution of the 44 PAH analytes provided detailed fingerprints that, with the aid of numerical analysis (PCA), readily distinguished the eight hydrocarbon sources. The widespread occurrence of non-petroleum (pyrogenic) PAH associated with coal soot/ash and creosote was responsible for many TAGM clean-up criteria exceedences – and not petroleum.

As such, the remedial investigation (RI) of complex sites can benefit from advance chemical fingerprinting data, which provides additional "forensic" detail compared to regulatory-required data. In this case, the soils were shown to contained significant TPH and PAH attributable to non-petroleum sources.

Environmental Stability of PAH Source Indices in Pyrogenic Tars

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Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants found in soil, sediments, and airborne particulates. While low levels of PAHs in the environment have natural origins, the majority of PAHs found in modern soils and sediments arise from myriad anthropogenic petrogenic and pyrogenic sources. Tars and tar products such as creosote produced from the industrial pyrolysis of coal or oil at former manufactured gas plants (MGPs) or in coking retorts are viscous, oily substances that contain significant concentrations of PAH, usually in excess of 30% w/w. Environmental chemists often are tasked with identifying pyrogenic tars and tar products in the environment, and distinguishing the chemical signatures of such substances from other point sources of PAHs, and/or ubiquitous anthropogenic background PAHs. Combustion and pyrolysis of organic matter can yield source-specific distributions of PAH compounds. Pyrogenic tars and tar products have unique PAH patterns (source signatures) that are a function of their industrial production. Among pyrogenic materials, certain diagnostic ratios of environmentally recalcitrant 4-, 5- and 6-ring PAHs have been identified as useful environmental markers for tracking the signature of tars and petroleum in the environment. The use of selected PAH source ratios is based on the concept that PAHs with similar properties (i.e., molecular weight, partial pressure, solubility, partition coefficients, and biotic/abiotic degradation) will weather at similar rates in the environment thereby yielding stable ratios. In this poster, we evaluate the stability of more than 30 high molecular weight PAH ratios during controlled studies of tar evaporation and aerobic biodegradation. The starting materials in these experiments consisted of relatively unweathered tars derived from coal and petroleum, respectively. The PAH ratios from these laboratory studies are compared to those measured in PAH residues found in tar-contaminated soils at a former MGP that operated with a carburetted water gas process.

Poster Session- MTBE

Tert-Butyl Alcohol (TBA) Biodegradation by a Mixed Bacterial Culture *YZ1* Enriched from Granular Activated Carbon (GAC)

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Tert-Butyl Alcohol (TBA) Biodegradation by a Mixed Bacterial Culture *YZ1* Enriched from Granular Activated Carbon (GAC)

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Tert-Butyl Alcohol (TBA) is a groundwater contaminant that is miscible in water and adsorbs poorly to aquifer solids; therefore pump and treat is the strategy employed near drinking water sources. Unlike other organic contaminants, air stripping and adsorption technologies are relatively inefficient for TBA. TBA biodegrades under aerobic conditions and cultures that develop within granular activated carbon (GAC) reactors are used as the primary TBA removal mechanism in a technology dubbed “Bio-GAC”. A TBA degrading enrichment culture was developed from GAC material (*YZ1* – this culture has unique metabolic properties from *KR1*, enriched from the same GAC material)to 1.) quantify TBA degradation kinetics under changing reactor conditions, to 2.) serve as an inoculum for GAC reactors in which native TBA degrading communities do not develop, and 3.) test low biomass versus high biomass inoculation strategies. Data suggests that mineralization of TBA in resting cell suspensions is fast, with up to 100% of the TBA mineralized to CO_2 within 80 hours. What’s more, culture could be starved for 7days without losing TBA degradation ability. Growing cultures continuously degrade 5mM TBA within 5 days; however, kinetics are slow relative to the resting cell suspensions, which may allow TBA breakthrough during periods of increased pumping in field reactors. The culture degraded TBA at extreme temperatures, 4°C and 60°C, which implied its application to cold groundwater. The culture is alkaliphile. The culture grows readily in freshwater media; the culture also adapted to high phosphate media, which is useful for agricultural areas where phosphate concentrations are high in TBA-contaminated groundwater. TBA was the sole electron donor and carbon source. These data will be used to develop a TBA-degrading bio-GAC reactor for wellhead treatment that can maintain activity during environmental fluctuations or changing (high versus low biomass) inoculation strategies

Poster Session- Remediation

River Remediation Utilizing Environmental Dredging Techniques in Response to Methylene Chloride Impacts

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Jeffrey W. LaRock, AMEC Earth and Environmental, Inc, Schenectady, NY
Paul J. Kurzanski, CSX Transportation, Inc, Jacksonville, FL

Heat Flow and Desaturation in Large-Scale Experiments of Thermal Remediation of DNAPL Sources in Aquifers

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DNAPL Remediation at Camp Lejeune using Soil Mixing with ZVI-Clay Injection

Christopher Bozzini, CH2M HILL, Charlotte, NC
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Innovative Application of Full Scale Six-Phase Heating for DNAPL Source Removal

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The Evaluation of Extraction and Cleanup Methods for the Determination of PCB Aroclors in Caulking and Sealing Material

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PAH Bioremediation

Michael L. Cook, CJH Environmental, Inc., Sharon, MA

A Case Study of Innovative Organoclay Remedial Technology at a Former Railroad Creosote Treating Site

Jerry Darlington, CETCO, Arlington Heights, IL
Jim Olsta, CETCO, Arlington Heights, IL

Comparison of Three *in situ* Treatment Technologies for the Remediation of Trichloroethylene Impacted Groundwater

<u>Eva Dmitrovic</u>, *Adventus Remediation Technologies, Mississauga, ON*
Fayaz Lakhwala, Adventus Americas, Inc., Union, NJ
Jim Mueller, Adventus Americas, Inc., Freeport, IL
James G.D. Peale, Maul Foster & Alongi, Inc., Portland, OR
Erik Bakkom, Maul Foster & Alongi, Inc., Portland OR

Achieving Quality Installations of Deep Permeable Reactive Barriers for Treatment of Chlorinated Solvent-Contaminated Groundwater

<u>Stephen J. Druschel</u>, *Golder Associates, Inc., Manchester, NH*
Nancy E. Kinner, University of New Hampshire, Durham, NH

Case Study - Innovative In-Situ Anaerobic Remediation to Treat Fuel-Oil Contamination

<u>Alexander Easterday</u>, *ECC, Marlborough, MA*
Robert Wasserman, ECC, Marlborough, MA
Curt Varner, TRC Environmental Corporation, Raleigh, NC
Eric C. Hince, Geovation, Inc., Florida, NY
Antonio Leite, US Navy, Groton, CT

Use of Electrical Imaging and Microscopy to Evaluate Distribution of Injected Nano-scale Zero Valent Iron

<u>Dan Elliott</u>, *The Whitman Companies, Inc., East Brunswick, NJ*
<u>Edward Sullivan</u>, *The Whitman Companies, Inc., East Brunswick, NJ*
Eric C. Hince, Geovation Consultants, Inc., Florida, NY
Christopher DelMonico, The Whitman Companies, Inc., East Brunswick, NJ

Combining Technologies for Source Area and Downgradient Contaminated Groundwater Remediation Using AS/SVE and iSOC Technology

<u>Craig Ellis</u>, *Environmental Compliance Services, Inc., Wakefield, MA*
Jamie Smith, Environmental Compliance Services, Inc., Wakefield, MA
James F. Begley, MT Environmental Restoration, Plymouth, MA

A Pilot Study using a Chemical Oxidant and Surfactant to Remediate Petroleum Hydrocarbons at an Active Gasoline Station

<u>Joseph Hayes,</u> *ECS, Richmond, VT*
Maureen Dooley, Regenesis, Wakefield, MA

Combined Chemical Oxidation and Volatilization Enhances Guaranteed Remediation Performance

<u>Patrick Hicks</u>, *ATC Associates, Inc, Raleigh, NC*

Combined Excavation and In-Situ Oxidation via $KMnO_4$ Injection

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Permeable Sorption Barriers for Groundwater Protection Includes Organoclay, Clay, Bentonite Geotechnical Fabric and Anaerobic Treatment of Pesticide Contaminated Soils

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George Alther, Biomin, Inc., Ferndale, MI

Small Column Experiment to Evaluate Compost Materials as Filter Media to Remove Colloidal Particles

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Retardation Properties of Clay Materials as Engineered Barriers in Repositories of High-level Waste

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Hana Vinsova, Institute of Chemical Technology, Prague, Czech Republic
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Thermally Enhanced Soil Vapor Extraction: the HeatTrode^{TM} System

Kevin P. McGrath, Earth Tech, Inc., Latham, NY
Donald J. Geisel, Donald J. Geisel & Associates, Inc., Clifton Park, NY
Anne Lewis-Russ, Earth Tech, Inc., Greenwood Village, CO

Remediation of a 2,000-Gallon Fuel Oil Release at a Private Residence via Soil Excavation, Groundwater Treatment, and Enhanced Bioremediation

Anne McNeil, ENPRO Services, Inc., Newburyport, MA
Geoffrey A. Brown, ENPRO Services, Inc., Newburyport, MA

PCB Remediation of a High-Hazard Dam

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Mark Mitsch, Weston & Sampson Engineers, Inc, Peabody, MA
Prasanta Bhunia, Weston & Sampson Engineers, Inc, Peabody, MA

High-Performance Attrition in a Wet-Mechanical Soil Washing Plant

Friedrich Schaaff, AKW Apparate + Verfahren GmbH, Hirschau, Germany
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Firing Range Closure to Prepare for Military Modernization

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Kim M. Plunkett, Commonwealth of Massachusetts Division of Capital Asset Management, Boston, MA
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Enhanced Chlorinated Solvent Dechlorination Using Groundwater Re-circulation for Effective Substrate Delivery

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Controlling Costs to Achieve Permanent Closure for a Quench Oil Site

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Biosparging of a Smear-Zone Plume of Residual Diesel in the Sub-Arctic

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River Remediation Utilizing Environmental Dredging Techniques in Response to Methylene Chloride Impacts

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On December 23, 2001 a freight train derailed approximately 150 feet from the Genesee River in Rochester, New York. As a result of this 27-car derailment, approximately 14,000 gallons of acetone and 16,000 gallons of methylene chloride were released into the environment. To address the release of acetone and methylene chloride, several phases of remedial activities were conducted at the Site beginning in December of 2001. Initial activities included delineation of the spill and monitoring of the Genesee River to assess water quality. These investigations indicated that elevated concentrations of methylene chloride and acetone were present in the river sediment and that a plume was directly east of the shoreline extending to the center of the channel. Bioassay studies from sediment collected in the channel indicated that growth and survival of invertebrate organisms in the river were not adversely affected by the concentrations of methylene chloride found in the sediments. Several river sediment-sampling events confirmed that the plume was stationary, but natural attenuation of the plume appeared to be limited. The impacted sediments were located within the Navigable Channel limits and state regulators insisted that bioassay studies and plume monitoring events were not sufficient.

This paper will discuss how dredging utilizing an environmental bucket and dredge cell approach proved to be an effective technology for removing a majority of impacted sediments while protecting the environment and community along with maintaining the river's navigability. Through the use of GPS technology dredging was conducted with accuracy and precision that increased optimization. Environmental parameters such as turbidity and chemical monitoring verified the effectiveness of the measures taken to protect the river. Implementation of a Community Air Monitoring Plan (CAMP) ensured protection of the surrounding communities.

Heat Flow and Desaturation in Large-Scale Experiments of Thermal Remediation of DNAPL Sources in Aquifers

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In-situ thermal remediation (ISTR) technologies are receiving increasing attention for remediation of dense non-aqueous phase liquid (DNAPL) source zones in soil and groundwater. A clear understanding of the mechanisms of ISTR is crucial in selection of appropriate sites and effective ISTR technologies for DNAPL source zone remediation. Large-scale physical model experiments have proven indispensable for incorporating thermal interactions between soil layers of different permeability. In this Strategic Environmental Research and Development Program (SERDP)-funded project, large-scale physical models are being used to address several essential research questions, including: (a) the relative significance of various contaminant removal mechanisms below the water table (e.g., steam stripping, volatilization, in-situ destruction); (b) the percentage of DNAPL source removal and accompanying change in water saturation at various treatment temperatures/durations through boiling; and (c) the potential for DNAPL mobilization through volatilization and recondensation and/or pool mobilization outside the target treatment zone during heating. Thermal conductive heating (TCH) is an ISTR method that takes advantage of the invariance of thermal conductivity across a wide range of soil types to effect treatment of DNAPL in lower-permeability and heterogeneous formations. TCH can complement steam-enhanced extraction, which is generally more applicable to higher-permeability formations. TCH accompanied by vacuum extraction is being employed in large-scale (containers 3 x 6 x 4.5m, and 6 x 6 x 4.5m) [width, length, height] controlled-release, closed mass balance experiments with geologically-relevant layering. In parallel, non-isothermal numerical modeling issimulating the controlling mechanisms and processes of the experiments. This research will answer key questions associated with the effectiveness of ISTR and lead to improvements in screening, selection, evaluation and design of field-scale ISTR systems.

DNAPL Remediation at Camp Lejeune using Soil Mixing with ZVI-Clay Injection

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Site 88 at Marine Corps Base Camp Lejeune, NC is the former Base dry cleaners. The dry cleaner was about 60 years old and located in a densely developed area. Historical activities resulted in a release of solvents, especially tetrachloroethene (PCE). CH2M HILL conducted the delineation of the source area using multimedia sampling and AGVIQ-CH2M HILL JV1 completed the remediation. The volume of contaminated soil was about 7,000 cubic yards, containing an estimated 14 tons (~2,100 gallons) of PCE. Prior to implementation, groundwater concentrations of PCE and daughter products totaled 145,000 μg/L and product was observed in several monitoring wells. Soil mixing with zero valent iron (ZVI) and clay addition was the selected for remediation because the patented technology is robust, can overcome subsurface heterogeneity, and reduces the soil conductivity thus reducing contaminant mobility. The ZVI-clay and soil mixture was injected using a 10-ft auger mounted on a crane to mix 146 overlapping columns to a depth of 20 feet below ground surface. After preparing the site by removing all monitoring wells, subsurface utilities and the former building slab, treatment occurred over 17 days with 200 tons of ZVI and 100 tons of bentonite mixed into the soil. Post-treatment monitoring of the site has included soil, groundwater, soil vapor sampling and analyses, and qualitative analysis using membrane interface probe (MIP) technology. The remedial action has worked well as PCE concentrations in soil have been reduced from 1,100 mg/kg to less than 1 mg/kg across most of the treatment area. Soil gas results have shown 99% reduction in PCE. In addition the hydraulic conductivity of the soil has been reduced by an order of magnitude, thus reducing future contaminant migration. After treatment was completed, the site was stabilized using concrete and a parking lot has been constructed over the entire area.

Innovative Application of Full Scale Six-Phase Heating for DNAPL Source Removal

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Full scale six-phase heating (SPH) was performed at IR Site 5, Alameda Point for DNAPL source removal within the 10,000 µg/L total contaminants of concern (COCs) contour of Plume 5-1, an area of roughly 15,000 ft^2, to a maximum depth of 20 ft bgs. The principal COCs were 1,1-DCA, 1,1-DCE, and 1,1,1-TCA.

The successful full scale application of SPH required technology innovation. Five standard SPH cells, each six electrodes arranged in a hexagonal pattern with a neutral electrode at its center, were used to heat the entire plume. Novel parallel operation of adjacent SPH cells, with appropriate electrode phasing, was required for interstitial area heating through electrical cross talk. Innovative multiple-member electrodes were utilized to achieve increased application rates and driven sheet-pile electrode members were cost effectively installed to provide greater surface area than the standard drilled electrodes.

The full scale SPH application at Plume 5-1 began on July 8, 2004 and was terminated November 5, 2004. The average plume temperature increased from an initial value of 22ºC to 92ºC within a 12-week period, and was maintained for 3 weeks prior to termination. Contour mapping of the temperature data confirm that all plume areas were heated to at least 90ºC. Daily mass removal rates, estimated from continuous and periodic vapor sampling, show that more than 3,000 pounds of VOCs were recovered. Groundwater concentrations were reduced from an average initial total COCs concentration of 54,000 micrograms per liter (µg/L) to less than 100 µg/L at the end of the active heating period, or a reduction of 99.8 percent. Follow-on sampling in March 2005 showed minimal rebound.

The full scale utilization of SPH at Plume 5-1 was the largest application of SPH to date, and proves that the technology can be scaled up for balanced, effective heating of a large area. In February of 2006 we began the installation of a SPH system for source removal at Plume 5-3, an area of roughly 40,000 ft^2, to 20 ft bgs. Operations should begin in May 2006.

The Evaluation of Extraction and Cleanup Methods for the Determination of PCB Aroclors in Caulking and Sealing Material

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Buildings that were built and/or refurbished before 1977 may well have caulking used to seal masonry joints and windows that contain PCB Aroclor 1254 and/or 1260. The Aroclors were used as a plasticzier and were added to the material to ease application and improve resiliency. The caulking material has been mainly used when there are dissimilar materials, like brick next to concrete, metal window framings, and roofing joints.

Several investigations took place in the 1990's in Germany, Sweden, and Finland. The studies established relationships between PCBs in caulking and levels in indoor air as well as in soil around the foundations of buildings containing these materials (Balfanz et al. 1993; Burkhardt et al. 1990; Pyy and Lyly 1998). This same relationship has been demonstrated here in the US by R.F. Herrick (2004) and his team at the Department of Environmental Health, Harvard School of Public Health, Boston, MA. This study surveyed the PCB content of caulking from 24 buildings in the Boston Area. Of the 24 buildings sampled, 13 contained caulking with detectable PCBs. Of these, 8 buildings contained caulking that exceeded the USEPA's hazardous waste standard of 50 ppm. The laboratory identified the PCB as Aroclor 1254 and Aroclor 1260.

Commercial laboratories, like NEA, are put to the test when analyzing caulk matrix. Caulking material itself is made of several different polymer components, many of which can interfere with the extraction and detection of PCBs. Typically, results are requested on a quick turnaround basis. So, the challenge is to optimize extraction and cleanup methods for this matrix. NEA has evaluated 4 extraction methods for processing caulk. The extraction methods are soxhlet, sonication, accelerated solvent extraction (ASE) and polytron homogenization. All extractions used 1:1 Hexane/Acetone. Several cleanup methods were also employed on the sample extracts including: acid wash, Florisil slurry, Florisil columns, and ultrasonication. NEA analyzed the samples by USEPA Method 8082 Aroclor analysis by GC/ECD. We will present an optimized method that is rugged, fast, cost effective, and has reproducible results.

PAH Bioremediation

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The property at 248 Lynn Road in Brockton, MA consists of a one family ranch house constructed using a slab-on-grade construction technique. Heating of the home was provided through a central heating unit located in the kitchen using an oil fired forced hot air ducting arrangement. The fuel oil tank was located outside the structure along the south wall of the home inside a small wooden shed attached to the house. Fuel was supplied to the heating unit via a small diameter copper tube placed beneath the floor slab. In late 1992/early 1993 it became evident that something was amiss with the fuel distribution system to the heater. A subsurface investigation report dated April 26, 1993 indicated that the fuel line from the AST to the heater had failed and that a significant, but unknown, quantity of fuel oil had been released to the subsurface soils beneath the floor slab. The extent of contamination appeared to be well defined. Several attempts were made to determine whether fuel oil had migrated outside the perimeter walls of the slab foundation with indications being that it had not done so. All the contaminants appeared to be located directly beneath the floor slab in the kitchen area, with some spread under the adjacent bedroom and living room areas. After several years of legal wrangling, an agreement was reached among the various potentially responsible parties to allow remediation to move forward. A release Abatement Measures Plan was prepared dated March 21, 2001 for bioremediation (PAH) of the property after several false starts negotiating a suitable contract agreement among the parties. Approximately one more year passed before all the appropriate approvals and contracts had been signed and remediation began.

This presentation chronicles the efforts made to remediate this property to a successful conclusion.

A Case Study of Innovative Organoclay Remedial Technology at a Former Railroad Creosote Treating Site

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The concept of permeable reactive barriers (PRB) had generated great interest in the field of groundwater remediation in the last few years. Organoclay media has become an option as the reactive material for this type of application due to its high adsorption capacity, high removal efficiency on a variety of organic species, cost and availability. The case study described below illustrated the use of organoclay media in construction of a permeable reactive barrier, as well as a reactive capping mat, to treat contaminated groundwater.

The groundwater at a former creosote railroad tie treating site was contaminated by NAPL (non-aqueous phase liquid). The contaminated groundwater was a threat to the nearby fresh water bay when NAPL and soluble organics were found seeping into the bay. The solution to stop this pollution spreading through the bay and into Lake Michigan was to install an organoclay reactive capping mat along the affected stretch of beach and a passive reactive wall behind the reactive capping mat.

Rolls of organoclay reactive capping mat were laid along a 5 m x 80 m stretch of beach. The reactive capping mat was covered with 15 cm of 18 mm stone and then 60 cm of riprap. As soon as the reactive capping mat was placed the sheen that had been seeping into the bay dissipated.

Bulk organoclay was mixed with 3 parts 6 mm gravel in a stockpile. Approximately 5 m behind the reactive capping mat, a continuous trenching machine placed the organoclay-gravel mix in a 45 cm wide by 3 m deep by 80 m long trench.

Comparison of Three *in situ* Treatment Technologies for the Remediation of Trichloroethylene Impacted Groundwater

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Adventus conducted a bench scale treatability study on groundwater impacted with trichloroethylene (TCE) from a site in the northwestern USA. The study tested the effectiveness of three commercially available *in situ* treatment technologies (emulsified oil, lactate, and EHC) for the removal of TCE. A series of columns were set up with soil and groundwater samples collected from the Site including an "as is" control and sterile control. Two columns were set up for each technology and one of the columns from each pair was inoculated with a *Dehalococcoides* microbial culture. Due to the low groundwater velocity at the Site, the columns were operated in batch mode rather than flow through systems. The columns were filled with impacted groundwater and the water within the column was recirculated for a given period of time (14, 21, or 28 days). The analytical results from the last 14-day contact period indicated that the total VOC concentration in the groundwater feed was 11,000 ppb and this was reduced to 244 ppb, 5,569 ppb, and 63ppb in response to the emulsified oil, lactate, and EHC treatments inoculated with the *Dehalococcoides* microbial culture, respectively. Complete results from the column testing will be presented.

EHC is a remediation product that uniquely combines controlled release solid carbon and zero valent iron (ZVI) to stimulate reductive dechlorination of organic solvents in the subsurface. EHC supports both biological and chemical removal of contaminants. The organic components of lactate and emulsified oil undergo microbial fermentation to produce fatty acids, which serve as electron donors for reductive dehalogenation. As such, these products lack the combined effects of biological and chemical processes that yield *in situ* chemical reduction (ISCR) of targeted contaminants. Cost data and engineering design variables will also be presented.

Achieving Quality Installations of Deep Permeable Reactive Barriers for Treatment of Chlorinated Solvent-Contaminated Groundwater

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In situ, passive groundwater treatment for volatile organic compounds may be accomplished by installing a permeable reactive barrier (PRB) ahead of the contamination plume. Reactive media may be zero valent metal, microbially-enhancing organic substrate, or sorbent material such as activated carbon. PRB construction appears so simple: dig a deep trench and fill it with reactive media, stand back and let treatment happen. However, it is the construction beneath the groundwater surface that makes the details complex, such as maintaining trench support, keying into underlying rock or preventing holes ("windows") in the reactive media. Quality is achieved by maximizing treatment, while having a reliable, well-understood installation. Simple in design, a PRB may be difficult to construct due to the constraints of working below the groundwater, particularly when depths totaling more than 30 feet are attempted. Meeting all goals of design will create a basis for trust between designers, constructors, owners, regulators and the community; stumbling through construction difficulty can destroy such trust. In this paper, construction techniques currently in use for PRB excavation and backfill are discussed and evaluated for potential implications in four PRB failure modes. Design and construction processes are assessed in a case study of a 400-foot long by 65-foot deep PRB installed for treatment of a large tetrachloroethene release in residual and lacustrine soils. A ten-step system is proposed to emphasize readiness and preparation during PRB installation as a method to achieve quality, gain trust and reduce costs.

Case Study - Innovative In-Situ Anaerobic Remediation to Treat Fuel-Oil Contamination

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This case study details the application of an innovative, anaerobic *in situ* technology to remediate petroleum contamination associated with a former No. 2 fuel oil underground storage tank at a military housing residential annex in Groton, Connecticut. The release site is located upgradient of a surface water receptor that serves as a secondary drinking water source for the City.
A remedial investigation was completed at the site to characterize the nature and extent of petroleum impacts, and several remedial alternatives were evaluated to treat hydrocarbon impacts to soil and groundwater. Several applicable remedial alternatives were considered, including excavation, aerobic *in situ* technologies, anaerobic *in situ* technologies, and traditional engineered remedial alternatives (i.e., soil vapor extraction/air sparging). While excavation was identified by regulators as the preferred remedial method, it was precluded from use given the site location, the prohibitive cost, and due to a large portion of the contaminant mass underlying the existing residential structure. Therefore, an anaerobic *in situ* treatment technology (denitrification-based bioremediation [DBB]) was recommended and selected as the remedial approach at this site. The acceptance of the DBB treatment technology by the regulators was the *first application of this remedial technology in the State of Connecticut.* In Sept 2003, baseline sampling was performed to document pre-remedial conditions. The nitrogen-based treatment solution was introduced to the subsurface through micro-wells and via passive diffusion gradients. Periodic soil and groundwater sampling activities were performed to assess treatment efficacy with respect to contaminant concentrations, and demonstrated that DBB successfully reduced the contaminant mass underlying the site (i.e., 50-60 percent reductions in sorbed-phase concentrations) while mitigating additional impacts to groundwater. The site-specific treatment program and post-treatment sampling activities were completed in July 2004. Additional monitoring data and focused treatments were completed in 2005 and 2006 which will be presented in this poster.

Use of Electrical Imaging and Microscopy to Evaluate Distribution of Injected Nano-scale Zero Valent Iron

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A pilot study was conducted using nano-scale zero valent iron (nZVI) and an emulsified soy oil product to promote dual abiotic and biotic degradation of TCE at a site in New Jersey. The nZVI and emulsified oil injections targeted a low permeability silt unit where most of the contaminant mass was bound. A sand aquifer overlies the silt unit. Pneumatic and hydraulic fracturing techniques were used to enhance the distribution of the injected amendments. A comparison of pre and post-injection Electrical Imaging (EI) surveys and ground water microscopy samples were used to evaluate the distribution of the nZVI particles achieved by the fracturing techniques.

The conductivity of saturated earth materials is dominated by the porosity and pore moisture chemistry. A decrease in the resistivity would be consistent with an increase in the conductivity of the saturating fluid due to the iron in the injected fluid. An increase in resistivity would be consistent with a decrease in the conductivity of the saturating fluid possibly due to the presence of high concentrations of chlorinated VOCs. The penetration depth of the EI survey was not sufficient to evaluate resistivity changes at the depth of injection. However, an increase in resistivity was noted in the sand aquifer interval just above the silt unit. Post-injection sampling data also showed a significant increase in TCE concentrations in this interval. This indicates that the injection techniques likely mobilized TCE mass upward from the silt unit into the sand aquifer.

The nZVI particles were observed via transmitted light microscopy and imaged with a CCD camera as angular, opaque objects ranging in size from less than 1 um to approximately 5 µm indicating that significant aggregation has occurred. nZVI particles were detected in samples collected from monitoring wells in the silt unit and the overlying sand unit at distances up to 25 feet from the injection points. This indicates that both of the fracturing techniques were successful in distributing the nZVI a significant distance from the injection points. Computer image analysis software running a particle-counting subroutine was utilized to count the number of nZVI particles in each sample. In general, higher nZVI particle counts were seen in the silt unit wells. No particles resembling nZVI were observed in the wells sampled prior to the nZVI injections to determine baseline conditions. To our knowledge, this is the first time these relatively inexpensive imaging and microscopic techniques were applied to the detection of injected nZVI in the field.

Combining Technologies for Source Area and Downgradient Contaminated Groundwater Remediation Using AS/SVE and iSOC Technology

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Remediation of groundwater contaminated by historical releases of gasoline at a Massachusetts site required a combination of technologies to address high concentration source area soil and groundwater contamination as well as a plume of contaminated groundwater that had migrated from the source area. The remedial action plan included source area air sparging and soil vapor extraction combined with enhanced monitored natural attenuation using the in-situ Submerged Oxygen Curtain (iSOC) System at a remote down gradient location. A case study of combined technologies implemented at the site will be presented that includes the basis for system design and the results of performance monitoring.

A Pilot Study using a Chemical Oxidant and Surfactant to Remediate Petroleum Hydrocarbons at an Active Gasoline Station

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This presentation will discuss the results of a pilot study involving bench-scale testing and a field injection program using a chemical oxidant, REGENOX^{TM} and a surfactant, BIOSOLVE® at an active gasoline station in Vermont. The objective of this pilot study was to field test the application of combining a chemical oxidant and surfactant to remediate residual gasoline related VOC contamination for possible full scale application to meet site closure criteria.

The pilot test was designed to address residual dissolved phase gasoline related VOC concentrations remaining in the subsurface near an existing gasoline dispenser island that were not completely remediated under a under Vermont's Pay for Performance Program. The REGENOX^{TM} product uses a solid alkaline oxidant that is activated through the action of a proprietary dual catalytic system. BIOSOLVE® is a water based biodegradable non-ionic surfactant that was specifically engineered as a remediation product for a wide range of petroleum hydrocarbons.

The results of bench-scale testing indicated that there was little reactivity between the REGENOX^{TM} and BIOSOLVE®, and that field testing was warranted to further evaluate this remedial approach. The purpose of including a surfactant in the injection program is to solubilize the adsorbed-phase contaminants making them more amenable to chemical oxidation.

The aqueous solution of oxidant and surfactant will be injected using conventional direct push drilling equipment and an injection pump over a depth interval of approximately 5 to 15 feet below ground surface. Prior to and following injection, a monitoring program will be instituted to evaluate the effectiveness of the surfactant and oxidant mixture at reducing VOCs in the test area.

Combined Chemical Oxidation and Volatilization Enhances Guaranteed Remediation Performance

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A guaranteed fixed price remediation project in Salt Lake City, UT was initiated in 2003. The site is a former dry cleaner facility, and is regulated under the Utah Voluntary Cleanup Program (UVCP). A cleaning solvent release resulted in a dissolved plume of Tetrachloroethene (PCE), Trichloroethene (TCE) cis 1,2-Dichloroethene (cisDCE), trans 1,2-Dichloroethene (trans DCE), and Vinyl chloride (VC) below the facility that migrated down gradient across the property. Buildings and traffic at the location restricts access to portions of the dissolved plume, and site geology and geochemistry is relatively complex. Thus, the project required a remediation approach with sufficient operational flexibility to compensate for the technical challenges presented by site conditions.

A combined approach using permanganate as a chemical oxidant, and in well volatilization (IWV) and traditional soil vapor extraction (SVE) was implemented at the site. The IWV and SVE components were installed and began operation in March 2004. The chemical oxidation process began on a pilot test scale in April 2004, and was implemented on a full-scale basis in August 2004. The enhanced distribution of the permanganate by the IWV system was considered to be a critical design component given the complex lithology at this site.

The chemical oxidant (3.5% sodium permanganate) injections were limited to 3,200 gallons in April and 5,100 gallons in August 2004. The IWV and SVE systems were operated until January 2005, at which time active remediation was suspended. Based on May 2005 groundwater monitoring, concentrations of dissolved solvent constituents have been reduced by 90% or more from baseline concentrations in portions of the plume, and have been completely eliminated in some monitoring wells. Negotiations with the UVCP regarding risk-based closure options are ongoing, and it is anticipated that closure will be obtained in the near future.

Combined Excavation and In-Situ Oxidation via $KMnO_4$ Injection

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Remediation usually requires the combined effects of different remediation technologies each playing a key role in focusing on the target media. The combined effects are required to achieve closure goals or remove the source of contamination.

The synergistic effect of combined soil excavation and oxidant ($KMnO_4$) injection to treat soil and groundwater impacted with PCE was demonstrated at a former dry cleaner site in Indiana. The source area soils were identified during a phased site investigation. The conceptual site model suggested that PCE was released from a section of broken drain line that ran from the former dry cleaner and tied into the sanitary sewer system. A corresponding dissolved phase plume was identified in the groundwater at this location and extending down gradient of the release.

Site re-development activities drove the schedule on this project, and minimized access to the plume. Traditional excavation was used to remove approximately 840 tons of PCE impacted soils in the source area. In conjunction with source soil removal, a series of $KMnO_4$ injection wells were installed to address the dissolved phase PCE near and down gradient of the source area.

The rapid removal of the source area soils has allowed the $KMnO_4$ injections to more effectively address dissolved contaminants without dealing with a large adsorbed phase source. Groundwater concentrations in the area immediately down gradient of the soil source area that were originally as high as 9,300 parts per billion (ppb) have decreased to below 200 ppb. Many monitoring wells in the area immediately down gradient of the former soil source area now have dissolved concentrations below the detection limit.

Permeable Sorption Barriers for Groundwater Protection Includes Organoclay, Clay, Bentonite Geotechnical Fabric and Anaerobic Treatment of Pesticide Contaminated Soils

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Approximately 29,000 tons of soils contaminated with DDT and toxaphene were treated with proprietary amendments designed to facilitate a combination of anaerobic reductive dechlorination and anaerobic oxidation biodegradation processes. After treatment, the soils were placed in a “biocell” designed for long-term containment and passive anaerobic bioremediation. Permeable sorption barriers were constructed as groundwater-protection components of the biocell. The lower barrier was constructed by amending native coarse-sand and gravel soils with a 3:1 mixture (weight/weight) comprised of 116,000 lbs. of montmorillonite and 40,000 lbs. of a proprietary “organoclay” specialty filtration media (Biomin, Inc.). This organoclay had been tested for its effectiveness to fixate such pesticides as alachlor, diazinon, metolachlor, 2,4-D, trifuralin, 2,4,5-T, and others. The clay materials were mechanically incorporated into the upper six inches of native soils and compacted to achieve a permeability estimated to be on the order of from 1×10^{-5} to 1×10^{-6} cm/sec (substantially lower than estimated “native” permeability of about 1×10^{-2} cm/sec). The clay minerals within the sorption barrier provide a selective capacity to adsorb more than 2×10^{10} mg of pesticides, an amount 10 times greater than the total mass of pesticides present in the soils prior to treatment. Based on calculations of estimated leak rates through the overlying geosynthetic clay liner (GCL), the clay-amended sorption barrier would provide protection for an estimated 7×10^{7} years against pesticides leaching at concentrations approaching their maximum solubility.

A Bentomat™ SDN geosynthetic clay liner (GCL) was installed immediately above the clay-amended sorption barrier (CETCO Lining Technologies). Bentomat™ SDN consists of a layer of sodium bentonite between two sheets of non-woven geotextile fabric. The GCL was installed immediately above the clay-organoclay sorption barrier, around the sides of the biocell and anchored into clean soil berms surrounding the biocell to provide further containment and long-term groundwater protection. Aside from the obvious protective benefits provided for by the GCL, the primary function of the GCL is to slow the rate of fluid flow through the overlying peat-amended biofiltration layer and hence to greatly increase the residence time of pore-water fluids in the biofiltration layer. The biofiltration layer is comprised of a mixture of >2,300 cubic yards of clean and low-pesticide-concentration soils (i.e., ± 0.5 - 10 mg/Kg) blended with >248,000 lbs. of aged peat. The peat-amended soils comprising the biofiltration layer were processed in a power screen and emplaced on the surface of the GCL via a mechanical conveyor system. The final installation of the biofiltration soil layer resulted in a ± one-foot thick lift immediately above the GCL. The amount of aged peat incorporated into the biofiltration layer provides a selective capacity to adsorb more than 9×10^{10} mg of pesticides, approximately 90 times the total mass of pesticides present in the soils prior to treatment. Based on calculations of estimated leak rates through the underlying GCL, the peat-amended biofiltration layer would provide protection for more than 2.5×10^{8} years against pesticides leaching to groundwater. The combination of the clay-amended sorption barrier, Bentomat GCL and peat-amended biofiltration layer provide a total selective capacity to adsorb more than 1.25 x 10^{11} mg of pesticides, (two orders of magnitude greater than the total mass of pesticides prior to treatment), and provide more than 3.5 x 10^{8} years protection against the leaching of pesticides to groundwater.

Small Column Experiment to Evaluate Compost Materials as Filter Media to Remove Colloidal Particles

STUDENT PRESENTER

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The treatment of low levels of PCB contamination in stormwater runoff or wastewater treatment effluent represents a significant cost to manufacturing and remediation facilities. Current regulatory requirements require the use of best available technology (BAT) which consists of activated carbon followed by filtration. Natural media filtration (NMR) represents a possibly significantly more economical process alternative to BAT. The goal of this research was to determine filtration efficiencies of colloidal particle in NMR columns.

In this study, mushroom and leaf compost materials were evaluated as a filter media to remove colloidal particles through a series of short pulse column experiments. The transport and deposition of model colloidal particles as a function of ionic strength and filter media were measured and evaluated by determining the first-order kinetic deposition rates. Next to two natural filter media, experiments were conducted also using sand and granular activated carbon.

The results of this experiment demonstrate that the solution ionic strength influences the dynamics of colloidal deposition and transport in heterogeneous porous media. Deposition rates depend also on the filter media; highest deposition rates were observed for granular activated carbon followed by leaf compost, mushroom composts and lowest deposition rates were found for sand. As expected, highest deposition rates were obtained at higher ionic strength. The significant change in deposition rate as a function of both ionic strength and filter media could be explained by DLVO theory. Electrostatic surface interactions between colloidal particles and porous media were examined through electrophoretic mobility analysis as a function of ionic strength and solution pH. Results of these measurements demonstrate that increasing ionic strength and the presence of divalent Ca^{2+}counterions lead to a decrease in electrophoretic mobility. This is consistent with predictions of the DLVO theory which predicts that at higher ionic strength and in the presence of divalent cations a compression of the double layer thickness occurs. Under these conditions more colloidal particles can be expected to deposit on the surface of porous media.

Overall the experiments suggest that the NMF process may efficiently filter colloidal particles from surface waters. However, surface water chemistry will significantly affect the filtration efficiencies.

Retardation Properties of Clay Materials as Engineered Barriers in Repositories of High-level Waste

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Research on a bentonite-based engineered barrier designated for safe underground disposal of high-level radioactive waste is a special multidisciplinary issue. To obtain the findings enabling the design of such construction, all experimental tools and procedures available must be used. With respect to extremely long time requirements for rheological stability and safety of the whole designed system, the physical, chemical and geophysical results of research were cumulated for physical modelling.

Bentonite was chosen as a buffer material surrounding the waste packages with spent fuel in deep waste repositories. The main merit of this material is very low permeability, high plasticity and its ability to seal the possible fractures by swelling in contact with water and therefore diffusion is the only possible mechanism of transport of radionuclides through the bentonite. Understanding of sorption and diffusion mechanism is essential in the assessment of radionuclide release through the bentonite buffer and backfill to the environment.

The effort has been done to interpret the sorption and diffusion data, particularly for radionuclides of cesium, stroncium and tritium and technecium as the representatives of multivalent elements. This information has important implications for modelling sorption and diffusion processes.

Experimental data allow a comparison of properties of bentonite before and after the load from the point of view of changes of its chemical and physico-chemical characteristics.

For performance and evaluation of experiments the through diffusion method has been applied and apparent diffusion coefficients (D_a) were evaluated by common analytical methods. In diffusion and sorption experiments the effect of particle mesh-size, different bulk densities and aerobic or anaerobic conditions on being in motion processes were studied, because oxidizing or reducing conditions influence chemical forms of multivalent elements.

The results obtained during sorption and diffusion study were applied as incoming parameters for the mathematical description of individual processes proceeded in the bentonite barrier. The essential aim of kinetic studies was to determine an optimum time to get the studied system into the equilibrium state, e.g. time when maximum values of distribution coefficients K_D and sorption yields are reached under given conditions.

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Thermally Enhanced Soil Vapor Extraction: the HeatTrode^{TM} System

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Thermally enhanced soil vapor extraction (TESVE) has been proven to be an effective remedial alternative for removing volatile organic compounds (VOCs) from unsaturated permeable soils. Methods used for heating the subsurface soils include hot air injection, electricity, or steam. Numerous case studies of these applications are available demonstrating the viability of TESVE.

Under a research grant from the New York State Energy Research and Development Authority, Donald J. Geisel & Associates, Inc. (DGA) conducted a field pilot test of their proprietary HeatTrode^{TM} System at a site containing sequestered free product in the soils from grade to the seasonally low water table. The free product included benzene, toluene, ethylbenzene, and xylene (BTEX) used in the manufacturing of phenolic compounds. Accidental releases from raw product, intermediate process, and final product storage tanks had saturated the soils with BTEX and semivolatile organic compounds (SVOCs) phenolic. A remedial investigation and feasibility study (RI/FS) of the site had determined that TESVE of the VOCs followed by bioventing of the SVOCs was the preferred remedial alternative for the site.

The HeatTrode^{TM} System is a hot water recirculatory system with collocated air extraction. Individual units can be adjusted and regulated to maintain both uniform heating throughout the remediation cell and balanced air withdrawal rates, effectively eliminating the formation of null zones (zones of no effect) within the area of treatment. The pilot test was conducted from March 2004 through September 2005. During the test near total removal of VOC contaminant mass was attained the soils while maintaining optimal conditions for reemergence of a microbial population for the eventual biodegradation of the residual phenolic compounds.

At the request of DGA, Earth Tech conducted an evaluation of the results of the pilot-test which, is reported in this case study. Earth Tech concluded that the application of the HeatTrode^{TM} System is an effective and efficient remedial alternative.

Remediation of a 2,000-Gallon Fuel Oil Release at a Private Residence via Soil Excavation, Groundwater Treatment, and Enhanced Bioremediation

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A release of approximately 2,000 gallons of fuel oil occurred at a residential property as a result of a leaking, subfloor fuel oil feed line. A neighbor discovered the release when he noticed oil breaking out of his lawn. ENPRO was contracted through the homeowner's insurance agency to cleanup the release. To initiate the cleanup, ENPRO obtained verbal approval from the MADEP to conduct an Immediate Response Action (IRA) at the site. In accordance with the IRA Plan, 400 tons of petroleum contaminated soil were excavated and recycled off site as asphalt batch material, 685 gallons of fuel oil were recovered from the subsurface and transported offsite for disposal, and soil and groundwater samples were collected to investigate the extent of contamination. Additionally, because the site bordered a Town-owned wetland area, ENPRO performed the IRA under a Notice of Intent.

Following these initial IRA activities, site conditions indicated that fuel oil contamination remained at concentrations requiring continued, accelerated response actions. ENPRO evaluated two remedial options for feasibility and cost effectiveness. The remedial alternative selected to further reduce fuel oil concentrations in site soil and groundwater was a product recovery and groundwater treatment system utilizing enhanced bioremediation. The system included an interceptor trench, a groundwater treatment system including an oil/water separator and bio-reactor, introduction of remedial additives, and re-injection of treated groundwater into the release area. The system operated for two years. During system operation and for one year after system shutdown, additional subsurface investigation was performed to document the effectiveness of the IRAs.

Based on the results of a Method 3 Risk Assessment, a condition of No Significant Risk was achieved for current and future site activities and uses. As such, ENPRO submitted a Class A-2 Response Action Outcome Statement, documenting the permanent solution to the MADEP.

PCB Remediation of a High-Hazard Dam

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The Fall of 2005 brought increased awareness of potentially hazardous and unsafe high-hazard dams in Massachusetts with a tense situation occurring in Taunton, Massachusetts. The Taunton dam came exceedingly close to breaching, potentially flooding numerous commercial areas and residential neighborhoods. Dam rehabilitation projects are very complicated and require painstaking care prior to implementing engineering controls and earthwork. However, when the dam structure itself is contaminated with concentrations of PCBs regulated by the Toxic Substance Control Act (TSCA) 40 CFR 761, the standard of care for precharacterization, excavation, confirmatory sampling, and disposal is increased dramatically. Prior to the rehabilitation of this High-Hazard dam in Worcester County, a full-scale remediation project was completed to remove PCB contaminated soil on the dam in accordance with Subparts N and O of the TSCA regulations. This paper will discuss the entire process of assessing the dam, developing the remediation strategy, implementing soil excavation activities while monitoring the structural integrity of the dam, and ensuring that PCB Remediation is in compliance with the TSCA regulations. We will also discuss the integration of the remediation work with the site civil work associated with the dam rehabilitation including:

- Reservoir dewatering and excavation for installation of intake structure
- Tailrace channel remediation and rehabilitation
- Compliance with TSCA, Massachusetts Contingency Plan (310 CMR 40.0000), Army Corps of Engineers 404 Clean Water Permit, and Massachusetts Wetland Regulations (310 CMR 10.00)
- Heavy equipment decontamination procedures, and
- Soil stockpile management

The project is currently ongoing and this paper will present results of the remediation effort.

High-Performance Attrition in a Wet-Mechanical Soil Washing Plant

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Contaminated sand fractions in soils need special attention during soil washing. Due to the high specific surface area particles < 200 µm are highly contaminated especially with hydrocarbons and heavy metals. AKW Apparate + Verfahren GmbH has developed a special attrition process with extraordinary decontamination possibilities of this particle size range (63µm – 2 mm). Their high-performance attritor is the main processing apparatus for the fines in a wet-mechanical soil and mineral waste washing plant measuring up to the high Swiss waste standards. The whole plant was designed and delivered within 12 months. The total capacity is approx. 30 t/h with a fines ratio of up to 40 %. The plant consists of a gravel and a sand purification unit, a process and a waste water treatment section.

The greatest part of the contaminants is in the organic part of the soil. In the gravel fraction a separation of the organic part removes the contaminants. In the fines and the sand fraction however the contaminants are due to the high specific surface area adsorptively bound to the particle surface. Here AKW Apparate + Verfahren GmbH developed a controlled high-performance attrition process. The sand fraction is fed to the high-performance attritor. There the surface of all sand particles has to be abraded by adhering to certain process parameters especially in regard to a high solids concentration (> 1300 g/l). The attritor is therefore equipped with a special sensor and a special control unit. After attrition the suspension consists of the abraded and now clean particles and the produced highly contaminated fine particles. Particles < 63 µm are separated by a hydrocyclone and fed to the waste water treatment plant. The powerful effect of the aggregates for the cleaning of the sand fraction was proved by different heterogeneous materials. The cleaned sand fraction is suitable to be an admixture to concrete or other applications.

Firing Range Closure to Prepare for Military Modernization

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The Camp Curtis Guild Site Improvement Project included site work activities centered on the excavation, handling, stabilization, and replacement within a designated Activity and Use Limitation (AUL) area of 7,800 tons of lead-contaminated granular and organic topsoil from two, currently inactive, firing ranges; Charlie Range and Delta Range. Related site-work elements included installation and maintenance of sedimentation/erosion controls, clearing and grubbing, subsurface GPR survey for potential unexploded ordinance (UXO) anomalies, demolition of small onsite structures, removal/abandonment of utilities, offsite disposal of construction/demolition debris, and additional earthwork related to excavation, handling, and placement of approximately 23,000 cy of clean granular soil to achieve finish grades. This work was performed in preparation for future construction of a new vehicle storage and maintenance facility. Key elements of the project included:

Excavation work including removal of soils from steeply sloped berm areas to depths ranging from 12-inches to 7 feet below ground surface
Identification of potential UXO anomalies required special investigations using low-impact, non-sparking, non-metal equipment by a licensed UXO clearance company. This work commenced in August and was completed in September, 2005.
With UXO support oversight by specialty contractor, contaminated soil excavation, handling, and stabilization commenced in late September, 2005-subsequent discovery of five UXO objects occurred during this work
As the work progressed, two additional issues came to light; 1. Substantial increase in the amount of soil requiring stabilization and 2. Accommodating the increased quantities required the AUL area be expanded.

By the end of the project, over 15,000 tons of soil from the two ranges had been stabilized. This represented an increase of almost 100% over the original contract amount. Intrusive earthwork activities and soil stabilization were completed on December 3, 2005. Related final grading and other ancillary earthwork items were completed by December 19, 2005.

Enhanced Chlorinated Solvent Dechlorination Using Groundwater Re-circulation for Effective Substrate Delivery

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A pilot demonstration was conducted in 2005 to assess the potential of enhanced anaerobic dechlorination to remediate groundwater and soil impacted with PCE and its' associated daughter products. Pilot test dimensions were 50 feet by 50 feet, and the saturated thickness of 15 feet. Groundwater was also impacted with diesel-range hydrocarbons (3-5 mg/L), which had already promoted the dechlorination of PCE to TCE, DCE, and VC in the saturated zone. A low-cost, nutrient-amended substrate was used to enhance the dechlorination of the chlorinated solvents to ethene/ethane.

A re-circulation approach was used to distribute the amended groundwater throughout the pilot demonstration area. The re-circulation approach utilized two extraction wells and three injection wells that were constructed at opposite ends of the test area. Three performance monitoring wells were constructed at increasing distances (10, 20, and 30 feet) from the injection wells. A trailer-mounted re-circulation system was used to re-circulate the amended groundwater. Groundwater from the two extraction wells was pumped into a 350-gallon tank mounted on the trailer where the substrate was added at a specific rate. Amended groundwater was then evenly injected into the three injection wells. Approximately 44,000 gallons of groundwater was amended and injected into the saturated zone over a period of three weeks using this system.

Groundwater performance monitoring data shows that within the first three weeks PCE and TCE were below detection limits, cis-DCE increased 3-8 fold, and VC increased from 0.1 to 2.5 fold in all monitoring wells. Data from week four and five show cis-DCE concentrations decreasing by 23-76%, VC concentrations decreasing by 3-51%, and ethene/ethane concentrations increasing by 76-660% in all monitoring wells. By week eight, three of the four monitoring wells had cis-DCE and VC concentrations below 5 ppb, and no rebound of PCE and TCE was observed.

Controlling Costs to Achieve Permanent Closure for a Quench Oil Site

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In 1992, emergency response actions were conducted at a site following the discovery of quench oil flowing from a spring and discharging to lagoons. The quench oil release was attributed to former underground storage tanks located within a rail-right-of-way. In 1994, an oil recovery interceptor trench was installed to capture migrating LNAPL. The site is classified under the Massachusetts cleanup regulations as having achieved a Temporary Solution.

This presentation will review cost-effective remedial measures evaluated and the success of the implemented measure to reach a Permanent Solution, cleanup of LNAPL. The existing remedial system consists of an impermeable barrier and product recovery trench with two product recovery systems installed in trench sumps.

Cost, site, and technology constraints were considered as part of the permanent remedial evaluation and included:

- Location within an active rail-right of way
- Shallow groundwater table and nearby wetlands
- Soil excavation and off-Site recycling of contaminated soil
- Dewatering excavations and treatment of groundwater
- More productive and cost-effective LNAPL recovery
- Expense of remedial action relative to the risk
- Integration of the existing LNAPL recovery system with the permanent action
- Technically feasible remedial alternatives to achieve a Permanent Solution

In order to evaluate reaching a Permanent Solution, a high-vacuum extraction pilot study was initiated over a three-month period, consisting of six biweekly high-vacuum extraction events. This pilot study was evaluated to optimize the current remedial system and remove higher volumes of free-phase product from the subsurface of the site. The high vacuum events conducted during the three-month period removed over 700 gallons of LNAPL compared to less than 100 gallons in the past three years utilizing the existing systems. Based on the success of the vacuum extraction, a Permanent Solution without excessive soil excavation or permanent remediation systems is achievable.

Biosparging of a Smear-Zone Plume of Residual Diesel in the Sub-Arctic

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Operations during the 1950s to early 1970s at the former fire-training pit at the Kodiak Airport (Kodiak, Alaska) contaminated a broad area adjacent to the Buskin River estuary with fuel (predominantly diesel). Although excavation has removed the primary source, fuel is smeared at residual saturation through a three-foot interval at the water table by tidal and seasonal fluctuations. Fluorescein dye moved rapidly through the underlying aquifer at up to 5 ft/day with high dispersion, but fuel-related textural changes in the smear zone appear to reduce permeability dramatically, inhibiting biodegradation by isolating the fuel from atmospheric or dissolved oxygen.

In a Fall 2005 pilot test, air sparging showed great promise as a means of aerating the smear zone. One injection well and an array of twelve tri-level piezometer/soil-gas samplers arranged along the arms of a cross at distances of 7.5 to 60 ft served to evaluate air sparging. The highly permeable aquifer matrix of sandy and silty gravels accommodated air injection at 102 scfm (the maximum that could be supplied) with a pressure of only 2 psig. Soil-gas measurements of oxygen, carbon dioxide, and methane confirmed the initial anaerobic conditions within the smear zone and demonstrated that four hours of sparging achieved atmospheric gas concentrations in nearly all monitoring points. The large radius of influence suggests that the low-permeability smear zone spread the injected air laterally. Importantly, gas flushing in the smear zone was nearly uniform rather than focused on preferential pathways.

Soil-gas chemistry returned to near-baseline conditions after one to two days. The rapid fall in oxygen probably reflected oxidation of abundant ferrous iron, but the rise in carbon dioxide may have been due to microbial respiration (along with unquantified desorption from mineral surfaces). An estimated maximum degradation rate of 400 mg/kg/yr offers the possibility that average fuel concentrations could reach the cleanup level in two or three years of treatment. The latest results from a multi-well test during the 2006 field season will be discussed.

Poster Session- Sediments

Applications of Electron Microscopy, ArcGIS Spacial Analyst and MINTEQA2 Model to Predict Phosphate Minerals in River Sediments

Asmare Atalay, Virginia State University, Petersburg, VA
Carol Bronick, Postdoctoral Associate
Kathleen Baker, Western Michigan University

Low Density Dredge Residuals, a Significant Impact to offsite Surficial Sediments?

Michael Bock, ENVIRON International Corporation, Portland, ME
Erik Martin, ENVIRON International Corporation.Portland, ME

Sediment Contamination in Cubatão River, Santos and São Vicente Estuaries, São Paulo, Brazil

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José Eduardo Bevilacqua, CETESB, São Paulo, Brazil
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Post-Dredging Residual Contaminant Impacts are a Reality

Chris Leuteritz, Anchor Environmental, L.L.C., Andover, MA

Modeling Copper Transport in the Sediments of Torch Lake, Houghton County, MI

Cory McDonald, Michigan Technological University, Houghton, MI

An Application of the Triad Approach to Maximize the Efficiency and Effectiveness of Remediation of Sediments

Jill Ann Parrett, EA Engineering, Science, and Technology, Inc., Warwick, RI
Timothy Regan, EA Engineering, Science, and Technology, Inc., Warwick, RI

Assessment and Interpretation of Field Duplicates-A Case Study of a Complex Sediment Investigation

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Applications of Electron Microscopy, ArcGIS Spacial Analyst and MINTEQA2 Model to Predict Phosphate Minerals in River Sediments

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Sediments are repositories of nutrients and other chemicals in surface waters. They are heterogeneous mixtures of assorted soil separates and organic matter. Phosphorus (P) flux into and out of sediments is controlled by P speciation and environmental conditions, such as temperature (T), dissolved oxygen (DO), redox conditions (Eh), and acidity/alkalinity (pH). This study was conducted to characterize chemical and physical parameters that affect P speciation in sediments of the James River, and to evaluate the experimental conditions under which sediment-bound P can become biologically available. Sediment cores were analyzed for T, pH, Eh, carbon (C) and metal ions. In a laboratory experiment, sediment samples were suspended in deionized water and equilibrated under different pH and aerobic/anaerobic conditions to assess P speciation and flux. The core sediment samples taken from a location near a former dairy farm showed the highest P concentrations while cores taken from downstream sites had lower P concentrations. Core samples with high P concentration correlated well with Fe and had non-uniform correlations with clay, Al and Ca that changed with cores depth. In controlled laboratory experiments, at pH 5, P was higher in anaerobic than in aerobic sediments. Higher Al precipitation occurred at low pH, which may reflect increased stability of Al phosphates in anaerobic conditions. Alternatively, increased Al concentration at pH 7 in aerobic conditions may indicate the stability of Al hydroxides as predicted by the MINTEQA2 speciation model. Elemental P distribution assessment using Scanning Electron Microscopy and application of ArcGIS Spacial Analyst inferred that at pH 4, P might be bound more to C and Al, than to Fe and Mn.

Low Density Dredge Residuals, a Significant Impact to offsite Surficial Sediments?

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Dredge residuals can be classified as either material missed by dredging operations or material lost during transport to the surface. Due to hydrodynamic considerations, low density material is more likely to be lost during retrieval. Sediments contain significant quantities of clay particles that form low density (< 2.4 g cm^{-3}) organo-mineral aggregates. This low density fraction in sediments has been shown to be highly enriched in organic material and is likely to be similarly enriched in hydrophobic chemicals, specifically organic contaminants such as polycyclic aromatic hydrocarbons and Polychlorinated biphenyls. Our simple model predicts that the loss of this material during dredging operations may result in significant offsite deposition of low-density material that is highly enriched in chemicals of potential concern. This enrichment is initially limited to the top several centimeters and is therefore underestimated using typical sampling techniques that integrate the top 15 cm of the sediment column. The persistence of this enrichment is dependent on the nature of physical and biological turbation. If the population of the benthic community has significant numbers of particle size selective surface deposit feeders, such as those common in estuarine environments, this surficial enrichment is predicted to be more persistent than otherwise predicted based on bulk bioturbation rates. The predictions of this model are consistent with reports of post remediation increases in the concentrations of chemicals of concern in sediment and biota.

Sediment Contamination in Cubatão River, Santos and São Vicente Estuaries, São Paulo, Brazil

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Studies in Cubatão Region and the adjacent Estuaries, in the 80´s, showed that water, sediment, mangrove and aquatic organisms were contaminated with inorganic and organic pollutants in toxic concentrations due to industrial activities (steel production, petrochemical plants and fertilizers manufacturing). Since then pollution control reduced industrial emissions, nevertheless, sediment contamination, Santos harbor dredging activities, bioaccumulation of contaminants are still important issues. In order to determine the degree of sediment contamination, its role in bioaccumulation and consequences to dredged material management, 23 sites in that region, including Santos Bay, were sampled, in 1999, for water, sediments, fish and shellfish. Samples were analyzed for heavy metals, PAHs, PCBs, PCDDs and PCDFs. Sediment results indicated an accumulation of TOC and Total N, and redox conditions indicated a strong decomposition of organic matter, especially in São Vicente and Santos Estuaries. Non point sources play a dominant role in organic accumulation due to insufficient waste municipal facilities. Considering the PEL (probable effect level) criteria, sediments were more contaminated at the Santos Estuary, where 5 million m^3 are dredged every year, for PAHs (11% >763 µg/Kg as benzo[a]pirene) and heavy metals (Hg (8% >0,696 µg/g), Pb (5% >112 µg/g) and Zn (3% >271 µg/g)). BHC (17% >0,99 µg/Kg as gama-BHC) and PCBs (2% >189 µg/Kg) were also found above PEL. Total PAHs reached concentrations of 800 mg/Kg and 2,3,7,8 TCDD was present in the sediments. PCBs in migratory fish (mullet, snook) were lower than in resident fish (mojarra). Mullets from Cubatão River, however, had higher values of dioxin and furans, indicating that bioaccumulation occurs during migration. Low values of PAHs were observed, except for benzo[a]pyrene and dibenzo[a,h]anthracene in oysters. Higher values of contaminants were found in bottom feeding organisms (blue crabs) than in herbivore species (mangrove crabs). Blue crabs and mullets are probably receiving most of their contaminants body burdens through sediments and/or benthic organisms ingestion.

Post-Dredging Residual Contaminant Impacts are a Reality

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During the remediation of contaminated sediments, low cleanup levels are typically set by the regulatory community. Dredging is often selected as the preferred remedial alternative to address contaminated sediments. During the execution of the remedy, confirmation samples are typically collected following completion of dredging to the design elevation. Typically these sampling results show recurring contaminant concentrations greater than the target remediation action level (RAL). On some projects, additional dredge passes are then attempted to remove the sediments with contaminant concentrations greater than the RAL. However, previous experience has indicated that these “cleanup passes” generate significantly diminished returns, as indicated by additional confirmation samples which show little or no reduction in concentration from the first pass dredging. The use of cleanup pass dredging without a well-defined completion point can lead to cost overruns, schedule overruns, and fingers being pointed between regulators, contractors, engineers, consultants, and clients for the failure of the selected remedy to achieve RALs.

Post-dredging residual contamination is a reality. Data from several recent dredging projects suggests the contaminant concentration of these residuals will be approximately equal to the average contaminant concentration of the mass of material slated for dredging. Additionally, the total mass of sediment characterized as residuals is ranges between 2 and 8 percent of the total contaminant mass of the original dredge prism.

The likelihood of contaminated dredge residuals should be planned for during the design and permit negotiation phases of the project. This is a critical step in the execution of a successful sediment remediation program involving dredging.

This paper presents the data from several projects regarding residual contamination after dredging. Additionally, the paper will discuss options for managing this residual contamination.

Modeling Copper Transport in the Sediments of Torch Lake, Houghton County, MI

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Torch Lake, a Great Lakes Area of Concern located in the Keweenaw Peninsula of Upper Michigan, has been heavily impacted by local copper mining activities. Toxic copper concentrations in surface sediments have nearly eliminated the benthic community. The EPA selected the "No Action" alternative for the sediments, which relies on contaminated sediments being covered by new, uncontaminated sediments. A model was developed to examine the diffusive transport of copper from the mining-era sediment into the post-mining sediment as well as from the post-mining sediment into the water column. The model was used to simulate the measured copper profiles in the sediments and to predict concentration profiles in the future. Deposition of new sediments has attenuated the flux of copper from the sediments into the lake. However, because “new” sediments contain more organic matter and therefore have a higher sorptive capacity for copper than the mining-era sediment, solid-phase copper concentrations in recently deposited sediment are actually twofold higher than concentrations in the original, "contaminated" sediments. Because upward-diffusing copper is mostly retained in the new sediments, copper concentrations in surface sediments are not predicted to decline below the toxic threshold in the foreseeable future.

An Application of the Triad Approach to Maximize the Efficiency and Effectiveness of Remediation of Sediments

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In 2005, remedial activities were conducted at a former textile mill and electroplating facility abutting the Woonasquatucket River, an urbanized American Heritage Designated River, in North Providence, Rhode Island. Contaminants of concern were chromium, primarily trivalent, and petroleum, primarily machine oils from plating wastes being discharged along the riverbank. Previous environmental investigations were used in the preparation of a conceptual site model, which determined that these wastes had adversely impacted nearly 200 linear feet of riverbank soil and sediment within the river. Due to potential adverse impacts of this contamination on the Woonasquatucket River, it was determined that impacted sediment and soil would be removed and transported off-site for disposal as part of a proposed Brownfield reuse proposal.

Through the Rhode Island Department of Environmental Management's Voluntary Cleanup Program, site-specific remedial objectives were established to address the ecologically sensitive nature of the impacted media and system. The remedial approach utilized a portable cofferdam system to bypass and de-water portions of the riverbed in conjunction with traditional excavation and engineered cap construction activities. Because the full extent of contaminated sediment could not be defined prior to river diversion and the need for rapid assessment during remedial activities, EA implemented the Triad Approach to maximize the efficiency of the remedial activities. To lessen the effects of diverting the river, EA's site geologist performed sediment screening using a combination of x-ray fluorescence (XRF) technology and hydrocarbon test kits in a field laboratory setting. These screening techniques provided real-time data to determine the extent of excavations without incurring equipment downtime pending receipt of laboratory data. Using these real-time measurement technologies, the project scope and conceptual site model were adapted during work activities to fully address the heavy metal and petroleum contamination of riverbank soils and riverbed sediment.

In conclusion, implementing the Triad Approach allowed for increased efficiency, reduction of project costs, improvement in the effectiveness of the standard remedial approach, and lessening of adverse impacts to the environment.

Assessment and Interpretation of Field Duplicates-A Case Study of a Complex Sediment Investigation

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For a high-profile river sediment characterization project located in the Northeast, multiple entities collected and analyzed samples over the last decade. During that time-period, the regulator's contractors collected several thousand samples that were analyzed for PCBs (Aroclors and congeners) and a variety of metals. Subsequently, the responsible party and its contractors collected several thousand additional samples for the same target analytes. Like most site characterization efforts, the collection and analysis of field duplicate samples was required.

During the evaluation of the historical site data prior to use for the generation of a conceptual site model, the project team was presented with the question of how to assess and utilize field duplicate data. The project team evaluated a number of approaches and the pros and cons of each of several approaches and selected a single approach to evaluation and utilization of the field duplicate data.

This presentation includes a case study utilizing the experience from a large sediment site characterization that included multiple field contractors. The work includes a discussion of the techniques used for the collection of field duplicate samples, the data quality assessment of the field duplicate sample results, and the use of the results in the conceptual site model.