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ABSTRACT BOOK



October 17-20, 2005

University of Massachusetts at Amherst

Analysis, Site Assessment, Fate,
Environmental and Human Risk Assessment,
Remediation and Regulation

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Analysis

Chemical Field Screening for Real Time Decision Making During Remedial Investigations

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Field Validation of Helium as a Tracer Gas During Soil Vapor Sample Collection

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A LC/MS Multi-Analyte Screening Method for Deleterious Organics in Water

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Chemical Field Screening for Real Time Decision Making During Remedial Investigations

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Chemical field screening techniques offer attractive analytical options to help mitigate the costs of hazardous waste site investigations. However, for many sites, litigation and risk assessment considerations, require that regulatory decisions are based upon thoroughly defensible high quality analytical data. From these perspectives, perceived limitations in the use of field screening techniques frequently include unacceptably high reporting limits, insufficiently definitive data, and matrix interferences.

In order to balance data quality needs and cost effectiveness, an integrated multi-analyte field screening and off-site analytical program was developed to drive field decision-making and chemical characterization, at a relatively complex 30-acre Superfund Site. The Site was an old industrial ash and cinder landfill that has been redeveloped into a mixed residential and commercial neighborhood. The presence of several dis-similar classes of chemical contaminants, including numerous metals, PAHs and PCBs, presented particular chemical characterization challenges and precluded the use of a single field screening methodology.

Under the field program, over 110 soil samples were successfully screened for multiple metals (XRF), PAHs (immunoassay) and PCBs (GC) by one chemist within six working days. The field screening program was noteworthy for its role in providing a clear and concise decision process for off-site analysis that would effectively address multiple federal and state regulatory requirements and associated risk assessment needs. The decision process was developed to utilize all of the field analytical data to determine an appropriate selection of samples for off-site analysis. Overall, the screening results demonstrated good correlation with off-site analytical results. The integrated analytical program successfully provided a comprehensive yet cost effective data set that facilitated an effective three dimensional chemical characterization of this large site, supported by a core database of appropriate quality.

Field Validation of Helium as a Tracer Gas During Soil Vapor Sample Collection

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The use of tracer gas is becoming a commonly specified field quality assurance method for identifying atmospheric short-circuiting during the collection of subsurface soil vapor samples. This paper presents the results of a field validation study of the use of helium as a tracer, utilizing a commercially available helium leak detector. The paper also presents observations on the frequency and degree of short-circuiting observed in soil vapor sampling from replicate installations of implants installed in differing soil types and depths.

The tracer gas field validation was conducted in two parts. The first part examined the ability of the method to detect short-circuiting in implants installed at four and eight feet below the ground surface. The implants were designed to short-circuit by introducing higher permeability material around the implant tubing and annular space. Following installation, a container was placed directly over the implant at the ground surface and filled with helium. Soil gas was then withdrawn from the implant and measured for helium. Conditions were varied and replicates were performed to investigate factors contributing to short-circuiting, and to establish response times and detection levels.

The second phase of the study investigated the frequency and magnitude of leakage, under typical field conditions and standard installation protocols. A total of sixty-four soil replicate vapor implants were installed by a field team experienced in soil vapor sampling. Thirty-two implants were installed in a sandy soil horizon and thirty-two in glacial till, to depths of four and eight feet below the ground surface. The frequency of atmospheric short circuiting was monitored as per the validated helium tracer field protocol, with consideration of soil type, depth, time and total volume of soil gas collected.

A LC/MS Multi-Analyte Screening Method for Deleterious Organics in Water

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The determination of deleterious organics in drinking water, or soil extract, is one of the particular areas of the Homeland Security Presidential Directive (HSPD-9) that will impact the EPA. It mandates that the EPA Office of Water expand monitoring and surveillance systems for recognizing a terrorist attack, or a significant change in water quality. This is a daunting task because of the breadth of organics, coupled with the numerous water sources required to be monitored.

The question is raised... what organics are present in this water? Whether it is drinking water, surface water, soil leachates, or wastewater, where does a chemist begin to answer this question? Time is critical.

The ability to perform a multi-analyte “screen” for numerous organics simultaneously would help maximize efforts to note the presence and significance of poisonous agents. This requires a broad analytical approach strategy utilizing the specificity of Liquid Chromatography / Mass Spectrometry (LC/MS and LC/MS/MS). Many of these organics are not amenable to Gas Chromatography / Mass Spectrometry (GC/MS). Universal detection with high sensitivity is the key. This approach can be adapted to any subset of analytes including explosives and perchlorate.

For non-MS detection methods, analyte resolution is critical for identification and quantification. However, the capability of MS to detect a single m/z (molecular weight/charge) gives analyte detection specificity that does not require chromatographic resolution. Thus, a “universal” reversed phase gradient providing a degree of analyte separation coupled with the specificity of mass spectrometry allows for the “screening” for multi-analytes simultaneously.

This presentation will discuss the development of a single, multi-analyte screening strategy for several deleterious pesticides and herbicides in drinking water using HPLC/ Electrospray Mass Spectrometry. This work is being conducted in collaboration with USEPA Central Region Laboratory Region 5. Several analytical issues will be raised to stimulate audience discussion and to solicit input to evolve this LC/MS strategy into a validated screening method template.

Arsenic

Arsenic-Rich Iron Floc Deposits in Seeps Downgradient of Solid Waste Landfills

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Tracing Pb Isotopic Compositions of Common Arsenical Pesticides in a Coastal Maine Watershed Containing Arsenic-enriched Groundwater

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Factors Influencing Arsenite Removal by Zero-Valent Iron

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Negotiating Achievable Arsenic Soil Cleanup Standards in the Context of High Natural Arsenic Background

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Copper, Chromium and Arsenic in Soil and Plants Near Coated and Uncoated CCA Wood

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In Vitro Gastrointestinal Bioavailability of Arsenic in Soils Collected Near CCA-Treated Utility Poles

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Microbes and Arsenic Contamination of Groundwater in Maine: is there a Link?

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Arsenic-Rich Iron Floc Deposits in Seeps Downgradient of Solid Waste Landfills

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Iron flocculate or “floc” deposits are commonly observed in groundwater discharge zones such as seeps, springs or stream margins downgradient of unlined solid waste landfills. Typically, these deposits are bright orange and may manifest as a surface coating on soil or sediment particles or as suspended particles loosely adhering to submerged rocks, plant stems or vegetative debris. Composed predominantly of amorphous iron oxy-hydroxides, these deposits generally have been regarded as aesthetically unpleasant, but environmentally benign. In recent years, there has been increased awareness of the widespread occurrence of elevated arsenic in sediments and groundwater. Research carried out at a municipal landfill in Maine indicates that naturally occurring arsenic exhibits redox-sensitive mobility and may be associated with iron as a dissolved constituent in leachate impacted (reduced) groundwater. If iron precipitates in discharge zones where reduced groundwaters are exposed to atmospheric oxygen, it follows that arsenic may co-precipitate with iron in these areas. To assess the prevalence of this problem within the lower Hudson Valley of southeastern NY, staff from the regional office of the New York State Department of Environmental Conservation (NYSDEC) and researchers from Columbia University’s Lamont-Doherty Earth Observatory sampled iron floc deposits at seven inactive solid waste landfills, and at one control site where iron floc deposition is derived from a natural spring. At six of seven landfill sites, arsenic concentrations exceeded the NYSDEC sediment guidance value of 30 mg/kg (severe effects level for aquatic life) at one or more sampling points. These results indicate that arsenic contamination is a potential concern downgradient of landfills wherever iron-stained leachate discharges are observed. Sampling and analysis of iron flocs associated with such leachates could provide a means of identifying landfills which may present risks to downgradient water supply wells, especially in cases where groundwater monitoring wells are not available for sampling.

Tracing Pb Isotopic Compositions of Common Arsenical Pesticides in a Coastal Maine Watershed Containing Arsenic-enriched Groundwater

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Arsenical pesticides and herbicides were extensively used on apple, blueberry, and potato crops in New England. Lead arsenate was the most heavily used arsenical pesticide until it was officially banned (USEPA, 1988). Arsenic and lead concentrations in stream sediments are higher in agricultural areas that used arsenical pesticides than in other areas; arsenic and lead concentrations are positively correlated ($r = 0.68$). Historical pesticide residues remain in soils and stream sediments when agricultural land previously contaminated with arsenical pesticides becomes residential. The common arsenical pesticides have similar Pb isotope compositions: $^{208}\text{Pb}/^{207}\text{Pb} = 2.3839\text{-}2.4721$, and $^{206}\text{Pb}/^{207}\text{Pb} = 1.1035\text{-}1.2010$. For other arsenical pesticides such as copper acetoarsenite (or Paris green), methyl arsonic acid and methane arsonic acid, as well as for arsanilic acid (used as feed additives to promote swine and poultry growth) range widely. The pesticides partially overlap the composition of the stream sediments from areas with the most extensive agricultural use. Soil profiles from a watershed containing arsenic-enriched groundwater contain labile Pb showing a moderate range in $^{206}\text{Pb}/^{207}\text{Pb} = 1.1870\text{-}1.2069$, and $^{208}\text{Pb}/^{207}\text{Pb} = 2.4519\text{-}2.4876$. The isotope values vary as a function of depth: the lowest Pb isotope ratios (e.g., $^{208}\text{Pb}/^{206}\text{Pb}$) representing labile lead (acid leach) are in the uppermost soil horizons. Lead contents decrease with depth in the soil profiles. Arsenic contents show no clear trend with depth. Labile lead in the profiles represents lead that is held in soluble minerals (Fe- and Mn-hydroxides, carbonate, etc.). Lead isotope compositions of stream sediments and soils from areas with heavy use of pesticides include contributions from rock, silicates, sulfides, and their weathering products, in addition to industrial lead (mostly from atmospheric deposition). In agricultural regions, the extensive use of arsenical pesticides and herbicides can also be a significant anthropogenic source of arsenic and lead to soils and sediments.

Factors Influencing Arsenite Removal by Zero-Valent Iron

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Arsenic (As) contamination of ground water is a world wide problem. Recently, laboratory and field scale experiments have shown that zero-valent iron (ZVI), a reactive material commonly used in permeable reactive barriers (PRBs) for ground water treatment, can remove arsenic from ground water.

The adsorption of As to iron (hydr)oxides, or iron corrosion products (ICPs), formed as a result of ZVI corrosion is the primary As removal mechanism by ZVI. While a Langmuir isotherm is generally accepted as the model to describe the adsorption capacity of As to ZVI, there is no consensus regarding the sorption kinetics and the water quality factors that affect them. In this study, laboratory-scale experiments were conducted to investigate the effects of pH, alkalinity, and mass transfer efficiency on the removal of arsenite [As(III)] by ZVI. The optimum pH range for As(III) removal was found to be between 7 and 8. The effect of alkalinity was found to be dependent on salinity, pH, and the concentrations of bicarbonate/carbonate and As(III). Inhibition of As(III) removal was observed only under conditions of high alkalinity and arsenic concentrations (alkalinity > 10 g CaCO₃ / L and 2.9 mg/L As(III)). Adverse alkalinity effects were not observed when As(III) concentration was low, 100 µg/L. The strong correlation between As(III) removal and increasing Reynolds number suggests that mass transfer efficiency plays a key role in the removal of As(III) by ZVI. A diffusion-limited adsorption model was developed to describe the removal of As(III) upon contact with ZVI as the result of adsorption to precipitated iron oxides. After an initial period of As(III) rapid adsorption to surface rusts formed during manufacturing and exposure to air, As(III) removal rate is most likely controlled by the continuous corrosion of iron and the diffusion of As(III) to adsorption sites in iron oxides.

Negotiating Achievable Arsenic Soil Cleanup Standards in the Context of High Natural Arsenic Background

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Highly mineralized desert regions pose exceptional challenges in remediation due to naturally occurring toxic metals in the soil background. Such can be the case in mine restoration, mill site and foundry remediation, or facilities with cooling water surface impoundments in arid climates. When background concentrations of metals exceed safe levels predicted by risk models or legislated action levels, cleanup stakeholders can find themselves at an impasse. In order to establish site-specific cleanup levels that maximize human health protection while fostering an achievable cleanup, owners, consultants, and regulators must negotiate cleanup levels in an economic, scientific, and political milieu. In the small residential community of Boulder City, Nevada naturally occurring arsenic in area soils range from about 3 to 9 mg/kg, yet current health-based cleanup goals recommend arsenic be controlled to below 0.39 mg/kg in a residential, one in a million, cancer endpoint model. The former US Bureau of Mines Metallurgical Research Laboratory site operated for half a century in the center of this community and resulted in uncontrolled soils and tailings with elevated levels of arsenic, lead, and chromium. By involving specialists in regulatory decisionmaking, risk assessment, dynamic site assessment, remediation and site engineering, an eighteen year stalemate was ended and a successful remediation and site closure was obtained.

Copper, Chromium and Arsenic in Soil and Plants Near Coated and Uncoated CCA Wood

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Chromated Copper Arsenate (CCA) was a widely used wood preservative, whose use was phased out partly due to concerns about CCA leaching into soil. In this study we determined the effects that coating CCA wood has on reducing leaching. Ten boxes were constructed, 6 of which were coated with film forming (FF) or penetrating finishes (PF), filled with soil, and weathered for 2 years. The soil was periodically sampled up to 2 years, and then romaine lettuce, arugula, basil and chives were grown under greenhouse conditions in these boxes. After 2 years, the average amount of As in the in soil 2 cm from the CCA wood was 29 (mg/kg, dry weight), 27 from wood coated with PF finishes and 6 in those coated with FF finishes. Soil As in samples 6 cm from the wood were near the background value of 3.4. Only the opaque, film-forming finishes were effective. The average amount of As in arugula grown 2 cm from the CCA wood was 60 (mg/kg, dry weight), 61 from wood coated with PF finishes and 24 in those coated with FF finishes. Similarly, the amounts in chives were, 75 (CCA), 75 (PF), 12 (FF); lettuce 5 (CCA), 5 (PF), 1.4 (FF); basil 6 (CCA), 10 (PF), 3 (FF). The amounts of As in plants grown in the control boxes were all <1. There was no reduction in plant As when grown next to the non-opaque finished wood, while the reduction in plant As ranged from 50-84% in plants grown next to the opaque finished wood. The reduction in arsenic in samples grown 6 cm from the wood compared to 2 cm from the wood ranged from 55-84%. The amounts of arsenic in the arugula and chives exceeded the British limit for plant As of 1 mg/kg (fresh weight).

In Vitro Gastrointestinal Bioavailability of Arsenic in Soils Collected Near CCA-Treated Utility Poles

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Chromated copper arsenate (CCA) has been widely used in North America to treat outdoor play structures and wood utility poles. However, there's a growing scientific concern about children exposure to the arsenic that leaches from these structures. Previous studies have shown that arsenic concentrations in soils beneath outdoor play structures or immediately adjacent to CCA-treated utility poles often exceed background levels.

Soil ingestion by children is an important pathway in assessing health risks associated with exposure to As-contaminated soils. In order to estimate the bioavailable arsenic from soil ingestion, in vitro gastro-intestinal methods that are based upon human gastrophysiology have been developed in last decade. The fraction of soil arsenic dissolved in the gastrointestinal system and potentially available for absorption can be defined as the bioaccessible As. The purpose of this study was: (1) to evaluate the bioaccessible arsenic in soils collected immediately near CCA-treated utility poles and (2): to assess the influence of various contaminated soil properties (particle-size distribution, pH, organic carbon, and arsenic fractionation) on bioaccessibility.

In November 2002, twelve CCA-treated utility poles were installed in four different locations (clayey, organic, and sandy environments) in the Montreal area (QC, Canada). After 18 months, soil samples immediately adjacent to each pole were collected and characterized. Bioaccessibility (in triplicates) was determined according to the in vitro gastrointestinal (IVG) method. This chemical extraction method is performed at 37°C with a gastric phase (1h, pH = 1,8, with pepsin) followed by an intestinal phase (1h, pH = 5,5, with bile and pancreatin). Bioaccessibility of arsenic in the certified reference material NIST SRM 2710 was also determined.

Bioaccessibility of arsenic ranged from 20.7 ± 2.9 % to 63.6 ± 1.2 % for the gastric phase and from 25.0 ± 2.7 % to 66.3 ± 2.3 % for the intestinal phase. Bioaccessible As was strongly influenced by soil organic carbon content and was independent of total arsenic content. Correlations between arsenic fractionation and bioaccessible arsenic in soils were determined.

Microbes and Arsenic Contamination of Groundwater in Maine: is there a Link?

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High arsenic concentrations occur naturally in groundwater in some locations and can result in serious health effects when the groundwater is used as a drinking water supply. The most infamous example is in Bangladesh, where millions of people have been exposed to unacceptably high arsenic concentrations since the 1970s and serious health impacts, such as cancer, have emerged. Here in the USA, there are several problem areas, among them, parts of Maine. In 2001, an isolate named NP4, later identified by 16S rRNA sequencing as a member of the genus *Sulfurospirillum*, was obtained from a contaminated well in Northport Maine. The well is among a cluster of wells with very high arsenic concentrations, and with no known anthropogenic sources of arsenic. At the time of sampling, the total arsenic concentration in the water was 1400 ppb. The presence of NP4 in groundwater, and its ability to reduce arsenate as well as a variety to other electron acceptors, including Fe(III) and Mn(IV), prompted a fluorescence in situ hybridization (FISH) study to determine its prevalence in the environment. Well water was taken from wells in the Northport area and in the Branch Lake area of Ellsworth, Maine, where the groundwater has much lower concentrations of arsenic, but with some readings still higher than the drinking water standard of 10 ppb. In the Northport area, NP4 accounted for as much as 16% of the total suspended bacterial population. While NP4 as a percentage of total bacterial numbers does not correlate with total As concentrations in groundwater, it does correlate with As(III). A positive correlation was also found between *Geobacter*, a genus that includes many iron-reducing bacteria, and total arsenic. These results indicate that microorganisms may be important in arsenic mobilization and speciation in groundwater.

Bioremediation

Mutagenicity of a Former Gasworks Soil During Bioremediation

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The Role of a Complex Microbial Community in Supporting Dehalococoides Bioaugmentation

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Margaret Findlay, Bioremediation Consulting, Inc., Watertown, MA
Donna Smoler, Bioremediation Consulting, Inc., Watertown, MA

In Situ Metals Remedation with Metals Remedation Compound (MRC®)

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Degradation of RDX with Reduced Humic Substances

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Enhanced Microbial Consortium Production in a Slurry Bioreactor for Creosote-Contaminated Soil Bioaugmentation Using Humic Acids

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Identification of Tetrachloroethene- and Vinyl Chloride-Dechlorinating Bacteria Enriched from Tetrachloroethene-Contaminated Groundwater and Sediments

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EHC™ for In Situ Bioremediation of Groundwater Containing Chloroethanes and other Chlorinated Solvents

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Mutagenicity of a Former Gasworks Soil During Bioremediation

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Although bioremediation is often assumed to be a detoxifying process, the production of degradation products can increase potential hazard. This study followed a pilot scale (750 L) bioslurry remediation of a PAC-contaminated soil from an aged gasworks site near Stockholm, Sweden. Chemical and biological analyses followed changes in the concentrations of PACs and PAC derivatives, and mutagenic activity at remediation days 0, 3, 7, 24 and 29. Sample extraction and fractionation employed pressurized fluid extraction and subsequent elution from partially deactivated silica. Two fractions (2 & 3), enriched in non-polar neutral (e.g., alkyl-PACs) and polar aromatic (e.g., N-heterocyclic) compounds, were analysed for mutagenic activity using the plate incorporation version of the *Salmonella* mutagenicity test on strains TA98, TA100, YG1041 and YG1042. The metabolically enhanced YG strains permitted enhanced detection of mutagenic nitroarenes and aromatic amines. Thorough chemical analysis revealed noteworthy carcinogenic PACs including benz[*a*]anthracene, benzo[*a*]pyrene and dibenz[*ah*]anthracene, as well as other PACs, alkyl-PACs, and O- and S-heterocyclics in fraction 2. Fraction 3 contained a variety of N-heterocyclic compounds and oxy-PACs. The heavier PACs, such as benzo[*b*]fluoranthene, showed modest declines (i.e., 14%) over the course of the remediation, while lighter PACs, such as anthracene, showed large reductions in concentration (i.e., 86%). Oxy-PACs, such as 4-oxapyrene-5-one and 1-acenaphthenone, increased in concentration during the remediation (i.e., 29% and 56%, respectively). The mutagenicity results showed a net 2- to 8-fold increase in frameshift mutagenic activity for the non-polar neutral fraction, and a 7- to 32-fold increase in the activity of the polar aromatic fraction. The patterns of mutagenic activity strongly suggest the production and accumulation of hitherto unidentified N-heterocyclics and/or other aromatic amines. Mutagenicity assessment of the identified compounds (currently underway) will determine the degree to which known compounds can account for the observed biological activity.

In Situ Metals Remediation with Metals Remediation Compound (MRC®)

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Contamination of groundwater by metals has not been widely addressed by engineered in situ remediation technologies, despite the documentation of metals contamination at greater than 50% of sites from the National Priorities List and at Department of Defense and Department of Energy locations. Metals Remediation Compound (MRC®) is a slow-release metals remediation product that removes dissolved metals from groundwater via in situ immobilization (precipitation and/or sorption to soil particles). The immobilized metals are stable under reducing conditions and may be stable under oxidizing conditions, depending on the identity of the metal and site specific geochemistry.

MRC consists of an organosulfur compound esterified to a carbon backbone. This organosulfur ester is embedded in a polylactate matrix, making MRC a thick, viscous liquid. Upon injection into an aquifer, the organosulfur compound is slowly released when the ester bonds in MRC are cleaved via hydrolysis by water and microbial enzymatic action. The organosulfur moiety interacts with metal ions, either to complex them or to reduce them and complex them sequentially. These complexes sorb strongly to soil, filter media, or other solid supports. MRC also slowly releases lactate, which acts as an electron donor and carbon source for naturally occurring bacteria and creates the optimal conditions for metals immobilization by the organosulfur compound. For sites with mixed metal and chlorinated solvent contamination, MRC provides a substrate for accelerated reductive dechlorination and metals immobilization.

MRC's ability to remove dissolved metals, such as arsenic, copper, chromium, cadmium, mercury, and lead, from solution has been tested in the laboratory and verified in situ via injection into metals-contaminated aquifers. Additionally, detailed modeling and kinetics calculations have been performed to investigate the stability of precipitated metals. Results from theoretical studies, as well as field applications for a variety of metals will be presented.

Degradation of RDX with Reduced Humic Substances

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Previous studies have indicated that humic substances and Fe(II) can abiotically transfer electrons to a variety of compounds. These include nitroaromatic and nitramine compounds, which can be reduced to less harmful metabolites. In this study, the potential for reduced humic substances and Fe(II) to degrade hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) was evaluated.

50 μM RDX was anaerobically incubated with 1mM, 500 μM , and 100 μM of chemically reduced AQDS (2,6-anthraquinone disulphonate) and biologically reduced AQDS, an analog for humic substances. RDX reduction was also investigated with 1.2 mM and 600 μM of soluble Fe(II).

RDX was completely degraded within 5 hours and 7 hours with 1mM and 500 μM of both of reduced AQDS, respectively. 100 μM of reduced AQDS reduced RDX to approximately 20 μM in 12 hours. Reduced AQDS transfers two electrons per mole in coupled oxidation/reduction reaction. RDX accepts six electrons per mole. Therefore three times as much reduced AQDS is needed to completely reduce RDX. Incubating the RDX with 100 μM of reduced AQDS resulted in reduction of two thirds of the 50 μM RDX. This was the predicted stoichiometry and demonstrates that RDX degradation is due to humics-mediated electron transfer. 50 μM RDX, however, was only reduced to 19 μM and 39 μM with 1.2 mM and 600 μM of soluble Fe(II) for 52 hours, respectively. The results of this study demonstrate that reduced AQDS can transfer electrons directly to RDX and will degrade RDX faster than soluble Fe(II).

These findings suggest that reduced humic substances react directly with RDX. This may eventually be used as a rapid and effective cleanup strategy in both Fe(III) rich and Fe(III) poor environments. Upcoming experiments include sediment incubations and cell suspensions of Fe(III)- and humics-reducing Bacteria (e.g. *Geobacter metallireducens*) to better evaluate anaerobic biodegradation of RDX under in situ conditions.

Enhanced Microbial Consortium Production in a Slurry Bioreactor for Creosote-Contaminated Soil Bioaugmentation Using Humic Acids

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The widespread contamination of soil by creosote in industrialized countries has created a need for reliable and cost-effective bioremediation processes. Polycyclic aromatic hydrocarbons (PAHs) in creosote are of particular concern because they represent up to 85% of its weight composition and many are carcinogenic and degrade poorly. Soil activation, a method based on the cultivation of an indigenous microbial consortium from a fraction of a contaminated soil for subsequent use as an inoculum for bioaugmentation of the same soil, was studied as a method for the bioremediation of creosote-contaminated soils. Since the bioavailability of PAHs is low due to their high hydrophobicity, humic acids were added during soil activation in soil slurry bioreactors to increase it. The effect of this organic material on the microbial consortium performance was investigated. Soil activation was performed in 8 L stainless steel soil slurry bioreactors operated in fed-batch mode with periodic addition of creosote in increasingly greater quantities. Half of the bioreactors were supplemented with humic acids. During the 70-day activation period, PAH concentration, pH, temperature and oxygen consumption were monitored. Microbial community performance was evaluated using phenanthrene, anthracene and pyrene mineralization tests, direct counts using the Live/Dead® BacLight™ method and total heterotrophic and PAH-specific microbial population counts using the spread plate method. During soil activation, the effective concentration of PAHs in the aqueous phase was increased in presence of humic acids. Humic acids also increased PAH degradation and mineralization rates and reduced the latency phase resulting in an enhanced microbial consortium performance for some PAHs. The enhanced microbial tolerance to increasing creosote concentration was also attributed to the addition of humic acids. These results indicate that the use of humic acids during creosote-contaminated soil activation efficiently enhances microbial consortium performance.

Identification of Tetrachloroethene- and Vinyl Chloride-Dechlorinating Bacteria Enriched from Tetrachloroethene-Contaminated Groundwater and Sediments

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We identified the dechlorinating bacteria enriched from a tetrachloroethene (PCE)-contaminated fractured rock aquifer at Rutgers University in Piscataway, NJ. This site is part of the Brunswick (Passaic) formation of the Newark Basin that makes up of much of northern NJ. Five sets of enrichments using groundwater containing 1% sediment fines were established (killed controls, live controls, electron donor only, electron donor + PCE, and electron donor + vinyl chloride (VC)). Chloroethenes and methane were determined and PCE, VC and electron donor (butyrate) were re-amended periodically. Enrichments were transferred over the course of two years. Complete dechlorination of chloroethenes to ethene was detected in all electron donor-amended bottles. Little dechlorination was observed in the live controls not receiving electron donors and or in the autoclaved controls. These results imply that the dechlorination is attributed to microbially mediated reduction and that the aquifer is electron donor limited. Molecular characterization was carried out using polymerase chain reaction (PCR) and denaturing gradient gel electrophoresis (DGGE). At least two different *Dehalococcoides*-like organisms were detected in second generation PCE- and VC-amended cultures by DGGE. A distinct band with a DNA sequence with high similarity to members of the *Geobacteraceae* was also present in PCE-amended cultures. PCR using primers specific for published dehalogenases yielded bands of the expected size for a PCE dehalogenase (PceA Y51 from *Desulfitobacterium* sp. Y51) and a TCE dehalogenase (TceA from *Dehalococcoides ethenogenes* 195) in PCE-amended cultures. PCR with primers specific for two VC dehalogenases (BvcA from *Dehalococcoides* sp. BAV1 and VcrA from *Dehalococcoides* sp. VS1) yielded bands of the expected size in both PCE and VC amended cultures. These findings suggest that the aquifer harbors a diverse chloroethene-dechlorinating community.

EHC™ for *In Situ* Bioremediation of Groundwater Containing Chloroethanes and other Chlorinated Solvents

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EHC™ bioremediation products uniquely combine various organic carbon sources with zero valent iron (ZVI) and/or other reduced metals to stimulate biological activity and direct reduction of organic compounds that are notoriously recalcitrant to biodegradation processes. We validated the ability of EHC to remove a mixture of chlorinated volatile organic compounds (CVOCs) from groundwater; 1,1,2-Trichloroethane (1,1,2-TCA), 1,2-dichloroethane (1,2-DCA) *cis*-1,2-Dichloroethylene (*cis*-1,2-DCE), vinyl chloride (VC), chloroform (CF), trichloroethylene (TCE), carbon tetrachloride (CT), tetrachloroethylene (PCE) and dichloromethane DCM. Following 62 days of continuous flow conditions, the concentration of 1,2-DCA decreased from 329,000 to 19 µg/L which corresponded to >99% removal of 1,2-DCA. Removal of all other compounds was also observed, yielding a total CVOC reduction of >99%. A chloride mass balance was conducted yielding excellent correlation between theoretical chloride concentration and CVOC removal.

A description of various conceptual designs for full-scale field implementation scenarios (EHC permeable reactive barrier [PRB] perhaps coupled with conventional ZVI PRB technology; source area treatment) will be presented along with cost analyses for a number of alternative installation techniques including an open trench PRB, hydraulic fracturing, pneumatic injection, or direct injection of an EHC slurry.

Bioremediation of Acid Mine Drainage Wastes

Prevention of Acid Drainage Generation from a Dump Consisting of Mining Wastes

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Use of Emulsified Edible-Oil for In-Situ Bioremediation of Acid Mine Drainage

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Sulfate-reducing Bacteria as Contaminants of Industrial Systems – Effects of pH on Sulfidogenic Activity

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Metal Immobilization by *In Situ* Bioprecipitation: Comments about Carbon Source Use, Process Efficiency and Sustainability

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Algal Bioremediation of the Berkeley Pit Lake System- An In Situ Test Using Limnocorrals

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Biotechnological Applications of Methane as Electron Donor for Biological Sulfate Reduction

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Prevention of Acid Drainage Generation from a Dump Consisting of Mining Wastes

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In the uranium deposit Curilo, Western Bulgaria, a dump consisting of about 800 tons of rich-in-pyrite mining wastes was, after rainfall, a large source of acid drainage waters. These waters had a pH in the range of about 2.3 – 3.5 and contained radionuclides (uranium, radium), heavy metals (copper, zinc, cadmium, lead, nickel, cobalt, iron, manganese), arsenic and sulphates in concentrations usually much higher than the relevant permissible levels for waters intended for use in the agriculture and/or industry. The generation of these pollutants was connected with the oxidative activity of the indigenous acidophilic chemolithotrophic bacteria inhabiting the dump. This activity was ceased by adding a multicomponent mixture to the top layer of the dump and on its surface. This mixture consisted of crushed limestone, different biodegradable solid organic substrates (cow manure, plant compost, hay) and soil. The rich-in-organics cover was maintained saturated with water and was inhabited by a mixed microbial community consisting mainly of heterotrophs. This community created a system characterized by a neutral pH and absence of molecular oxygen, i.e. conditions not favorable for the acidophilic chemolithotrophs. As a result of this, during an experimental period of more than 5 years, the dump effluents after rainfall had a pH around the neutral point and contained no pollutants in concentrations higher than the relevant permissible levels.

Sulfate-reducing Bacteria as Contaminants of Industrial Systems – Effects of pH on Sulfidogenic Activity

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Sulfate-reducing bacteria (SRB) are ubiquitous in anaerobic environments such as soils, sediments, wastewaters and gastrointestinal systems. Due to the high oxygen tolerance of some SRB they are also commonly found in temporary oxic habitats such as biofilms, algal mats, activated sludge and a large variety of industrial systems. SRB play a major role in the turnover of organic matter in many ecosystems and further may effect immobilization of toxic heavy metals from AMD water, souring of oil and gas bearing formations and cause corrosion of iron and steel constructions.

In order to either inhibit or exploit the metabolic activity of SRB it is important to know the physico-chemical limits for survival and growth of these bacteria. The present talk will discuss the effects of pH on the activity of extant SRB and present data from a study of the microbial population within the piping system of a Danish district heating plant. During this study several novel types of alkaliphilic sulfidogenic anaerobes were isolated and characterized. These strains may be involved in metal corrosion occasionally observed in the piping systems of district heating plants. A novel alkaliphilic sulfate-reducing bacterium was isolated from biofilm on a mild steel surface. This bacterium (strain RT2) grew at pH values up to approx. 10 at 40°C. Our results also indicate that anaerobic bacteria capable of reducing elemental sulfur, sulfite and thiosulfate could be as important as the SRB in producing hydrogen sulfide in the piping system of the plant.

Metal Immobilization by *In Situ* Bioprecipitation: Comments about Carbon Source Use, Process Efficiency and Sustainability

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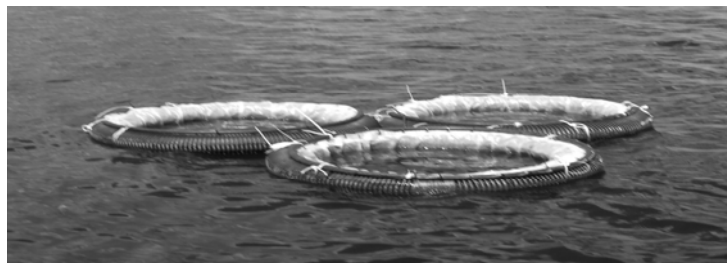
About 45% of the contaminated sites are dealing with heavy metal problems. Metals are spread in the environment by mining activities, surface treatment and non ferrous processing. As heavy metals can not be degraded, removal or immobilization (leading to bioavailability reduction) are the only risk reducing measures that exist. Next to the often used but expensive pump and treat technologies, *heavy metals* can be immobilized by inducing sulfate reducing bacteria to transform the sulfates, that are very often present in the same groundwater (due to the metal mining or processing activities), into sulfides. These sulfides will precipitate the metals as insoluble metal sulfides. At the moment several studies have demonstrated the feasibility of this *In Situ* Bioprecipitation Process (ISBP) as well at lab scale (batch and column tests) as at field scale. However some questions arise concerning the continuation of the process, the efficiency and the sustainability of the precipitates. The presented study will try to answer these questions. The study is based on more than 10 different studies, all done by the same authors, on different groundwaters and aquifer samples.

The presentation will give an overview of the guidelines necessary for a correct and successful bioprecipitation process with stable metal sulfide precipitates. It will pay attention to the influence of the carbon source on the complexing of the metals and the efficiency of the induction of the bioprecipitation process, the possible negative influence of acetate inhibition, the influence on the competence between sulfate reducers and methanogenic bacteria and the influence of low pH on the ISBP. These results will allow the correct implementation of the ISBP with an eye on longevity and sustainability of the process and present the ISBP as a much more sustainable alternative to the pump and treat technology as measure for heavy metals contaminated groundwaters.

Algal Bioremediation of the Berkeley Pit Lake System- An In-Situ Test Using Limnocorrals

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Introduction:

Through various metabolic, physiological, and biochemical processes, algae have the potential to reduce soluble metal ions in acid mine waters. Laboratory experimentation, conducted at Montana Tech of The University of Montana, has demonstrated that algal species indigenous to the Berkeley Pit Lake System have the potential to reduce soluble metal concentrations as much as 50 percent in small tissue culture flasks and Imhoff cones. The Berkeley Pit Lake is located in Butte, Montana, near the headwaters of one of the largest U.S. Environmental Protection Agency Superfund sites in the United States. To properly test bioremediation potential of algae in the Berkeley Pit system, an in-situ experiment was performed, using nine, 1m-by-3m polyethylene acid/metal resistant limnocorrals. Limnocorrals are an enclosed experimental apparatus (test tube); used to simulate actual physical, chemical, and biological conditions of the lake environment within a controlled volume of water, allowing for manipulation of one to several aspects of the natural environment.

Methods:

On June 15, 2004, nine limnocorrals were deployed into the Berkeley Pit Lake system. Experimental manipulation in this experiment consisted of nitrification of limnocorrals using nitrate and phosphate concentrations to stimulate algal growth. It is hypothesized that if properly nitrified, dissolved metal concentrations in the Berkeley Pit will decrease due to increasing algal biomass. Total algae counts, bacteria counts, dissolved metal analysis, and various physical parameters were monitored over a six month course. Nitrified limnocorral (2-levels) were compared to non-nitrified (control) limnocorrals to determine if eutrification of the Berkeley Pit is a viable option for remediation.

Results & conclusion:

With the addition of inorganic nutrients, algae can be grown to high concentrations (10^6 cells/mL) in the Berkeley Pit Lake. As a result, reduction of dissolved metals from water may occur in conjunction with heterotrophic growth.

Biotechnological Applications of Methane as Electron Donor for Biological Sulfate Reduction

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Biological sulfate reduction is a process used to remove oxidized sulfur compounds and metals from wastewater of the mining and metallurgical industry. Sulfate is biologically reduced to sulfide, which precipitates with metals to form metal sulfides. The metal sulfides are removed from the water by sedimentation and reused in the metallurgical industry as raw material. For sulfate reduction an electron donor is required. A widely used electron donor, for large-scale applications, is hydrogen. Hydrogen is produced from methane in natural gas or biogas via a process called steam reforming. However, this process requires high temperatures and pressures, resulting in a high-energy loss. Therefore, the emission of the greenhouse gas carbon dioxide and the costs of the wastewater treatment would be greatly reduced if methane could be used directly as electron donor for biological sulfate reduction.

Biological sulfate reduction with methane as electron donor occurs in deep-sea sediments. Recent research provided evidence for the involvement of a syntrophic consortium of methanogens and sulfate reducers. It is believed that methanogens form hydrogen or acetate via “reversed methanogenesis” and that these compounds serve as electron donors for sulfate reducing bacteria.

Our research examines if methane can be used as electron donor for the reduction of oxidized sulfur compounds (sulfate, sulfite and thiosulfate) in a “high rate” bioreactor. Biomass from anaerobic reactors and deep-sea sediments is screened for sulfide production coupled to methane oxidation, in continuous membrane reactors. In addition, the effect of different co-substrates is investigated.

Chemical Oxidation

Field Results with an Alkaline In-Situ Chemical Oxidation Process

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Steve Peck, Regenesis, Oceanside, CA

Michelle Von Arb, Regenesis, San Clemente, CA

Maryam Azad, Applied Power Concepts, Anaheim, CA

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ISCO of DNAPLs: Applicability Based on 2-Dimensional Transport Studies of DNAPL Entrapment and Oxidant Delivery Techniques

Michelle Crimi, Colorado School of Mines, Golden, CO

Sarah Seitz, Aquifer Solutions, Evergreen, CO

James Kopp, Colorado School of Mines Golden, CO

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The Permanganate Soil Oxidant Demand: A Critical Parameter For ISCO Remediation

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Field Scale Comparison of Activated Persulfate and Modified Fenton's Reagent for Treatment of Chlorinated Benzene Compounds

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Field Results with an Alkaline In-Situ Chemical Oxidation Process

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Regenesis has recently developed an in situ chemical oxidation process designed to treat organic contaminants. As with other chemical oxidation products, this product is used to target high concentration source areas in the saturated and vadose zones, often followed by treatment technologies such as bioremediation as a polishing step. The RegenOx™ product uses a solid oxidant that is activated to a very high performance level through the action of a proprietary dual catalytic complex and which operates under alkaline conditions with certain advantages.

Regenesis initiated a field test program in conjunction with several engineering consulting firms. RegenOx was tested at various sites throughout the United States, including gasoline stations, dry cleaning facilities, former manufactured gas plants and a chemical packaging facility among others.

The typical field test was conducted using direct injection points in a defined area. After the initial injection event, monitoring wells within and adjacent to the test area were monitored for oxidation-reduction potential (ORP), pH, dissolved oxygen (DO), the contaminants of concern (COCs), the RegenOx oxidant, anions, and cations. As scheduled, a second and some cases third injection event were conducted at the sites and monitoring was continued. The wells were monitored just prior to injection and at daily, weekly and monthly intervals.

This presentation discusses the basic technology and laboratory data, in addition to the design of the field test program and the evaluation of the data collected from the tests.

ISCO of DNAPLs: Applicability Based on 2-Dimensional Transport Studies of DNAPL Entrapment and Oxidant Delivery Techniques

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In situ chemical oxidation (ISCO) is a rapidly emerging technology for remediation of organic contaminants at hazardous waste sites in the U.S. and abroad. While much is known about oxidative destruction of aqueous phase contaminants, there are important knowledge gaps with respect to ISCO for remediation of dense non-aqueous phase liquid (DNAPL) contaminants. DNAPLs present a particular challenge due to their low solubility and high density, which can result in release of the contaminant to ground water above regulatory limits over extensive time frames. Successful application of ISCO at DNAPL sites requires comprehensive understanding of the conditions that will impact subsurface oxidant delivery and transport to the point of reaction, and of the conditions that will affect the rate and extent of the subsequent reactions.

Current research at the Colorado School of Mines is examining the reaction and transport processes that impact the efficiency and effectiveness of ISCO of DNAPLs. One experimental system this research employs is a two-dimensional, flow-through cell to assess oxidation effects as a function of representative porous media structures, DNAPL mass levels and entrapment architectures, and oxidant type and delivery techniques. Twelve experimental runs are planned (7 completed to date) to evaluate the impacts of these experimental conditions. ISCO effects are represented by (1) treatment-induced changes in DNAPL mass transfer, (2) contaminant distribution in the transport cell, (3) contaminant plume mass flux, (4) oxidant consumption, (5) % DNAPL destroyed, and (6) changes in system geochemistry (e.g., byproducts, solids, pH,

ionic content, etc.). The measurements to determine these effects are made with respect to space and time.

Results of these experimental studies will provide the basis for future guidance on ISCO of DNAPLs so that it can be selected as a preferred remedy when appropriate, and be implemented to reliably achieve risk-based cleanup or other performance objectives.

The Permanganate Soil Oxidant Demand: A Critical Parameter For ISCO Remediation

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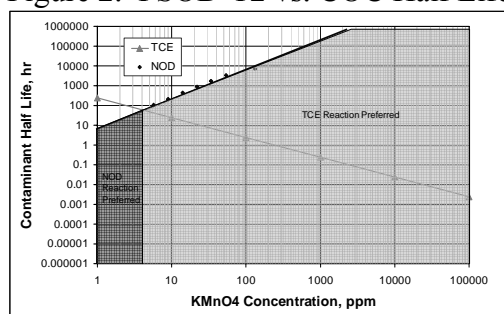
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The key design parameter to consider when applying ISCO is the background permanganate soil oxidant demand (PSOD) of the treatment zone. The PSOD is the degree to which naturally occurring materials in the soil matrix will compete with the target contamination for oxidizing reagent. When estimating the dosage of oxidant reagent required to treat the target contaminant, it is critical that all potential oxidant demands including reduced soil minerals and natural organic matter (NOM) are considered. A high SOD can increase the use of an oxidizing agent that the method becomes cost-prohibitive relative to alternate technologies. Without consideration of all these potential oxidant demands in the application design process, the required amount of oxidant delivered may be underestimated and ISCO could be ineffective. This paper will describe two emerging procedures for determining the PSOD at a potential remediation site. The first method (PSOD-T1) is a preliminary screening tool (2 day test) that is rapid and inexpensive to perform. It is intended to provide general information on the amount of permanganate (potassium or sodium) that could be consumed by natural materials (organic and inorganic) and any contaminants of concern (COC) in soils at a potential remediation site. Its value is in providing a first pass evaluation on the potential application of permanganate technology (e.g. is it economically viable). This procedure provides level I screening information. It is not intended to be exclusively used to obtain specific engineering data required for full-scale implementation.

The second procedure, PSOD-T2 (7 day test), is a more detailed procedure intended to provide additional site information. The PSOD-T2 provides comprehensive site data including a more extensive sampling methodology, increased reaction data points and the ability to obtain reaction kinetics. Data generated from the PSOD-T2 procedure can provide a predictive demand curve allowing the determination of longer demand values. It can also provide the rate constant and half-life information on the SOD of the soil that can then be related to the expected half-life for the site contaminant of concern. An example of this is shown below for TCE.

Figure 2. PSOD-T2 vs. COC Half Life



As shown, application of permanganate at concentrations shown in the red zone would react with the soil components in preference to the TCE. As the permanganate concentration increases (green zone) the permanganate will react more readily with TCE than the natural occurring soil components. Therefore, based on a kinetic analysis of the PSOD-2 results for this soil and the COC primarily comprised of TCE, a minimum permanganate concentration of 4 ppm needs to be maintained to effectively react with TCE.

Oxidation of TNT, HMX and RDX by Iron-Chelate Activated Persulfate

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Destruction of organic compounds by direct or by free-radical-based activated persulfate ($S_2O_8^{2-}$) oxidations is gaining interest as an *in situ* chemical oxidation technology. Persulfate oxidation is generally conducted under heat-, photo-, acid-, base- or metal-activated conditions because oxidation rates can be greatly accelerated, resulting from the formation of a variety free radical species. In this work we demonstrate the efficacy of using activated persulfate to destroy energetic compounds. Destruction of the compounds 2,4,6-Trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and their degradation products were investigated in aqueous and soil slurry batch reactors at 20°C. In this paper we compare the kinetics of parent compound removal to mineralization using Fe-EDTA as the activator. Mass balances using ^{14}C -labeled parent compounds and by-products, solids and trapped CO_2 enabled an analysis of the extent of mineralization achieved under various initial conditions. Because of the high persulfate and sulfate concentrations present in the experimental systems, numerous modifications of normally routine analytical methods were necessary to enable analysis and mass balancing of carbon and nitrogen species, as well as other products of oxidation including the Fe-chelate.

Persulfate Oxidation of TCE at Ambient Temperature: Kinetics and Influence of Radical Scavengers

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Improper disposal or accidental release of volatile organic compounds (VOCs) such as trichloroethylene (TCE) has resulted in thousands of incidents of groundwater contamination that pose significant threats to public health and environmental quality. Previous laboratory studies have demonstrated that persulfate anion, that has been thermally or chemically activated to produce a powerful oxidant known as the sulfate free radical ($\text{SO}_4^{\cdot-}$, $E^\circ = 2.6 \text{ V}$), can be effectively used for treating TCE contamination in soils. This laboratory study examines the use of unactivated persulfate anion for TCE degradation. The basis of this investigation was to test the hypothesis that slow persulfate decomposition at ambient temperatures (e.g., 20°C), resulting in limited $\text{SO}_4^{\cdot-}$ formation, can be used to effectively oxidize TCE given an extended reaction time. It was determined that the reaction efficiency depends upon competing reactions that may scavenge the free radicals. Initial experiments evaluated the reaction kinetics of persulfate oxidation of TCE at 10° , 20° and 30°C in an aqueous phase. The role of sulfate free radical scavengers, e.g., hydrogen and hydroxyl ions (i.e., pH), alkalinity species, chloride ion (i.e., degradation products of TCE), and the influence of solution ionic strength were investigated. Pseudo-first-order TCE degradation rates under experimental conditions of phosphate buffered pH 7, ionic strength 0.1, and persulfate/TCE molar ratio 50/1 were determined to be 0.006, 0.018, and 0.074 hour^{-1} for system temperatures of 10, 20, and 30°C , respectively. It was evident that the TCE degradation rate was a little lower than that under acid conditions at 20°C . The influence of other radical scavengers was minor on the rate of TCE degradation at ambient temperature. The environmental application of unactivated persulfate anion for subsurface remediation, i.e., in situ chemical oxidation (ISCO), represents an alternative to use of oxidants such as permanganate or Fenton's Reagent.

Field Scale Comparison of Activated Persulfate and Modified Fenton's Reagent for Treatment of Chlorinated Benzene Compounds

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A field scale pilot demonstration comparing the in situ chemical oxidation technologies (ISCO) modified Fenton's reagent and activated persulfate was performed in November 2004 at the Eastland Woolen Mills Superfund site (site) in Corinna, Maine. Each 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.

Modified Fenton's reagent is based on the decomposition of hydrogen peroxide in the presence of iron that results in the formation of: 1) the hydroxyl radical, a powerful and relatively non-selective oxidant, 2) superoxide, a reductant and nucleophile, and 3) hydroperoxide, a nucleophile. Activated persulfate is based on the decomposition of persulfate in a reaction with Fe (II) which forms the sulfate free radical, a powerful oxidant.

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). The modified Fenton's reagent area was further divided into two test areas with different geochemical conditions; i.e., one injection well was treated with acid and one injection well was left at natural pH conditions prior to peroxide injection. A relatively large volume of acid (one pore volume of up to 11% sulfuric acid) was required to adjust the pH to the optimal range (i.e., <3.0), indicating a fairly high aquifer buffering capacity. This confirmed prior bench testing which had indicated that this system was buffered at approximately pH 6.2, presumably due to the presence of significant amounts of carbonate minerals in the soils. Both injection wells in the modified Fenton's test area were then treated with one pore volume of 10 percent hydrogen peroxide. In each instance hydrogen peroxide was applied without catalyst as the bench test indicated that there was sufficient naturally occurring catalyst. Within the activated persulfate test area, one pore volume of approximately 130 g/L sodium persulfate solution was applied to the activated

persulfate area. The persulfate solution was activated using a catalyst solution of Fe (II) and citric acid.

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). Chlorobenzene groundwater concentrations in the injection wells decreased by up to 40 percent. However, chlorobenzene concentrations in groundwater sampled from multiple monitoring wells within 10 feet of the injection wells showed little change in comparison to the baseline results. Post-treatment soil samples in this area exhibited little change or increases in chlorobenzene concentrations. Field parameters collected during the application indicated the distribution of dissolved oxygen over the entire 10 ft ROI; however, significant concentrations of peroxide were not observed in the same monitoring wells.

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. Several monitoring locations in the persulfate area also exhibited groundwater concentration decreases of greater than 80 percent. A few monitoring locations in close proximity to the most contaminated area did exhibit increases in groundwater concentrations, but this was likely the result of displacement of highly impacted pore water from the DNAPL impacted areas.

Both Fenton's reagent and activated persulfate are viable ISCO technologies that have been successfully applied to several sites. The results of these pilot tests underscore the importance of site specific characteristics when applying ISCO technologies. This side by side demonstration clearly indicated that activated persulfate was the more effective technology for this particular site. The greater stability of the persulfate in the subsurface likely resulted in better distribution of the oxidant as compared to peroxide. Furthermore, if the buffering capacity observed in the bench test is due to carbonates, as suspected, the results suggest that the sulfate free radical may not be as limited in carbonate systems as the hydroxyl radical. This is significant since it is well known that the hydroxyl radical is scavenged by carbonates and as a result modified Fenton's reagent is often not applied in systems containing significant amounts of carbonate minerals.

As a result of these pilot tests activated persulfate was recommended and selected for use in the full scale application.

Ecological Restoration and Natural Treatment Systems Remediation

Site Remediation, Sediment Removal and Comprehensive Ecological and Riparian Corridor Restoration for a Former MGP Site along a Tidal Freshwater River in Taunton, Massachusetts

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Community and Business Coordination, Outreach and Input for an MGP Remedial Closure and Restoration Program to Facilitate Redevelopment Opportunities along the Taunton River in Massachusetts

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Integrating Community Values into River Restoration: Neponset River Environmental Literacy Projects

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Treatment of Recovered Groundwater Containing 1,4-dioxane: Year-round Phytovolatilization by Irrigating Stands of Deciduous and Coniferous Trees

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Greenhouse Results, Substrate Matrix Selection and the Full-scale Design of a Vertical Flow Constructed Wetland for Chlorinated VOCs at a Site in North Carolina

John H. Pardue, Louisiana State University, Baton Rouge, LA

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Field-scale Assessment of Phytotechnology Applied to Sites Impacted with Weathered Hydrocarbons

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Site Remediation, Sediment Removal and Comprehensive Ecological and Riparian Corridor Restoration for a Former MGP Site along a Tidal Freshwater River in Taunton, Massachusetts

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On behalf of Nisource, Inc. ENSR International provided technical services for developing regulatory strategy, preparing a comprehensive environmental permitting approach, and overseeing dredging operations for an MGP Site Closure. In addition ENSR designed and implemented an ecological and riparian corridor restoration program involving 500 lf of bank restoration, revegetation and enhancement, 1.5 acres of palustrine wetland restoration and 250 lf of freshwater intertidal wetland restoration along the Taunton River in Massachusetts. Regulatory constraints included a multi-tiered environmental permitting program, presence of a state-listed endangered species in the waterway, specific dredging implementation work windows, and the opportunity for extensive public comment throughout the process. The site closure remedy involved on-site consolidation, containment and capping combined with the dredging of 10,000 cubic yards of sediment from the River with upland disposal. Physical constraints affecting design and construction of the restored bank and intertidal wetland were examined prior to design, and included analysis of current velocity, tidal hydraulics, riverbank substrate, and ice shear. Methodology employed to determine appropriate elevation for macrophyte establishment included analysis of pre-excavation conditions, unaffected wetlands within the same system, estimation of non-tidal hydrologic inputs, and consideration of future settling and sediment accretion. Engineering controls were included in the wetland design to prevent sloughing away from the riverbank, while accounting for future settling of the planting surface and maintenance of an appropriate elevation for maximum plant growth. This paper provides an overview of the entire project with an emphasis on the opportunities for cost-effective ecological restoration post-site closure.

Community and Business Coordination, Outreach and Input for an MGP Remedial Closure and Restoration Program to Facilitate Redevelopment Opportunities along the Taunton River in Massachusetts

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Nisource, Inc. and ENSR International worked together to develop a focused community and local business coordination and outreach program during the early planning stages of a comprehensive MGP site remediation and closure program along the Taunton River in Massachusetts. The Site Closure involved on-site consolidation and capping, dredging of 10,000 cubic yards of sediments from a tidal freshwater river, excavation and restoration of 1.5 acres of palustrine wetlands, restoration and revegetation of 500 lf of riverine bank, and restoration of 250 lf of intertidal wetlands along the riverbank. This program included working very closely with the Taunton Industrial Commission, the Weir Village Corporation, the Massachusetts Department of Environmental Protection, the Massachusetts Executive Office of Environmental Affairs (EOEA), the City's Mayor's Office and the public community to promote an understanding of the project remedial objectives, restoration initiatives, and to solicit input on future re-use scenarios. Nisource and ENSR were successful in petitioning the EOEA for a site specific Riverfront Area Densely Developed Area Petition which once effective relaxed some regulatory restrictions to promote redevelopment of a former industrial corridor. Further, by taking an up-front pro-active community involvement approach, Nisource was able to get all stakeholders on board with the project at an early stage which facilitated regulatory approvals (as all permits required extensive opportunity for public comment), resulted in partnering relationships with the local redevelopment commissions and businesses which facilitated project implementation and avoided any delays associated with the local community. This presentation provides an overview of the stakeholder outreach program for the project.

Integrating Community Values into River Restoration: Neponset River Environmental Literacy Project

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The Massachusetts Riverways Program is leading inter-agency efforts to evaluate technologies and approaches to achieve ecological restoration and contaminant remediation goals in the lower Neponset River. The benefits of restoration alternatives, including engineered fishways, dam breaching, and dam removal, and remediation options, including natural attenuation, bioengineering, in-situ stabilization, capping, and excavation and disposal, vary widely when assessed for effectiveness, ease of implementation, and compatibility with resource management goals. Each alternative can also affect a wide range of community interests which in turn influence community preferences.

Traditional public education and outreach activities associated with environmental decision-making incorporate the easily quantified (data, reports), the previously documented (historic photos and narratives), and the commonly observed (built and natural environment). Riverways is collaborating with the University of Massachusetts at Amherst to capture the social values of the people who live, work, and recreate in the lower Neponset River as a basis for effectively communicating complex technical data associated with environmental restoration and contaminant remediation.

Valuable insights regarding the effectiveness of public outreach strategies designed to communicate technical information to the general public have been gained through a search of the professional and scientific literature related to public involvement in watershed and river management and restoration. A greater understanding of stakeholder interests and values has emerged from focus groups and interviews involving community members and leaders of non-governmental organizations. Additional clarity regarding the “boundaries” of the current state of the science, particularly what is known and unknown about public and environmental health in the lower Neponset River, has been provided by a team of environmental remediation and restoration practitioners. This foundation of knowledge will inform the design of public outreach activities to explore fish passage, river ecology, and water and sediment quality as well as alternatives for ecological restoration and contaminant remediation.

Treatment of Recovered Groundwater Containing 1,4-dioxane: Year-round Phytovolatilization by Irrigating Stands of Deciduous and Coniferous Trees

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Groundwater at a site in North Carolina is contaminated with 1,4-dioxane and chlorinated aliphatic compounds. The dissolved-phase contaminants, originating from a former chemical manufacturing facility, are migrating toward a municipal water supply. The migration of the contaminant plume can be effectively controlled by a series of recently installed groundwater recovery wells located up-gradient of the water supply. These wells will pump year-round at a combined rate of approximately 50 gpm, and natural systems will be used to treat the recovered groundwater. The water will be routed to a constructed treatment wetlands to remove chlorinated aliphatics (Pardue's presentation), and effluent from the wetlands will be used to irrigate upland stands of deciduous and coniferous trees to remove 1,4-dioxane. This latter contaminant is highly water-soluble and resistant to biodegradation, and therefore will pass mostly untreated through the wetlands. However, 1,4-dioxane will be readily taken up, translocated and volatilized by the trees in the upland phytoremediation system. Once in the atmosphere, the 1,4-dioxane will be quickly degraded by UV-light. The phytoremediation system will be located on a closed municipal landfill that is adjacent to the site. In order to prevent the formation of dioxane containing leachate, all of the recovered groundwater used to irrigate the trees must be used via transpiration. The size of the upland phytoremediation system was determined based on estimations of water balance (transpiration rates vs. precipitation and irrigation rates). The recovered groundwater has moderate concentrations of carbonates that would accumulate in the root-zone if a stand of conifer trees, for example, were irrigated continuously with the water. Therefore, two different tree stands will be irrigated with the recovered groundwater: A mixed deciduous stand in the summer, when reference evapotranspiration (ET) is high, and a mixed coniferous stand in the winter, when ET is low. Summer rains (or tap-water irrigation) will leach carbonate salts from the root-zone of the conifer stand, and winter rains will leach salts from the dormant deciduous stand. The conifer stand (30 acres) will be larger than the deciduous stand (7 acres) because of low wintertime ET. A mixed stand of deciduous trees is included in the design because these trees grow much faster than conifers, and it is important to get the system at least partially on-line as soon as possible. Candidate coniferous and deciduous tree species were selected for the full-scale phytoremediation system based on the results of preliminary greenhouse studies assessing the phytovolatilization potential for 1,4-dioxane, and tolerance of the groundwater. A small-scale pilot on the landfill is now in progress to demonstrate that tree stands can be irrigated with recovered groundwater while maintaining a water balance (i.e. no leachate formation). These preliminary greenhouse and pilot projects will be discussed, as well as the design of the full-scale system.

Greenhouse Results, Substrate Matrix Selection and the Full-scale Design of a Vertical Flow Constructed Wetland for Chlorinated VOCs at a Site in North Carolina

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Greenhouse and bench-scale studies were performed to develop design criteria for a constructed wetland treating a complex mixture of chlorinated ethenes and ethanes from extracted groundwater and surface water at a site in North Carolina. Three sets of measurements and experiments were utilized to estimate design parameters: a). measurements of soil sorption and geotechnical properties for candidate peat and compost mixtures, b). batch microcosms to establish the compatibility of a mixed culture containing *Dehalococcoides* sp. with the selected compost mixture and c). vertical upflow wetland mesocosms to estimate spatial sorption and biodegradation parameters. An available compost mixture was identified with suitable bulk density, hydraulic conductivity, and sorption characteristics. Anaerobic batch microcosm studies demonstrated the compatibility of the mixed culture containing *Dehalococcoides* sp. with the selected mixture, first using trichloroethene as a benchmark compound, then a synthetic groundwater containing the complex mixture of chlorinated ethenes and ethanes representing the site in North Carolina. Complete dechlorination of both the benchmark compound and the chlorinated ethene/ethane mixture were observed to non-toxic end products, ethene and ethane. Upflow mesocosm studies demonstrated that very high removal efficiencies can be achieved with characteristic daughter product formation of chlorinated ethenes and ethanes. Synthesis of this information into a full-scale design for a ~50 gpm flow will be discussed.

Field-scale Assessment of Phytotechnology Applied to Sites Impacted with Weathered Hydrocarbons

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Phytotechnologies involve the plant-assisted bioremediation of organic and inorganic contaminants and are essentially a form of ecological engineering that depends on natural, synergistic relationships among plants, microorganisms and the environment. Since 1998, our research has focused on assessing the effectiveness of phytotechnologies as a means of reducing petroleum hydrocarbon concentrations in soils contaminated with weathered oil product. The overall focus of this research is to gain a better understanding of: (i) the pool of phytoremediation species found in Canada; (ii) how phytoremediation operates under unique Canadian climatic conditions; (iii) the mechanisms employed by phytoremediator plants to restore contaminated sites; and (iv) the agronomic requirements needed to maximize phytoremediation as an efficient and cost-effective cleanup technology. Starting in 2002, field studies were initiated to provide the type of ‘field performance data’ needed to determine appropriate uses of the newly emerging phytotechnologies. To address this need, field trials were established at sites impacted with weathered hydrocarbons in Saskatchewan and Alberta. As of fall 2004, three full growing seasons have been completed at the Saskatchewan site, and two full growing seasons have been completed at the Alberta site. The data indicate that there have been significant reductions in TPH concentration at both sites. Reductions in TPH concentration were greater in plots amended with fertilizer and compost than in plots receiving no fertilizer or amendment. Moreover, TPH concentrations were lower in the vegetated plots than in the unplanted plots. As well, site-specific plant mixes generally out performed a standard seed mix that was included at both sites. Whereas reductions in TPH concentration were reflected in all four CCME TPH-fractions, they were more pronounced in the F2 (equivalent C-numbers C10–C16) and F3 (equivalent C-numbers C16–C34) fractions.

Ecoterrorism: Research Issues

Securing the Water Supply: Using Detailed Simulations to Anticipate the Spread of Contaminants

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Lessons Learned from Chernobyl

George Markowsky, University of Maine, Orono, ME

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Resilient Communication Networks for Environmental Emergencies

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Pathogen Capture in Water Using Floating Film

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Thoughts from Twenty Years of Living with Plague

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Securing the Water Supply: Using Detailed Simulations to Anticipate the Spread of Contaminants

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New computational methods assist in preparation for attacks on the water supply. A computer simulation technique is demonstrated that can help predict the spread of contamination in any reservoir. This simulation capability allows "war gaming" of contamination scenarios so that emergency response agencies can determine (1) Where monitoring stations should be placed, (2) How long before the contaminant reaches the water supply intake, (3) How the contaminant's spread can be slowed by the use of booms or by altering flows at dams and gates. The simulation is demonstrated and validated using a particularly vulnerable part of the Massachusetts water supply, the Wachusett Reservoir. The Thomas Basin in the Wachusett Reservoir receives water from the Quabbin Reservoir, but is crossed by a state highway and bordered by active rail lines. Contamination at this point, which is possible through both accidental and malicious means, would soon deprive over 2.5 million people in the greater Boston area of drinking water from both the Quabbin and Wachusett Reservoirs. A three-dimensional computational fluid dynamics model is used to estimate the hydraulic residence time for the Thomas Basin in the Wachusett Reservoir in central Massachusetts. The simulation includes accurate depiction of basin bathymetry and inlet and outlet geometries. It is determined that mean hydraulic residence time is 3 to 4 days, approximately half of what would be expected with traditional models. The presence of a primary flow path, large scale eddies and stagnation zones contribute to the faster travel times. The incorporation of wind-driven circulation and thermal stratification effects is discussed. Under windy conditions, contaminants take much longer to reach the water supply intake.

Lessons Learned from Chernobyl

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The International Scientific–Information Center on Bio-Ecosystems (ISIC) in Kiev, Ukraine, has spent the last 15 years studying the consequences of the Chernobyl nuclear disaster with the goal of finding ways to reduce the harmful effects to ecology and humans. The techniques they have developed have been used to help Ukraine recover from the effects of the Chernobyl accident, but they also apply more widely to deal with a variety of hazardous substances.

Based on its studies of the Chernobyl accident, and the countermeasures taken to recover from it, ISIC has developed an optimal set of remediation and protection methods to protect ecosystems against radiation and other pollution (heavy metals, herbicides, and pesticides).

ISIC has developed a database detailing the ecological and socio-economic problems of the contaminated regions of Ukraine, including the Compulsory Evacuation Area. This database also contains information about the countermeasures applied and a metric of their effectiveness. ISIC will be continuing this research with the goal of creating an expert computer system for monitoring and forecasting of emergency situations, and the selection of countermeasures to minimize the impacts and risks of accidents. This talk summarizes the work of ISIC and provides an overview of some of its projects.

Resilient Communication Networks for Environmental Emergencies

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In this paper, we introduce a low-cost and easily setup wireless multimedia transmission system that can assist patient care during disasters. With real-time transfer of data from video cameras, sensors and display of information on the devices (PDAs, laptops) of EMT (Emergency Medical Team) from multiple disaster sites to the control center, the system enables disaster managers to quickly obtain patients' status information from the entire disaster area, to assist the diagnosis and treatment of patients, reducing mortality and morbidity in disaster situation. Moreover, the disaster managers in the command center can remotely control the information sent from the disaster sites. We have implemented the system prototype over the wireless network and successfully demonstrated simultaneous transmission of video, sensor information, medical image and text patient information from multiple disaster sites to the control center. The experiments conducted on the system prototype validate our system design.

Pathogen Capture in Water Using Floating Film

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Identifying pathogens in drinking water can be a challenge when they occur in low concentration. Floating films and micelles synthesized from lipids and glycoproteins offer an affordable and inconspicuous means of selectively concentrating pathogens at the surface of drinking water reservoirs where they can be collected for analysis. Studies by a number of scientists have demonstrated that bacteria, viruses and biotoxins can be captured by exploiting the affinity of their surface adhesins for specific sugar sequences present on host tissue surfaces. These sugar sequences can be present in glycoproteins of other species, thus providing a source of raw material. Based on these observations, it appeared possible to design glycoprotein films to capture human pathogens that express adhesins in water. Floating biocapture films are prepared by adding oil to glycoprotein solutions. Amphipathic molecules line up in a uniform sheet at the oil-water interface, with hydrated carbohydrate moieties facing the aqueous phase. Agitation of the film produces buoyant spheres (micelles) filled with oil and coated with protein molecules exposing complex carbohydrates to the milieu.

Currently, biocapture films made from commercial yeast-derived invertase are being tested to assess the binding capacity and specificity for *E. coli* expressing Type 1 fimbriae. A mutant afimbriated *E. coli* strain is used as a control. Within a short mixing time, invertase micelles capture fimbriated *E. coli*, with no significant binding of the afimbriated strain. In future studies, methods of selective capture in multi-species aqueous systems will be explored. Micelle size, mixing time and other variables will be tested to determine the efficiency, sensitivity and selectivity of biocapture films. This technology may provide the basis of an affordable and unobtrusive large-area water surveillance system.

Thoughts from Twenty Years of Living with Plague

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Yersinia pestis, the causative agent of plague, produces fulminant life-threatening infections in a wide variety of mammalian species. These properties--high virulence and the ready availability of good animal models--have allowed for productive research leading to discovery of principles later shown to be of broad importance relevant to many unrelated pathogens. *Y. pestis* has also been an organism of great concern with respect to biological warfare, bioterrorism, and biodefense. Key aspects of plague biology and its potential for misuse will be discussed. In addition, a scheme for early detection of potential outbreaks based on methods in routine use for protection of laboratory workers and applicable to a wide range of diseases will be presented.

Environmental Biotechnology

Visualization and Enumeration of Microorganisms Growing Under Denitrifying Conditions with Multi-Color FISH

Eric Hince, Geovation Technologies, Inc., Florida, NY

Use of Proteomics in Bioremediation

Rolf U. Halden, Johns Hopkins Bloomberg School of Public Health, Baltimore, MD

Monitoring Bioremediation by Analyzing *In Situ* Gene Expression

Derek R. Lovley, University of Massachusetts, Amherst, MA

Barriers to the Adoption of “Cutting Edge” Research to Solve “Real World” Problems

Robert J. Steffan, Shaw Environmental, Inc., Lawrenceville, NJ

The Use of Stable Isotopes in Nucleic Acid and Lipid Analysis for Assessing Bioremediation Potentials

Aaron D. Peacock, The University of Tennessee Center for Biomarker Analysis, Knoxville, TN

Greg Davis, Microbial Insights Inc., Rockford, TN

Kerry Sublette, University of Tulsa, Tulsa, OK

Bill Holmes, University of Michigan, Ann Arbor, MI

Investments in Environmental Genomics: Relevance to U.S. DOE Missions

Robert T. Anderson, U.S. Department of Energy, Washington, DC

Visualization and Enumeration of Microorganisms Growing Under Denitrifying Conditions with Multi-Color FISH

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Molecular, culture-independent methods have revolutionized our current understanding of the microbial ecology of many natural and anthropogenic environments. Fluorescence in-situ hybridization (“FISH”) is emerging as a powerful and quantitative genomic-based method for investigating the relative abundance of microorganisms in environmental samples. Multi-color FISH (“mFISH”) involves the simultaneous hybridization of a sample with multiple oligonucleotide probes conjugated to different color fluorochromes so as to provide quantitative information on different sub-populations in the same sample. mFISH also enables the simultaneous visualization of spatial arrangements of microbes in mixed consortia to investigate the potential for mutualistic or syntrophic interactions among different organisms.

mFISH data and images will be presented from an ongoing denitrification-based bioremediation (“DBB”) project at a DoD-owned hydrocarbon contamination site. Initial DGGE and PCR screening of ground-water samples were used to identify bacteria, archaea and fungi present within the DBB treatment zone and to help design mFISH assays targeting microorganisms suspected to be numerically important members of the DBB consortia. Multiple probes targeting the 16S or 23S rRNA of various taxonomic classes of microorganisms, from Domain- to Genus-specific probes, are being used to enumerate members of the DBB consortia. Probes being used include Domain-level probes EUB338 (eubacteria), ARC915 (archaea), and PF2 (yeast) and division- or phyla-specific probes BETA42a (β -proteobacteria), GAM42a (γ -proteobacteria), ALF968 (α -proteobacteria), DELTA495 (δ -proteobacteria) and CFB560 (*Cytophaga-Flexibacter-Bacteroides*). Group- and genus-specific probes are being used to target sub-populations of bacteria shown by DGGE to be among those consistently found at DBB treatment sites including members of the *Comamonadaceae* (BONE23a), *Burkholderiales* (SUBU1237) and *Pseudomonas* spp. (PS56a). Probes were labeled with Oregon Green, Cy3, or Cy5 for CCD imaging with a Nikon 90i epi-fluorescent microscope and narrow-band filter sets. Initial mFISH results have revealed an abundance of β -proteobacteria and dimorphic, *Yarrowia*-like fungi in dense DBB consortia comprised of $\geq 10^7$ total cells/mL. A dual-probe mFISH assay for bacteria (Cy3-labeled EUB338) and yeast (Cy5-labeled PF2) revealed clusters of mixed bacteria and small yeast in contact with one another, raising the possibility of some type of mutualism or opportunistic association.

Preliminary results indicate promising potential for mFISH assays using both the BETA42a (Oregon Green) and GAM42a (Cy5) probes. BETA42a and GAM42a differ by only one base, so they are normally used with a competitor probe, i.e., the labeled probe to be imaged (e.g., BETA42a) together with the unlabelled “competitor” probe (e.g., GAM42a) to minimize erroneous hybridizations. Preliminary results suggest both probes can be imaged simultaneously with different color fluorochromes while minimizing errant hybridizations. mFISH assays that combine multiple probes may enable more rapid and cost effective enumeration and examination of important groups of microorganisms for monitoring *in-situ* bioremediation programs.

Monitoring Bioremediation by Analyzing *In Situ* Gene Expression

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In general, *in situ* bioremediation of groundwater contamination is an empirical practice because there is little information on the metabolic state of the microorganisms involved in bioremediation and it is not possible to accurately predict how these microorganisms might respond to various strategies to modify the subsurface environment in order to promote bioremediation. However, the sequencing of the genomes of microorganisms involved in bioremediation is leading to the development of genome-based *in silico* models which can be used to interpret gene expression data from the environment to infer the physiological state of the microorganisms in the subsurface as well as to predict the likely response of these microorganisms to potential bioremediation strategies. For example, adding organic electron donors to stimulate dissimilatory metal reduction and promote the reductive precipitation of uranium has proven to be an effective strategy to immobilize uranium in uranium-contaminated subsurface environments. *Geobacter* species, which are capable of U(VI) reduction, are the predominant members of the microbial community during this *in situ* uranium bioremediation, accounting for over 95% of the microorganisms in the groundwater. However, little was known about the *in situ* metabolic state of the *Geobacter* species during this process. Quantitative analysis of *in situ* levels of transcripts for key genes involved in nutrient uptake and metabolism of acetate provided insights into additional nutrients that might be added to the groundwater to better promote the growth of *Geobacter* species and demonstrated that rates of metabolism of *Geobacter* were directly linked to how much acetate was added to the groundwater. This systems biology approach to groundwater bioremediation, which is readily applicable to other processes such as reductive dechlorination, has the potential to change groundwater bioremediation from an empirical practice to science.

Barriers to the Adoption of “Cutting Edge” Research to Solve “Real World” Problems

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Each year extensive research is performed to address remediation of contaminated sites. Most of this research, however, never finds its way into practical application. The application of molecular biology tools for site assessment and remediation monitoring provides a useful example to address the difficulty of bridging the gap between remediation research and application. These tools have been used for >20 years to study biodegradation and microbial ecology. Early environmental applications of molecular tools employed colony hybridization to identify degradative genes in bacterial colonies growing on Petri plates. This technique was useful, but limited by the need to culture organisms. Consequently, techniques were developed to isolate DNA directly from environmental samples, and ultimately, a PCR method was demonstrated whereby target DNA in environmental samples could be amplified and detected at extremely low levels without cell culturing. Despite these early advancements and more than 15 years of continued development, molecular tools are still infrequently used outside of academic laboratories. Reasons of the slow adoption of molecular biology tools are likely many. Notably, the environmental remediation business is dominated by environmental engineers and hydrogeologists who may not be familiar with these techniques or capable of interpreting the resulting data. Equally important, scientists developing the techniques often fail to understand the technical requirements of the remediation business, and they often can not address the important practical requirement of correlating molecular biology data with remedial design needs. Ultimately, the benefits of the using these techniques and the utility of the resulting data often are difficult to convey to those paying for the services. Likewise, the commercial uncertainty of the techniques has limited the number of analytical laboratories willing or able to provide these services. In the final analysis, the use of molecular tools will likely increase as practitioners find them useful for serving their clients, but widespread adoption of the techniques will require a concerted collaboration between developers and practitioners to generate better tools that address practical remediation concerns.

The Use of Stable Isotopes in Nucleic Acid and Lipid Analysis for Assessing Bioremediation Potentials

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In situ monitored natural attenuation or enhanced passive remediation in many situations is the most cost-effective way to remediate groundwater contaminated with low concentrations of contaminants. The key to demonstrating the potential effectiveness of monitored natural attenuation (MNA) at a site is establishing cause and effect relationships, which provide direct evidence that desired bioprocesses are occurring, or are likely to occur. Currently, comprehensive groundwater monitoring programs or microcosm studies are implemented to attempt to ascertain these relationships. In practice, these approaches are often time consuming, costly, and difficulties with data interpretation or scale-up often occur. Experience has led to the conclusion that, while these approaches are theoretically and technically sound, the data obtained is often inconsistent and/or conflicting, and the insight gained from such approaches does not lead to knowledge of attenuation capacity. Most importantly, with current approaches, it is often difficult or impossible to demonstrate convincingly that desired bioprocesses are occurring *in situ*. Thus, NMA/EPR are not always employed to their best use. Over the past couple of years the Center for Biomarker analysis has developed specialized molecular biology tools that integrate Stable Isotope Probing (SIP) which provides direct evidence of contaminant degradation or remediation. This talk will present background information on the development of these tools as well as case studies from several sites with contaminants ranging from BTEX to Uranium.

Investments in Environmental Genomics: Relevance to U.S. DOE Missions

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The Department of Energy has, as one of its missions, the responsibility for cleaning up numerous sites contaminated with radionuclides resulting from Cold War era processing of uranium. At many of these sites the occurrence of contamination across vast volumes of the subsurface precludes the use of conventional remediation techniques. Microbial communities found in the subsurface are capable of transforming radionuclides to insoluble forms thereby limiting further transport of contaminants. In order to understand the influence of microorganisms on contaminant transport the office of Biological and Environmental Research (BER) is exploring the use of environmental genomics to describe bioremediation processes within the subsurface. BER via the Genomics:GTL program has embarked on an ambitious and large scale effort to sequence the genomes of microorganisms found in the subsurface, and many other environments, and comprehensively understand the physiology of these organisms. Investigations within the Environmental Remediation Sciences Division (ERSD) of BER are applying molecular biology techniques to in situ bioremediation studies in an effort to understand subsurface biogeochemistry. BER envisions the coupling of genomic information, gene expression assays and biogeochemical information from the environment in a systems biology approach will enhance the understanding of contaminant biotransformation in the environment and promote a more quantitative view of in situ bioremediation processes.

Environmental Fate

Vadose Zone Hydraulic Process- Infiltration and Percolation- and Their Function in Hazardous Materials Transport

Alton Day Stone, Alton Engineering, Sterling, MA

James C. O'Shaughnessy, Worcester Polytechnic Institute, Worcester, MA

Evaluation of NAPL Migration Resulting from Big Dig Activities

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

Kelley Race, Weston & Sampson Engineers, Inc., Peabody, MA

Ken Bisceglia, Weston & Sampson Engineers, Inc., Peabody, MA

DNAPL Dissolution- Evaluating Natural Depletion Over Time

Jeffrey A. Johnson, The RETEC Group, Inc., Houston, TX

Bart Germond, Focus Environmental Services, Inc., Galway, NY

Vadose Zone Hydraulic Processes – Infiltration and Percolation – and their Function in Hazardous Materials Transport

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The release of most hazardous materials occurs through spillage or other deposition on the ground (soil) surface, either in the liquid-phase - e.g. gasoline or solvent spill, or solid-phase - e.g. lead paint chips, and deposition of atmospheric particulates. The transport of surface deposited hazardous materials to an underlying water supply aquifer is of great concern, and necessitates liquid and dissolved-phase transport through the *vados* or *unsaturated zone*. Vadose zone flow is very complex, being a function of several interdependent (and dependent) variables, that is not easily described or modeled and commonly is not well understood by environmental professionals. The importance of unsaturated flow cannot be ignored; risk characterization models and associated substances-specific risk levels, involve vadose zone transport modeling at some level. Understanding of vadose zone processes permits adaptation of site-specific data to the general transport models. This paper describes the basic mechanisms of vadose zone flow, in particular *infiltration* and *percolation*, and their relationship to hazardous materials transport. Infiltration is the movement of water through the soil surface into the underlying soil column. Percolation is the subsequent movement of water, usually downward, through the subsurface soil. Both mechanisms involve two hydraulic phenomenon – gravity drainage through macropores and capillary flow through micropore - that are highly dependent on soil type and structure. This paper focuses on one-dimensional downward vertical flow ($\partial v/\partial z$) as described by the *Buckingham-Darcy* and *Richards Equations*. One-dimensional flow is adequate for practical description of most common engineering applications. The results of bench scale experiments using soils common to New England, including outwash sands, marine clay and till, are used to illustrate transport mechanisms.

Evaluation of NAPL Migration Resulting from Big Dig Activities

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The Big Dig required numerous complex construction projects to complete arguably one of the biggest civil engineering projects of mankind. One of these projects involved the installation of an access road to service the numerous construction vehicles through a dense, highly populated area of South Boston. This road was installed adjacent to a bus maintenance facility that contained several feet of light non-aqueous phase liquid (LNAPL - Diesel#1 and gasoline) over a 2.5-acre area. LNAPL migration from this site was influenced by a myriad of complex urban subsurface conditions including:

- Numerous active and abandoned utility ducts and conduits
- An MBTA red-line tunnel
- An active aboveground rail line and bus maintenance facility
- A regional stormwater pump station
- Underdrain system to control groundwater for the newly installed Big Dig access road and
- Complex, heterogeneous urban stratigraphy including urban fill and interbedded clay lenses

This paper will evaluate and discuss the fate and transport/hydrogeologic characteristics of the site and how these characteristics influenced LNAPL migration toward the underdrain system of the access road. Also, we will discuss how these data were used to design the multi-million dollar, multiphase extraction system including measures to intercept LNAPL prior to reaching the stormwater pump station. The remediation system contains the following processes LNAPL separation, groundwater and soil vapor treatment via carbon adsorption, metals precipitation, and bioremediation complex.

DNAPL Dissolution – Evaluating Natural Depletion Over Time

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The transfer of mass between a non-aqueous phase liquid and the aqueous phase is complex and a function of numerous physical and chemical conditions. Factors that influence the rate of dissolution include surface area of exposure, groundwater velocity, dispersion, diffusion, viscosity, and chemical interactions between the residual and dissolved phases. These various processes can be simplified into three general factors: (1) groundwater velocity, (2) the concentration difference between the effective solubility of the dissolved species in the residual phase and the dissolved concentration, and (3) a mass transfer coefficient (Pfannkuch, 1984). Over time, with residual mass depletion, the total mass transfer to the water phase decreases producing lower dissolved phase concentrations.

This paper presents data from residual trichloroethylene (TCE) that has been monitored for over a decade under natural conditions. The results of the monitoring indicate the mass flux from the residual NAPL to the aqueous phase has continually decreased through time. Specifically, analyses indicate that the mass transfer rate decreased by a factor of 5 from 1991 to 2002. The continual depletion of the source reduced the estimated source mass by approximately 65 percent. As a result, the dissolved TCE concentrations produced from the residual NAPL has decreased continually over time – ranging from 7 to 20 ppm per year. In one area, the decrease in mass transfer appears to be occurring in a “step-like” fashion, which is thought to be the result of the physical depletion of residual mass within the pore network.

The long-term monitoring of dissolved concentrations over time without influence of remedial activities provide useful insights into the rates of natural depletion of a NAPL within a groundwater system.

Environmental Forensics

“Is this Diesel Mine...?”: Advances in Forensic Identification of Petroleum Related Releases into the Environment

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Estimating the Timing of a Chlorinated Solvent Release: A Case Study

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Polycyclic Aromatic Hydrocarbon Characterization in Differing Watersheds in Northwest Ohio

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DNA Fingerprinting - Tools of Tomorrow's Forensics

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Environmental Forensic Methods for Soil Gas and Vapor Intrusion Investigations

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Differentiation of PAHs from Coal, Creosote, and Combustion-related Background Sources in Stream Sediments

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“Is this Diesel Mine...?”: Advances in Forensic Identification of Petroleum Related Releases into the Environment

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Recent developments in forensic hydrocarbon fingerprint analysis have enabled specific markers found in diesel to be characterized and identified. The fingerprinting and data interpretation techniques include the recognition of distribution patterns of hydrocarbons (alkylated naphthalene, phenanthrene, dibenzothiophene, fluorene, chrysene and phenol isomers); analysis of “source-specific marker” compounds (individual saturated hydrocarbons, including n-alkanes ($n-C_5$ through $n-C_{40}$), alkylcyclohexane, homologues series, recalcitrant isoprenoids: pristane and phytane); the determination of diagnostic ratios of specific petroleum and non-petroleum constituents; and the application of various statistical and numerical analysis tools (Compound Ratio Analysis Technique (CORAT)). A spill sample was analysed to identify the possible source and origin of the diesel. Samples were subjected to analysis by Iatroscan, and gas chromatography, utilising both flame ionisation and time of flight mass spectral detection techniques (TOF-MS) in comparison to known reference materials. The analysis showed that the diesel came from the suspected source which allowed the regulator to prosecute.

Estimating the Timing of a Chlorinated Solvent Release: A Case Study

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Soil and ground water samples on- and off-site implicated a solvent recycling facility as the source of chlorinated solvents on and downgradient of the facility in soil and ground water. The timing of the releases, however, was a factor in determining liability for remediation at the site. In particular, whether the releases occurred before or after 1990 was in question. The primary solvents released at the facility were believed to be PCE, TCE, and 1,1,1-TCA. Four methods were used to assess the likely timing of the releases. The site operational history, focusing on materials handling and spill control procedures, was evaluated. Second, locations at which contamination was found were evaluated in the context of the site development and grading history. Third, transport rates in the vadose and saturated zones were evaluated to determine the likely time required for chlorinated solvents to move from the source locations to the locations at which they were found in samples from monitoring wells and surface water. Fourth, a sequential degradation model incorporating both biotic and abiotic degradation pathways was used to estimate the amount of time chlorinated solvents in ground water had been undergoing degradation. Degradation rates were estimated from a combination of site and literature data. The abiotic degradation rate of 1,1,1-TCA to 1,1-DCE was based on rates reported in the literature, and other degradation rates were constrained by a rates reported in the literature taken in context of the site geochemical conditions. The model was calibrated by varying degradation rates, within appropriate constraints, until the variation in the estimated time of degradation for compounds reported in each well was minimized. These four methods each supported the hypothesis that there were significant chlorinated solvent releases prior to 1990.

Polycyclic Aromatic Hydrocarbon Characterization in Differing Watersheds in Northwest Ohio

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Polycyclic aromatic hydrocarbons (PAH) are ubiquitous contaminants traceable to both petrogenic (natural) and anthropogenic (human-related) sources. Characterization of their sources can be determined using a modified method described by Stout *et al.* (2001). PAH contamination was characterized in three unique watersheds in Northwest Ohio. Otter Creek, deemed a dead stream, is an Area of Concern in Lucas County that has been highly altered from its original wooded character by human activities. Seven miles long, it passes through urban and industrial areas to empty into Maumee Bay and Lake Erie. The Maumee River, carrying the highest sediment load in the region, passes through rural, agricultural areas. The Ottawa River, also an Area of Concern, runs through industrial areas and municipal landfills. Sediment samples taken from both the river bottoms and 15 cm depths were collected in late 2004 and early 2005 from several sites along the waterways. The relative abundances of specific branched and unbranched PAH compounds denote their pyrogenic, petrogenic, or biogenic origins.

DNA Fingerprinting - Tools of Tomorrow's Forensics

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Microorganisms, being ubiquitous in any environment, extremely diverse and versatile, may record any effect of present or past contamination. Finding the right tools to look into microbial changes in environment will offer powerful forensic methods. Modern DNA fingerprinting techniques, using PCR reaction to amplify the targeted gene require tiny amount of sample, may be automated and are very specific, providing such forensic tools. To date, in forensic studies, DNA fingerprinting techniques are commonly used to track down criminals, test the parentage of children, and to follow the evolution of species. In environmental forensics, DNA fingerprinting is yet to be used. So far, the study and monitoring of microbial communities in different contaminated environments based on DNA fingerprinting methods have been well established and applied. Based on such studies, the changes induced by different contaminants may be monitored, too. Since microbial communities contain groups with ability to metabolize basically any contaminant present, specific changes or shifts in microbial population will be induced by specific contaminants. The potential to track the passage of contaminants even long time after they are gone by DNA fingerprinting of a certain gene responsible for metabolizing the contaminant, is very high. So is the potential of tracking the source and age of contamination.

This presentation will review some of the main DNA fingerprinting methods available (PCR based) to monitor microbial changes in the environment with potential environmental forensics applicability. Some practical applications of DNA fingerprinting technique in criminal forensics and environmental studies will be also presented. It is our hope and conviction that such methods will be the basis for developing standardized forensic techniques of tomorrow, applicable in any environment and for any contaminants.

Environmental Forensic Methods for Soil Gas and Vapor Intrusion Investigations

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Powerful methods are available for differentiating hydrocarbon contaminated soil gas from ambient chemicals in indoor air. However, the techniques used during many soil gas and indoor air quality assessments lack a standard approach that can differentiate household chemicals from vapor derived from subsurface hydrocarbon contamination. Consequently, environmental contaminants like benzene from in-house sources could be inaccurately attributed to emission from subsurface NAPL. This problem becomes even more complex in the presence multiple subsurface vapor plumes derived from fugitive gasoline, fuel products, and tar. The primary obstacle is that standard methods for characterizing the composition of indoor air, potential sources, and background air do not adequately measure a sufficient number of chemicals to accurately determine makeup and—and hence sources—of chemicals found in indoor air.

The selection of appropriate analytical methods is critically important in the source identification of indoor air chemicals. Standard Methods such as EPA TO-14 that are used for measuring regulated compounds include few of the diagnostic hydrocarbons required for source identification and differentiation purposes. As a result, the application of standard methods must be extended to include additional compounds needed for source identification purposes. In addition, the sensitivity of the standard methods must be increased to detect diagnostic compounds at low concentrations approximately 1,000 times lower than most site assessment techniques. Recent advances in measurement methods using EPA TO-15 have demonstrated critical improvements in sensitivity and analyte richness for improved hydrocarbon source identification. Two case studies demonstrate the improved capability of TO-15 enhancements for the differentiation of gasoline, diesel and tar vapors from background signatures in indoor air.

Differentiation of PAHs from Coal, Creosote, and Combustion-related Background Sources in Stream Sediments

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment from a variety of sources: atmospheric soot residues from burning petroleum/wood/coal, surface runoff, urban/industrial outfalls, petroleum uses and releases, and others. In aquatic environments, sediments are a primary sink for hydrophobic compounds, such as PAHs. PAHs also constitute the predominant hydrocarbon fraction in creosote, and are typically the constituents of concern for sediment remedial investigations associated with wood-treating sites. A case study is presented where coal particles were identified as a major source of elevated PAH concentrations in sediments downstream of known site releases, and the primary source of PAHs in a stream branch where site releases were suspected, but proved to be insignificant. Relatively simple interpretative techniques were applied to PAH delineation data generated using conventional analytical methods. The preliminary evaluation identified two potentially distinct PAH signatures, representing site-related creosote sources and site-unrelated coal sources. Comprehensive PAH “fingerprinting” was performed on selected samples to confirm source identifications, and particles were analyzed microscopically to confirm their coal origins. The findings were used as the technical basis for significantly reducing remedial liability.

Environmental Stewardship and Proactive Management at Small Arms Ranges

Environmental Range Management

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Environmental Management at Operating Outdoor Small Arms Firing Ranges

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Update of the RangeSafe Program

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Suppression of Tungsten's Leachability in Water

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A Challenge for the Applicability of Regulatory Leaching Tests for Assessing Lead Leachability in Shooting Range Soils: Comparison of TCLP and SPLP

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Use of Predictive Models for Characterization of Trap And Skeet Ranges: Case Studies and Model Results

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Environmental Range Management – An Overview of National Environmental Policy Act Requirements and Engineered Solutions to Achieve Them

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Current Federal regulations mandate the preparation of planning documentation for the construction of new outdoor firing ranges, alternative reuse of existing firing ranges and construction of indoor firing ranges. Typically, two types of planning documentation are required: Intra-service planning documentation (often a component of master planning or real property development planning); and Externally-consumable National Environmental Policy Act (NEPA) documentation that provides a legally-required public interface to the planning process. This documentation should address all aspects of environmental planning to include assessing the impacts of construction, operation, long term management, and ultimately, closure. With environmental management a key issue receiving every increasing regulatory scrutiny and public pressure at operational ranges, best management practices (BMPs) guidelines are being developed. The BMPs stress that the primary goal of any environmental management plan is to manage potential impacts posed by range activities on the environment, public health and/or public welfare. To achieve this goal while maintaining NEPA compliance, it is imperative to keep lead on-site and in its metallic form, while minimizing the potential of projectiles impacting wetlands or surface waters, and reducing noise impacts to surrounding properties. These considerations must be addressed during both environmental master planning and range design to ensure cost effective implementation.

This presentation provides a layperson overview of NEPA requirements and real-world engineered solutions to meet them in a format suitable for use in an operational range Environmental Management Plan (EMP).

Environmental Management at Operating Outdoor Small Arms Firing Ranges

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The Interstate Technology Regulatory Council (ITRC) subgroup on Small Arms Ranges has published (February 2005) its document, “Environmental Management at Operating Outdoor Small Arms Firing Ranges.” In addition to making this document widely available on its web page (http://www.itrcweb.org/gd_SMART.asp), the ITRC also provides free internet based training and class room training (2005) which aids small arms range managers in proactively managing environmental issues on their ranges.

Constituents from small arms projectiles, targets, and primers used at a range can potentially migrate in the environment. Depending on the depth of groundwater, climate, soil chemistry, or proximity to surface water at the range, constituents can reach groundwater or surface waters.

Well-designed and -managed ranges should incur only manageable environmental issues during operation. Environmental conditions at operating ranges need to be evaluated, however, to delineate any existing and potential risks to the environment. Upon identifying a problem, measures should be undertaken to correct, prevent or minimize adverse environmental impacts.

The ITRC document and training are intended to help minimize potential exposures to lead and other materials associated with shooting ranges. They are designed to assist range operators in developing, using, and monitoring environmental management plans at their active outdoor small arms firing ranges. The central task in formulating an environmental management plan is the selection and implementation of effective and reliable pollution prevention and mitigation measures, otherwise referred to as “best management practices” (BMPs). The document and training developed by a partnership among state and federal environmental representatives, Department of Defense, shooting sports industry, and stakeholders, focuses on providing range operators with the guidance they need to identify and undertake BMPs that are appropriate for and tailored to the site-specific environmental conditions at their ranges.

Suppression of Tungsten's Leachability in Water

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The next generation of bullets and other projectiles for use in small arms is relying on new and at the same time non-toxic materials to reproduce the density and properties of lead. The primary materials of choice for the high-density components are tungsten and tungsten alloys. The experimental data of a leachability study of pure tungsten and ceramic-coated tungsten is presented.

The extent and rate of tungsten's leachability in water under aerobic conditions first of all depends on the pH. For the studied pH range 1.5 - 8.5, a pH of 8.5 revealed the most pronounced leachability. Tungsten's leachability at pH 1.5 is negligible. The first step of the interaction between tungsten and the oxygen-containing water can be described as follows: $W + H_2O + 1.5 O_2 \rightarrow WO_4^{2-} + 2 H^+$. Secondly, monotungstate, WO_4^{2-} , reacts with H^+ , resulting in the formation of the soluble metatungstate anion $[H_2W_{12}O_{40}]^{6-}$: $12 WO_4^{2-} + 18 H^+ \rightarrow [H_2W_{12}O_{40}]^{6-} + 8 H_2O$.

Tungsten's leachability strongly depends on the surface area. In descending order of surface area, a tungsten powder is a worst-case scenario followed by a pressed tungsten powder compact, and finally, a sintered tungsten powder part.

By addition of selected metals M, the leachability of tungsten can be significantly suppressed. The cation M^{n+} interacts with $[H_2W_{12}O_{40}]^{6-}$, producing tungstates like $M^{II}WO_4$ and $M^{III}_2(WO_4)_3$, which are characterized by an extremely low solubility. The addition of selected metals to tungsten powder suppresses the leachability of tungsten to a great extent and at the same time exhibits only a minor leachability.

An alternative way to prevent or greatly minimize the leachability of tungsten consists in adding selected salts or oxides to tungsten. The solubility of the selected compounds must be slightly higher than the solubility of the tungstates to be formed.

A Challenge for the Applicability of Regulatory Leaching Tests for Assessing Lead Leachability in Shooting Range Soils: Comparison of TCLP and SPLP

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Contamination of lead (Pb) from use of Pb bullets at shooting range sites has drawn considerable environmental attention. Treatments and/or disposal of contaminated range soils depend upon the leaching potential of Pb. The toxicity characteristic leaching procedure (TCLP) is the current USEPA standard protocol to evaluate metal leachability. However, application of TCLP to assess Pb leachability from contaminated range soils may be questionable. This study determined Pb leachability in range soils using two USEPA regulatory leaching methods, i.e. TCLP and synthetic precipitation leaching procedure (SPLP). Possible mechanisms that are responsible for Pb leaching in each leaching protocol were elucidated via X-ray powder diffraction. Soil samples were collected from the backstop berms at four shooting ranges, with Pb concentrations as high as 60,600 mg kg⁻¹ soil. Lead concentrations in the TCLP leachate ranged from 3 to 350 mg L⁻¹, with all but one soil exceeding the USEPA non-hazardous waste disposal limit of 5 mg L⁻¹. Furthermore, continued dissolution of metallic Pb and re-precipitation of cerussite prevented the TCLP extraction from reaching equilibrium at the standard leaching time of 18 h. Thus, the standard one-point TCLP test would either over- or under-estimate Pb leachability in range soils. SPLP-Pb levels ranged from 0.021 to 2.6 mg/L, with all soils above the USEPA regulatory limit of 0.015 mg/L. The analytical SPLP results in all soils agreed well with a modeling prediction. In contrast to TCLP, SPLP leaching readily reached equilibrium within standard time of 18h, regardless of pH and Pb concentrations, and the acidic rainfall environment that the SPLP fluid simulates is identical to the condition that the shooting range soil is actually exposed to. Therefore, SPLP is a more appropriate leaching test than TCLP for assessing lead leachability in range soils. This is very important in helping the USEPA in regulating the evaluation of Pb leachability and subsequent treatment of shooting range soils.

Use of Predictive Models for Characterization of Trap And Skeet Ranges: Case Studies and Model Results

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The distribution of lead shot in the soils surrounding trap and skeet ranges typically follows predictable patterns, which can be estimated using empirical models. This is possible because the geometry of the ranges is standardized, and the trajectories of the shot sizes that are commonly used vary within narrowly defined limits. Based on an analysis of standard shotgun range layouts and the results of previous site characterization investigations, geometric projections were developed of typical lead-shot distribution patterns associated with trap ranges, skeet ranges, and combined trap/skeet installations. The projections were used to develop scaled, graphic overlays (templates), which depict the likely horizontal limits of shot deposition, as well as those areas likely to contain the greatest accumulations of lead shot. Using conventional GIS or CAD software, the templates can be electronically registered over site plans or digital aerial photographs, using features such as shooting stations and trap houses as reference points. The templates can be used to develop an initial framework for site reconnaissance, as well as a preliminary inventory of potential ecological receptors (*e.g.*, wetlands or surface water bodies). The templates enable the focused delineation of lead and associated contaminants (*e.g.*, antimony and arsenic) in soils at the margins of the shot-fall zone, and also beneath areas where the highest metal concentrations are likely to occur. They can also be used to decipher overlapping shot-fall patterns at multiple range facilities, and are especially useful in the investigation of closed ranges, where shot deposition patterns can be reconstructed relative to features identified in historic aerial photographs or site plans. A variation of the same approach can be applied to sporting clays courses, providing that both the present and historic alignments of the stations and target throwers are known.

Evolving Strategies for Dealing with Contaminated Sediments

Managing Contaminated Dredged Sediments in New England: A Valuable Experience Base

Thomas J. Fredette, US Army Corps of Engineers, New England District, Concord, MA

Case Study – Remediation of the New Bedford Harbor Superfund Site

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Mark Anderson, U.S. Army Corps of Engineers, New England District, Concord, MA

Jim Brown, U.S. Environmental Protection Agency, Boston, MA

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Excavation of PCB-Contaminated Sediment Adjacent to the Intake of a 12-MGD Drinking Water Plant

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Effectiveness of *in situ* Cement Stabilization for Remediation of Sediment Containing Coal Tar Derived Hydrocarbons

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David Templeton, Anchor Environmental, LLC, Seattle, WA

Tim Metcalf, Honeywell International Inc., Morristown, NJ

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Monitoring the Uplift of a Low-Permeability Sediment Cap Due to Gas Entrapment Beneath the Cap: Findings of the First 18 Months

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Optimization of PCB Dechlorination by Palladized Magnesium in Marine Sediments

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Managing Contaminated Dredged Sediments in New England: A Valuable Experience Base

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Environmental management of contaminated aquatic sediments from dredging projects in New England began in 1967 when the Providence Harbor channel was specifically dredged so that the more contaminated sediments were removed first followed by the cleaner sediments in order to bury the contaminants deeper in the deposit at the designated offshore disposal site. This was followed by a similar sequencing of the dredging of New Haven channel in 1974. Little is known about the success of these operations as there are no records of monitoring. However, later observations that the marine benthos actively recolonized these sites suggests they met at least one factor of success.

The first fully planned and monitored capping operation was conducted from 1978 to 1979 when sediments from Stamford Harbor were dredged, placed in two separate mounds at an offshore site in Long Island Sound, and subsequently capped with sediments from New Haven. This project involved extensive monitoring and reporting. Use of a different management technique, that of a confined aquatic disposal (CAD) cell, was first done in 1981 when about 5,000 cubic yards of nitrobenzene contaminated sediments were buried below the I-95 bridge in Norwalk, CT. Similar to the early capping efforts, little is known about any monitoring to document the success of the operation. However, since these early efforts, dozens of dredging projects in New England have been managed using open water capping. More recently, CAD cells have been used for projects in Hyannis, Boston, and Providence. Much of this later work has been extensively documented, monitored, and published. Although the bulk of this information resides in grey literature, access to much of it has become easier with the advent of the internet.

The past several years have seen a dramatic increase in the number of contaminated soil and sediment remediation projects being undertaken in a variety of upland and aquatic settings. As a consequence the number of corporations and individuals conducting this work has also risen. It is likely that many practitioners of sediment remediation may be unaware of the experience and lessons that have been learned through the long existing history of projects conducted with dredged sediments. This presentation is one small effort to help bridge this gap and hopefully keep at least a few wheels from being reinvented.

Case Study – Remediation of the New Bedford Harbor Superfund Site

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New Bedford Harbor is a small urbanized estuary located on the waters of Buzzards Bay approximately 50 miles south of Boston. The sediments in many areas of the Harbor are contaminated with polychlorinated biphenyls (PCBs) and metals, primarily from the manufacture of electrical components which occurred at several areas around the Harbor between the 1940s and mid-1970s. Based on human health concerns and ecological risk assessments, the USEPA designated New Bedford Harbor as a Superfund Site in 1982. Through an Interagency Agreement between the USEPA and the USACE New England District, the USACE is responsible for carrying out the design and implementation of the remedial measures.

The 18,000 acre New Bedford Harbor Superfund Site extends from the shallow northern reaches of the Acushnet River estuary, south through the commercial harbor of New Bedford, and out into Buzzards Bay. A wide range of contaminant concentrations exist in both subtidal sediments and intertidal marsh areas, with multiple defined remediation goals based location/exposure potential and a total of more than 800,000 cubic yards of sediment designated for removal. As a result, remediation at this challenging site has proceeded down multiple pathways.

Initial remedial efforts included a pilot test of dredging technologies in 1989, dredging of a limited area with the highest sediment contamination levels in 1994-95, and removal/restoration of shoreline areas with high exposure potential in 2001-03. Construction of a dewatering and water treatment facility was completed in 2003, and full-scale remedial dredging was initiated in 2004. A pilot capping project is currently being performed in 2005. This presentation will provide an overview of the 15+ year history of remediation efforts at the Site that highlights the evolution of strategies for dealing with contaminated sediments.

Excavation of PCB-Contaminated Sediment Adjacent to the Intake of a 12-MGD Drinking Water Plant

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The ROD for the former Westinghouse plant in Sharon, Pennsylvania issued in February 2003 included the removal of approximately 4,000 CY of PCB-contaminated sediment from several locations along the Shenango River to a cleanup goal of 1.0 mg/kg. Delineation sampling indicated a maximum total PCB concentration of about 400 mg/kg, although 97% of the sediment samples were less than 50 mg/kg, and 88% of the samples were less than 10 mg/kg. Remediation planning was complicated by the presence of a 12 MGD drinking water plant with a surface intake less than 200 feet from the remediation areas, along with an active 24-inch cast iron water line crossing the river underneath the riverbed. Given the water depth and composition of the riverbed, as well as potential flow velocities during high flow periods, it was determined that the best means of protecting the water plant intake during the remediation would be to isolate the excavation areas using sheet piling, with placement of silt screens around the intake as well as downstream of the pile installation areas. In addition, a mobile laboratory was brought on site to provide rapid analysis of surface water samples at quantitation limits of 0.05 µg/l, in order to provide reassurance to all interested parties that the water supply would not be impacted by the work.

Remediation commenced in late summer 2004, and to date, more than 1400 surface water samples have been collected downstream of active work areas, including more than 540 samples collected directly from the water plant intake. PCBs have been detected in only one of the water samples collected from the intake (0.07 µg/l), and only 17 other samples collected downstream of work areas were found to contain PCBs (up to 0.54 µg/l). The sediment remediation, delayed by Hurricanes Frances and Ivan, is expected to be completed in September 2005.

Effectiveness of *in situ* Cement Stabilization for Remediation of Sediment Containing Coal Tar Derived Hydrocarbons

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Sediments adjacent to a former coal tar processing facility are associated with intermittent releases of hydrocarbon droplets and sheen to the overlying marine water column, particularly during low tide. *In situ* sediment stabilization with Portland cement was one of the alternatives considered for a response action to control sheen in accordance with Surface Water Quality Standards. The remedial design concept consisted of driving large-diameter caissons through the sediment and into the underlying clay aquitard, mixing Portland cement inside the caissons (approximately 15 percent by weight) using an auger or similar piece of equipment, and removing minor amounts of surficial sediment that had bulked up above the original mudline. The caissons would then be pulled, offset in a systematic overlapping pattern, and the process repeated until the sheen-producing area had been stabilized.

Bench-scale laboratory testing was conducted on composite samples of both untreated and stabilized sediments from the area to better characterize the effectiveness of cement stabilization for controlling sheen. The bench-scale tests included the Sequential Batch Leaching Test (SBLT), a U. S. Army Corps of Engineers protocol (Myers et al., 1992) that simulates the effects of contaminated sediment on pore-water chemistry, and a more qualitative Static Sheen Test, per USEPA (40 CFR Chapter 1, Part 435). Tests were conducted on sediments treated with 10, 15, and 20 percent dry cement, 15 percent cement slurry, and, for comparison, 10 percent organoclay, a hydrocarbon adsorbent. Sediment mixtures were allowed to cure for seven days before testing.

The bench-scale test results indicate *in situ* stabilization as a stand-alone technology would not be effective at controlling sheen; the response action would require additional components, such as the addition of a thick cap or placement of sediments in a confined disposal facility, to achieve this objective. Even the most effective stabilization mixtures leached polycyclic aromatic hydrocarbons (PAHs) and mid-range aromatic and aliphatic hydrocarbons at concentrations well above their effective solubilities, indicating a strong tendency for continued sheen production. Performing the appropriate bench-scale tests cost-effectively demonstrated the need for a different approach to designing and implementing an effective remedial solution for this site.

Monitoring the Uplift of a Low-Permeability Sediment Cap Due to Gas Entrapment Beneath the Cap: Findings of the First 18 Months

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The Hazardous Substances Research Center (HSRC), in conjunction with Battelle, Horne Engineering, and HydroQual, Inc., is conducting a major field study of “active” sediment caps on the Anacostia River near Washington, DC. As a part of this overall study, the potential uplift and deformation of low-permeability sediment cap constructed with AquaBlok™ is being studied using highly sensitive, in-place horizontal inclinometers. The potential for low permeability sediment caps to be uplifted by increases in sediment pore pressures due to the designed restriction of groundwater discharge caused by the cap or by transient tidal fluctuations has been shown to be significant in some riverine and estuarine settings. Uplift could potentially cause cracking and jointing of the low permeability cap substantially increasing its hydraulic conductivity and, consequently, compromising the cap’s ability to restrict contaminant flux.

The research project involves construction of several pilot scale sediment caps. One such pilot scale sediment cap consists of six inches of AquaBlok™ overlain with six inches of sand. A 100-foot long horizontal inclinometer casing was constructed within the 100 by 80 foot pilot-scale cap overlying the AquaBlok™. A string of ten in-place horizontal inclinometers is housed in the casing and has been measuring uplift or deformation of the cap since March 26, 2004. The data have recorded initial settlement of the cap due to sediment consolidation. Following initial settlement, the further offshore portion of the cap began to slowly uplift a total of about one inch over a period of 40 days before suddenly uplifting more than two feet. Uplift events of similar magnitude occurred intermittently throughout the summer and early fall of 2004. Initial indications point to instability caused by a buildup of decomposition gas from the sediments under the cap. Bathymetric surveys have revealed that the cap is thinner in the area of observed instability. The cap has been relatively dormant during the late fall and winter likely corresponding to declining temperatures and concomitant reductions in gas generation. Monitoring will continue throughout 2005 to observe whether a renewed cycle of uplift events occurs when temperatures rise again in the spring and summer.

Optimization of PCB Dechlorination by Palladized Magnesium in Marine Sediments

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Currently, marine sediments contaminated with Polychlorinated Biphenyls (PCBs) are treated ex-situ through dredging followed by landfill. This form of treatment can be very costly, has high impacts on the marine environment, and can further disturb and disperse PCBs from the sediments. Capping and monitored natural recovery are two other viable options, both of which suffer from leaving contamination in place. This research focuses on the optimization of in-situ treatment of marine sediments contaminated with PCBs by dechlorination with palladized magnesium. Three sediments (New Bedford Harbor, MA, Housatonic River, MA, and Hudson River, NY) have been tested for dechlorination with palladized magnesium (4 μm magnesium particles coated with 0.1% by weight palladium). High PCB removals were observed for sandy sediments with low organic carbon content, whereas lower removals were seen for sediments with higher organic carbon content. Desorption experiments using Tenax beads were conducted to see whether PCB desorption from sediment was a rate limiting step for dechlorination. Sediment characteristics such as PCB concentration, organic carbon content, particle size distribution and water content are being used to optimize the percent addition of palladized magnesium to each sediment. A study will also be conducted to see how well the solvent d-Limonene extracts PCBs from the sediment and makes them available to react with the palladized magnesium. The results from these studies will be presented.

Heavy Metals

Trace Metal Distributions in Connecticut Soils

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Dissolution Kinetics of Metallic Tungsten In The Presence of Common Alloying Elements

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Pragmatic Approach to Remediation of Mercury in Wastewater: Source Characterization, Implementation and Results

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Comparative Analysis of Sorptive Capacities of Toledo Soils for Heavy Metal Remediation

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Influence of Aging in Soil on the Dermal Penetration of Hexavalent and Trivalent Chromium

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Predicting Mercury Cycling and Methylation in NY/NJ Harbor

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Trace Metal Distributions in Connecticut Soils

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Improvements to state and federal highways, airports, harbors, and railroads in Connecticut are commonly preceded by environmental investigations to determine whether excavation and dewatering activities will generate regulated wastes. As part of the investigations, soils in the construction corridors are routinely tested for waste characterization parameters including PCBs, VOCs, PAHs, ETPH, RCRA metals by mass analysis, RCRA metals by SPLP and TCLP, ignitability, corrosivity, and reactivity. The organic parameters almost exclusively reflect anthropogenic pollutants. The RCRA metals, and occasionally sulfide, represent natural background levels as well as various sources of pollution.

The focus of this investigation is the distribution of trace metals in native and anthropogenic (disturbed) soils. Native soils are primarily Entisols and Inceptisols that developed on glacial till, glaciofluvial and glaciolacustrine deposits, eolian sediments, alluvium, and organic deposits. Anthropogenic soils, mainly Entisols, formed on a variety of parent materials including hydraulic fill pumped from offshore sandbars, soil manufactured with reclaimed bituminous pavement, estuarine silts, combustion by-products (coal ash, cinders and slag, casting sand), and the aforementioned native soils when used as borrow materials along transportation corridors and in rights-of-way for public utilities.

The total population of samples is separable into groups that (1) approximate natural background levels of metals, and (2) reflect anthropogenic pollutants to a greater or lesser degree. Natural background is represented by samples removed from intensive pollutant inputs, such as along rural highways and with increasing depth below grade. Metal concentrations are elevated as a function of proximity to source, as with shallow soils along major highways, and in response to parent material that may also be an industrial waste. Certain metals, for instance arsenic, may achieve natural background levels exceeding state remediation standards.

Dissolution Kinetics of Metallic Tungsten in the Presence of Common Alloying Elements

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To avoid potential environmental insults that could arise from the use of tungsten made materials in general and new tungsten-based munitions, it is necessary to fully understand how these materials will behave after they have been released to the environment. Previous research reports that tungsten dissolves in large quantities reaching up to 500 mg/L in aqueous solutions. The amount of tungsten dissolved appears to be dependent on the alloying elements. This research aims at further understanding the processes involved in the leaching of metallic tungsten once released into the environment by studying the dissolution kinetics of tungsten powder alone and in the presence of other metallic powders (90:10 binary mixtures with Co, Cu, Ni, and Fe). The initial conditions for the dissolution reactors were; pH between 6.9 and 7.2, ORP between 260 and 290 mv, dissolved oxygen between 6.6 and 7.8 mg/L. The variations of pH, ORP, dissolved oxygen and dissolved metal concentration were followed over a 46 days period. A reduction in pH was measured in all the reactors but very substantial (>4 pH units) for the W:Cu mixture. The magnitude of pH reduction was in the order: W:Cu > W (Sigma Aldrich) > W (munitions grade) > W:Fe > W:Ni > W:Co. Reductions in dissolved oxygen occurred in all the reactors with very large reductions recorded for the W:Cu and W:Fe mixtures (82 and 95%, respectively). The ORP behavior was more erratic, a large reduction in ORP was measured for the W:Fe mixture while for munitions grade W, W:Ni and W:Co mixtures the value was fairly constant. Increased ORP values were observed in the reactors containing W from Sigma Aldrich and W:Cu mixture. Modeling of the dissolution kinetics and speciation changes over the period of study was performed using the Visual Minteq (version 2.31) software. The information gathered sheds some light on the dissolution behavior of tungsten alloys in the environment.

Pragmatic Approach to Remediation of Mercury in Wastewater: Source Characterization, Implementation and Results

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Beginning in 2003, a large pharmaceutical research and development company was experiencing dissolved mercury in their wastewater, often exceeding concentrations allowed by their Industrial Discharge Permit with the local POTW. Previous sewer cleaning efforts resulted in limited improvement. However, in the intervening time, more stringent analytical methods were adopted and lower discharge limits increased the potential for repeat non-compliance in their discharge. The company retained Solutions-IES to implement intensive source characterization activities to identify the problem and develop a remediation plan.

Monitoring data from sewage discharge outfalls identified general campus areas that were contributing to the elevated mercury. The source characterization activities indicated that fumehood, laboratory, and utility closet sink traps contained significant mercury concentrations, as did selected laboratory and sanitary waste manholes and the campus Energy Center. The first remediation phase focused on removing trapped mercury from the interior facility infrastructure upstream of the impacted outfalls. Review of engineering drawings indicated three sink trap types and a complex laboratory and sanitary waste handling infrastructure. Different cleaning procedures were tested on each type of sink before full-scale implementation. Solutions-IES then oversaw cleaning and testing of 292 laboratory and fumehood sink traps, 28 utility closet sink traps, selected exterior laboratory and sanitary waste manholes, and floor drains. Dissolved mercury concentrations were reduced by 12% to 98% when comparing post-cleanup to baseline samples.

The second remediation phase involved cleaning accumulated biomass and scale from over 3,000 feet of exterior laboratory and sanitary waste collection systems upstream of the impacted outfalls, using pipe location and cleaning techniques similar to those used to locate, clean and evaluate municipal collection systems. Over 13,000 gallons of water and solids were removed from the system, containing approximately 3.5 grams of mercury. Although a seemingly small amount, its removal resulted in system-wide reduction by up to 99% with measured concentrations now generally below the permit discharge limits.

Comparative Analysis of Sorptive Capacities of Toledo Soils for Heavy Metal Remediation

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In-situ treatment for remediation of pollutants is a technologically expanding field because of the wide range of pollutants that now exist in the ecosystem and lack of a solution capable of removing every type of pollutant. Heavy metals are persistent in the ecosystem due to anthropogenic impacts. The use of soils for remediation of heavy metal contamination is becoming more popular because of ease of implementation and cost effectiveness. The ideal soils to use would be local soils within proximity to the project to minimize transport costs. The soils chosen for this study have a range and variability of heavy metal sorption capacities. The soils were taken from known polluted sites and from sites where the soils are being proposed for heavy metal containment. The results of the study may influence which soil is to be used for the remediation of heavy metal contamination.

Influence of Aging in Soil on the Dermal Penetration of Hexavalent and Trivalent Chromium

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Soil and groundwater are contaminated with chromium in thousands of sites in the United States and in the developed world. Although direct dermal contact with high concentrations of chromium, especially Cr (VI) compounds, can produce skin burns, blisters, and skin ulcers, sensitive individuals may develop rashes and erythema from contact with chromium in soil. Health risk assessments often do not consider the amount of soil-sorbed metal that is absorbed by the body but rely on the total concentration of metal in soil that can be extracted by rigorous procedures. This practice can overestimate health risks and soil remediation goals because metals can be sequestered in soil with time (“aging”) thereby decreasing bioavailability. The influence of aging on the dermal penetration of Cr (III) as chromic chloride or Cr (VI) as sodium chromate was evaluated in two soils – Atsion (a sand) and Keyport (a sandy clay loam). Dermal penetration was measured *in vitro* through dermatomed pig skin by Teflon flow-through diffusion cell methodology. After four months in soil, the dermal penetration of both species was decreased by 91 - 97% relative to pure chromium (without soil). Furthermore, the dermal penetrations of Cr (III) and Cr (IV) were reduced more by aging in the Atsion soil (83% and 68%, respectively) than in the Keyport soil (40% and 57%, respectively) relative to chromium in freshly treated soils. The data suggest that an increase in environmentally acceptable endpoints for chromium will be dependent on soil type and time in soil. (Supported through funding from the Hazardous Substance Management Research Center and the New Jersey Commission on Science and Technology).

Predicting Mercury Cycling and Methylation in NY/NJ Harbor

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The NY and NJ harbor has been impacted by historical discharges of mercury, and continues to receive mercury inputs from a combination of sources including combined sewer overflows, treatment plant discharges, stormwater runoff, river discharges, and atmospheric inputs. We have developed a mercury cycling model as part of a larger effort to simulate the fate and transport of contaminants including mercury in the New York and New Jersey harbor and nearby water bodies in part to evaluate how natural attenuation and remedial management of the area may affect fish tissue mercury concentrations in the future. Understanding and predicting mercury impacts on aquatic organisms is particularly challenging, due to the complex transformations that mercury can undergo in water and sediments including the formation of methylmercury. Methylmercury is much more toxic and much more likely to bioaccumulate than other forms of mercury, and its formation is dependent on a number of environmental factors including the availability of mercury, and suitable conditions in aquatic sediments where methylation largely occurs. Our modeling approach is based on the considerable information in the scientific literature linking mercury methylation to the activity of sulfate reducing bacteria. Our model also includes the simulation of processes related to carbon diagenesis, including sulfate reduction, in order to predict sediment interactions and oxygen demand on the quality of the water column. These simulated sulfate reduction rates were also used as one of the key factors responsible for determining methylation rates. The advantage of this approach is that methylation rates are predicted in a mechanistic framework, and are not used as a calibration parameter to fit observed methylmercury concentrations. This approach allows direct linkages between mercury methylation and other water quality factors, and can provide explanations for season patterns in methylation rates, and for differences in rates observed in different water bodies.

Indoor Air

A Vadose Zone Soil Gas Sampler- Its Design, Implementation and Performance

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A Practical Approach to Distinguishing Vapor Intrusion Indoor Air Impacts from Background

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Indoor Air As A Source of VOC Contamination in Shallow Soils Below Buildings

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Overview of Two Large-Scale Residential Sub-Slab Depressurization System Installation Programs

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A Vadose Zone Soil Gas Sampler – Its Design, Implementation and Performance

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Human health risks resulting from the inhalation of vapors from volatile organic chemicals (VOCs) in contaminated soils and groundwater are sometimes the most critical risks that must be addressed during the environmental risk management and remediation of contaminated sites. Potential indoor air quality impacts can be assessed by collecting air samples indoors and submitting them for laboratory chemical analyses. However, indoor air quality is often affected by VOC vapors released indoors by cigarette smoke, building materials and household solvents and thus may not be a reliable indicator of the impact caused by subsurface contamination. Many U.S. and Canadian environmental regulatory agencies have accepted an indirect method of assessment. The method is comprised of soil gas sampling near the basement or ground floor slab of a building and transport modeling to estimate soil gas flow rates and VOC flux into a building. The VOC flux concentration is then used to evaluate the potential human exposure to soil or groundwater derived VOCs and estimate the associated human health risks. The soil gas transport model most commonly used is the Johnson and Ettinger model which is an axisymmetric analytical model. Since 2001 O'Connor Associates has been using a soil gas sampler (SGS) and sampling procedures specifically designed for collecting representative soil gas samples in the vadose zone adjacent to a building basement or a ground floor slab. Using the SGS and a vacuum canister, a constant volume of representative soil gas can be collected at a fixed location for every sampling event. In order to more accurately simulate soil gas transport, a 3-D finite element soil gas transport code has been adapted to study the influence of such factors as soil type, degree of saturation, sampler volume, sampling rate, proximity to the building structure and atmospheric pressure variations. These results are then used to evaluate the design requirements and performance of the SGS. This paper presents comparative analytical results for samples collected from indoor air, sub-slab backfill and SGSs along with predicted sub-slab and indoor VOC concentrations.

A Practical Approach to Distinguishing Vapor Intrusion Indoor Air Impacts from Background

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Evaluating the origins of indoor air impacts at a contaminated site requires a well thought out qualitative and quantitative evaluation. When the potential for vapor intrusion (i.e., migration of volatile organic compounds from contaminated soil, groundwater or soil gas into indoor air) has been identified the following three consecutive steps are typically taken: (1) field screening of soil vapor from probes, (2) laboratory analysis of soil vapor from probes, and (3) laboratory analysis of indoor air samples. Based on site-specific information steps may be combined, skipped or added. The purpose of this session is to introduce vapor intrusion assessment methods and to present assessment methods that may be used to distinguish between contaminants in indoor air that are attributable to vapor intrusion and those that are attributable to background sources.

The presence of numerous background sources of volatile organic compounds (VOCs) in residential, commercial and industrial buildings and human health risks posed by low VOC concentrations makes assessing and remediating the source of contaminants in indoor air a complex problem. Through a combination of assessment and data evaluation techniques one can help determine if the contaminants detected in indoor air are attributable to the release being assessed.

The presentation shall include:

- Introduction
- Assessing Vapor Intrusion – Why, When and How?
- Sampling Indoor Air – Why, When and How?
- Where are the contaminants coming from?
 - Common background sources of VOCs
 - Site Specific, Federal and State Background
 - Using tracer gases
 - Seasonal Fluctuations
 - Comparing indoor air data to soil vapor data
 - Establishing ratios: indoor air data to soil vapor data
 - Interpreting ratios
 - Case Study
 - Distinguishing vapor intrusion indoor air impacts from background

Indoor Air As A Source of VOC Contamination in Shallow Soils Below Buildings

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Both USEPA and many state guidance documents recommend sub-slab sampling as a key component of site investigations to determine if vapor migration from underlying soil is a completed exposure pathway (USEPA, 2002; WIDHFS, 2003; San Diego County, 2004; PADEP, 2004). If VOCs are detected in the sub-slab, then migration from the subsurface is assumed to be occurring and further evaluation is required to determine the extent of the impact. This guidance is predicated on the assumption that VOCs detected in sub-slab samples have originated from deeper within the subsurface. However, detection of VOCs in sub-slab samples is not sufficient to conclude that VOCs are migrating from the subsurface towards a building. VOCs detected in sub-slab samples can originate from indoor sources, migrating through the slab by diffusion or advection. Commonly used conceptual models of vapor intrusion include VOC migration from the subsurface into buildings but do not consider the potential for VOC migration from buildings into the subsurface (USEPA, 2002, Johnson and Ettinger, 1991, Parker 2003).

However, the advective and diffusive forces that result in the migration of VOCs from the subsurface into buildings are equally likely to result in the migration of VOCs from buildings into the subsurface under conditions under suitable pressure or concentration gradients. In this paper we present: i) simple analytical modeling indicating that indoor sources of VOCs may cause sub-slab impacts through advection across the building foundation, ii) field analyses from a site where indoor sources rather than subsurface contamination was the source of VOCs detected in sub-slab samples, and iii) recommendations for field investigation methods to allow the discrimination of subsurface versus indoor sources of sub-slab VOCs.

Overview of Two Large-Scale Residential Sub-Slab Depressurization System Installation Programs

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Sub-slab depressurization (SSD) systems, commonly used to mitigate radon, create a vacuum beneath a building to prevent soil gas from entering the building as a result of pressure gradients that naturally exist between the building and the sub-slab region; the extracted soil gas is then vented directly to the atmosphere. This paper describes two large-scale residential SSD system installation case studies. The SSD systems were designed and installed to mitigate intrusion of soil gas, which contained low levels of volatile organic compounds, into (1) 100+ individual houses and (2) several buildings in a multi-structure condominium complex.

The SSD installation methodology consisted of the following components: stakeholder involvement, site assessment, feasibility study, pilot testing/design, installation, performance testing, and operations & maintenance. Public meetings were held and homeowner feedback was elicited to achieve an end product that not only mitigated vapor intrusion, but also was acceptable to the homeowner. The system design process incorporated the results of site-specific assessments and field pilot testing. These systems were installed in a design-build fashion using a variety of construction techniques. Following installation, the SSD systems were performance tested to ensure that the resulting suction field encompassed the entire sub-slab area.

Numerous examples of the SSD system installations are presented. SSD system designs/components and construction techniques, issues, and challenges specific to the two case studies are discussed. System performance data and lessons learned from the SSD installations also are presented. In addition, a comparison of the operation of the engineered SSD systems to several radon mitigation systems previously installed using typical radon industry techniques is conducted to reveal some interesting results.

Legal / Regulatory

In Situ Source Control Remediation of High Explosives

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Dan Kwiecinski, MKM Engineers, Inc., Albuquerque, NM

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How Will Your Institutional Controls Be Working In 2035?

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

In Situ Source Control Remediation of High Explosives

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This paper describes ongoing results of in situ source control interim corrective measure (ICM) pilot testing at the U.S. Department of Energy (DOE) Pantex Plant, located in Amarillo, Texas. ICM pilot tests are ongoing at Pantex for two HE source control technologies, one targeted for vadose zone remediation and the other a groundwater reactive barrier. In situ ozone treatment of the vadose zone is being implemented as an ICM pilot test at Pantex in order to reduce the mass of HE constituents migrating vertically downward to the groundwater. Remediating the vadose zone soils and HE dissolved in vadose zone pore water is an important element of the overall source control program at the site. The in situ ozone system involves injection of ozone gas into the vadose zone soils. Ozone gas (O₃) is a strong oxidizer that is capable of completely degrading RDX and other HE constituents. Additionally, ozone degrades to oxygen gas which promotes biodegradation as a secondary treatment mechanism. Ozone injection was pulsed in order to maximize the benefit of biodegradation during the intervals between injection pulses. Current results are presented describing the ozone subsurface delivery radius of influence and the level of HE treatment obtained. A reactive barrier ICM pilot test using is also being implemented at Pantex as part of the source control measures. The reactive barrier is a chemical reduction barrier involving the injection into two wells of sodium dithionite that acts to reduce naturally occurring iron in the subsurface to Fe²⁺. The Fe²⁺ is immobilized within the aquifer matrix, and serves as a semi-permanent reductant that treats HE migrating in groundwater through the reactive zone. This project is the first field-scale application of ISRM technology for high explosives treatment. The field-scale design for ISRM implementation was based on site hydraulics, on reduction reaction stoichiometry, and on reactive transport characteristics of the sodium dithionite. Current results are presented describing the dithionite delivery radius of influence and the barrier performance.

How Will Your Institutional Controls Be Working In 2035?

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Risk-based cleanups are on the rise. Brownfield's are a hot topic. When leaving waste in-place how do you make sure land use controls will work and remain viable ten, twenty or thirty years from now? How can you ensure that today's Superfund site can be transformed into a real estate asset?

Many consulting firms and insurance companies offer liability transfer services and long-term O&M, but you or your client likely will still have to certify annually that controls are in place and working. This presentation will discuss the legal and environmental landscape existing today with respect to Risk-Based Corrective Action (RBCA) and land use controls. Will restrictions run with the land over time? Who will enforce them and how? How can municipalities shoulder the burden and should they? What about environmental insurance? What other services may be available to control potential migration address the public perception of risk?

Insurance policies relating to institutional or land use controls are just becoming available on the market. Will the coverage work as advertised? How can environmental professionals prepare a site so that conditions and investigations support a RBCA determination, effective liability transfer or an insurance underwriter's analysis? This presentation, by an experienced environmental attorney, will help answer these questions using real world examples. Audience participation is encouraged.

MTBE

Occurrence of Methyl-tert-Butyl Ether in Source Waters to Public and Private Wells in New Hampshire

Denise M. Argue, US Geological Survey, Pembroke, NH

Joseph D. Ayotte, US Geological Survey, Pembroke, NH

Frederick J. McGarry, New Hampshire Department of Environmental Services, Concord, NH

Accelerated Natural Attenuation of MTBE with Oxygen Release Compound (ORC®)

Stephen S. Koenigsberg, Regenesis, San Clemente, CA

Anna Willett, Regenesis, San Clemente, CA

An Estimate of the National Cost for Remediation of MTBE Releases from Existing Lust Sites

Frank Sweet, ENSR International, Westford, MA

Mark D. Kauffman, ENSR International, Westford, MA

Tabatha Pellerin, ENSR International, Westford, MA

Dave Espy, ENSR International, Westford, MA

Mike Mills, ENSR International, Westford, MA

MTBE: Coverage for this “Spreading” Problem

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

John N. Ellison, Anderson Kill & Olick, P.C., Philadelphia, PA

Accelerated Natural Attenuation of MTBE with Oxygen Release Compound (ORC®)

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Oxygen Release Compound (ORC®) is patented formulation of phosphate-intercalated magnesium peroxide that slowly releases oxygen and facilitates the aerobic degradation of a range of environmental contaminants including petroleum hydrocarbons and fuel oxygenates. Since 1994, ORC has been used on over 8,000 sites worldwide and has been the subject of an extensive body of independent, peer reviewed literature. ORC technology has now been clearly established as a sensible strategy for enhancing natural attenuation on sites where capital and management intensive options are either undesirable or contraindicated.

With respect to MTBE, as early as 1996, consultants using ORC noticed that MTBE concentrations decreased at a higher than expected rate. Working on this foundation, a number of subsequent laboratory and field experiments have demonstrated that oxygen can indeed enhance the remediation of MTBE; a concept that has since been verified in other quarters. At present we have information on over 500 sites where MTBE is the primary or co-contaminant. Fourteen of these applications are the subject of peer-reviewed publications. To date, we have inquired on and attempted to examine 86 of the 500 sites. 65% of the sites (56) were too early to evaluate or had insufficient data, leaving a population of 30 sites that could be fully vetted.

The preliminary results show that 9 sites (25.7%) demonstrated excellent results, 18 sites (51.4%) demonstrated moderate degradation and 7 sites (22.8%) demonstrated poor degradation. The poor results are of interest in that it is a significantly greater number than the 3% negative performance seen with BTEX remediation on a larger sample size (n= 600). This may be a function of the relative recalcitrance of MTBE degradation, but it may also have a component that relates to the microbial status of the aquifer. A detailed examination of representative cases will be presented. One such example is as follows.

At a U.S. Coast Guard support facility in Elizabeth City, NC, MTBE was detected in groundwater. The release of petroleum constituents was related to the 10,000-gallon fiberglass underground storage tank (UST) and a series of underground transfer lines used to deliver JP-4 and JP-5 jet fuel to the aircrafts at the facility. ORC was applied via direct push technology into both the source area and dissolved plume area. Each ORC application was designed to satisfy oxygen requirements for MTBE and BTEX biodegradation and other naturally occurring oxygen sinks in the aquifer. Post treatment monitoring of the aquifer quality parameters indicated effective enhancement of biological activity and substantial decrease in dissolved MTBE and BTEX concentrations. Maximum MTBE concentrations of 510 ppb in the source area and 390 ppb in the plume area were recorded prior to treatment. The MTBE concentrations in both source and plume areas decreased to below quantifiable limits approximately 3 months after treatment. After seven months, the dissolved MTBE mass was reduced 100%, and subsequent monitoring events have shown no rebound in MTBE concentrations.

An Estimate of the National Cost for Remediation of MTBE Releases from Existing LUST Sites

Frank Sweet, Mark D. Kauffman, Tabatha Pellerin, Dave Espy, Mike Mills, ENSR International, Westford, MA

Methyl tertiary butyl ether (MTBE) is an oxygenated gasoline additive that has been used in the U.S. since the late 1970s. Gasoline from leaking underground storage tanks (LUSTs) can contaminate soil and groundwater with a range of petroleum hydrocarbons and gasoline additives such as MTBE. This study compiles available published literature to quantify the cost of MTBE remediation. Most available sources provide an estimate of either the number of LUST sites across the US or an estimated cost to remediate LUST sites, but few sources contain both of these essential parameters. This paper compiles key parameters from an array of published sources to quantify an overall national cost of MTBE remediation, separate from remediation costs that do not include MTBE. In addition, our internal experience with actual data, including investigation and remediation projects for retail petroleum clients across the US, was used to supplement and validate information obtained from published data sources. Available state-specific data relative to the numbers of sites, cleanup levels, and costs were compiled and statistically interpreted. The development of this study included a limited external peer review, by a team who then participated in public panel discussions. Through this process the research and results were subsequently expanded to include a sensitivity analysis and estimate of the total cost to remediate the nation's existing LUST sites as well as a clearer description of the study limitations.

MTBE: Coverage for this “Spreading” Problem

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Environmental professionals need to understand the legal issues involving MTBE-related claims and insurance coverage. Legal actions involving MTBE contamination are on the rise.

Throughout the United States, litigation has included MTBE claims based on negligence, conspiracy, property damage and product liability. In April 2002, for example, after an 11-month trial brought by a California public utility against MTBE producers, oil refineries and gasoline retailers, a jury found that gasoline containing MTBE was a defective product and decided in favor of large awards to plaintiffs. As a possible harbinger of what is to come, a number of law firms now include information relating to MTBE on their websites.

As MTBE-based claims increase, disputes concerning insurance coverage for those claims will also most assuredly increase. This presentation will provide a framework for helping to determine how insurance policies cover MTBE-related claims. For example, if government requirements to use MTBE result in legal actions relating to substances or commercial products exempted from Superfund liability, can insurance companies successfully deny coverage based on a pollution exclusion?

Standard liability insurance forms generally provide coverage for damage to the environment arising from MTBE. First, the large majority of jurisdictions that have addressed the issue of the “legal obligation to pay” hold that amounts paid to address government mandates in administrative enforcement actions are amounts which the policyholder “is legally obligated to pay as damages.” Therefore, costs to investigate and remediate MTBE contamination in response to a government directive should be construed “as damages” which a policyholder is legally obligated to pay. Second, environmental contamination arising from gasoline containing MTBE is “property damage” and courts uniformly hold so. Such damage generally is to the property of a third-party because most states designate groundwater as a resource held in trust for all people so actual or potential threats to groundwater from MTBE are considered damage to the property of another. Third, “property damage” takes place or “triggers” coverage as long as the gasoline spill or leak was released into the environment at least, in part, during the policy period(s) at issue.

To deny insurance coverage for MTBE-related environmental damages, the insurance companies have (with varying degrees of success) relied upon: (1) the “expected or intended”/no “occurrence” defense; and (2) various forms of “pollution” exclusions. Policyholders should be sure this fine print actually applies before taking “no coverage” for an answer. While coverage for MTBE-related liabilities will not come easily, policyholders and environmental professionals need to know what evidence is necessary to support a claim for MTBE coverage.

Ozone

Rapid Removal of Chloroethenes at Industrial Sites

Barrett E. Culp, RMT, Inc., Greenville, SC

Greg Mitchell, RMT, Inc., Greenville, SC

Steven Schroeder, RMT, Inc., Greenville, SC

William Kerfoot, Kerfoot Technologies, Inc., Mashpee, MA

Mark Miesfeldt, RMT, Inc., Greenville, SC

In-Situ Chemical Oxidation of Pentachlorophenol Using Microbubble Perozone™ Technology

Christopher Watt, LACO Associates, Eureka, CA

In-Situ 1,4 Dioxane Remediation in HVOC Sites

William B. Kerfoot, Kerfoot Technologies, Inc., Mashpee, MA

Andrew Brokowski, Kerfoot Technologies, Inc., Mashpee, MA

In-Situ Remediation of MTBE and Petroleum Product Spills Utilizing Ozone Injection

Scott Miller, Resource Control Corporation, Moorestown, NJ

Paul Rosenwinkel, Resource Control Corporation, Moorestown, NJ

Jeffrey Dey, Resource Control Corporation, Moorestown, NJ

Application of Vapor Phase Ozone to Remediate BTEX, MTBE, and EDB Groundwater Plumes

Scott M. Lato, Advanced Environmental Technologies, LLC, Tallahassee, FL

Chemical Basis for pH, Eh (Pourbaix) Changes Observed During Low-Mass Air/ Oxygen/ Ozone Injection for Petroleum Treatment

William B. Kerfoot, Kerfoot Technologies, Inc., Mashpee, MA

Rapid Removal of Chloroethenes at Industrial Sites

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Air sparging with trenches had failed to remove groundwater and soil contamination at a superfund site in Piedmont soils in South Carolina. The major contaminants to be removed were 1,2 Dichloroethene (DCE) and Trichloroethene (TCE). A costing of alternatives showed that life cycle costs of using microbubble ozone would be the lowest cost choice when compared with groundwater pump and treat, air sparging, and liquid oxidation (permanganate). In spring 2001, field pilot studies were performed to verify expected removal rate and injection well radius of influence. Initial testing for 12 weeks on two ozone sparging wells showed over 50% removal. During 2001-2002, full-scale design and construction was completed with nine ozone microbubble sparging wells with recirculation capability. In October 2002 the system was started. After 12 months of treatment, all monitoring wells but one were at recommended MCLs (minimum concentration limits). After 18 months of treatment, all wells met closure requirements. Continued monitoring showed no rebound.

A Western Massachusetts site is ongoing with chloroethene treatment by ozone and Perozone™. Different approaches to contaminant removal were required at two soil regions on the site.

In-Situ Chemical Oxidation of Pentachlorophenol Using Microbubble Perozone™ Technology

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A proprietary ozone and hydrogen peroxide sparging system was operated for 10 months at a former lumber mill located on the margin of an estuarine environment. Target compounds, intrinsic groundwater parameters, and chloride ion were monitored in the area groundwater. In addition, pre and post-treatment intrinsic soil conditions were documented.

The strongly poised (up to 1% organic carbon and 2.5% ferric iron by weight) water-logged sediments resisted change in electron pressure (oxidation-reduction potential) during oxidant sparging. This elevated reduction capacity appeared to limit effective distribution of the oxidants. Increased injection times and installation of additional sparge points allowed for sufficient oxidant distribution.

After nearly one year of treatment, dissolved chlorophenol concentrations were reduced 95% and soil sampling has confirmed the gradual destruction of sorbed-phase chlorophenols.

In-Situ 1,4 Dioxane Remediation in HVOC Sites

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Increasingly, 1,4 Diethylene Dioxide (1,4 Dioxane) is being found as a co-contaminant at chloroethene spill sites. The highly soluble compound has been employed as a solvent for lacquers, paints, and varnishes and as a corrosion inhibitor. The compound has shown limited removal (<5% to 30% TOC) during biodegradability tests. Bench-scale testing has shown good removal (69-78%) with exposure to microbubble ozone or peroxide-coated ozone injected into aqueous soil slurries while in the presence of elevated chloroethene concentrations.

The bench-scale tests were conducted in a pressurized glass reaction cell enclosed in a vented chamber. Gas and liquid were introduced with a miniaturized Laminar Spargepoint®. A slurry solution was maintained in suspension with stirring by a Teflon-coated bar. Aqueous subsamples were removed at the beginning of the test and at 120, 240, and 480 minutes following the start of the test.

The bench-scale tests revealed a removal rate of about 0.15% per minute, thus effective for in-situ treatment. Field tests of 1,4 Dioxane removal with Perozone™ have exhibited similar effective treatment. Examples of observed attenuation rates will be discussed.

In-Situ Remediation of MTBE and Petroleum Product Spills Utilizing Ozone Injection

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Numerous gasoline and oil spill sites located in New Jersey and Pennsylvania have been remediated using ozone injection either as a primary technology or by bundling ozone injection with more conventional remedial technologies including total phase extraction (TPE) or air sparging and soil venting AS/SVE). The bulk of the petroleum mass in the source area were remediated within the first two quarters using TPE or SVE. Soil and groundwater were then addressed via air, oxygen and ozone injection as a gas or suspended in re-circulated groundwater. Remediation has commonly been achieved in 6 to 18 months of active treatment.

MTBE (Methyl-tert butyl-Ether) have been detected at these sites at dissolved concentrations up to 100,000 ug/L along with BTEX dissolved compound concentrations, up to 43,000 ug/L, (Benzene, Toluene, Ethylbenzene, Xylenes). TBA has also been detected at dissolved concentrations as high as 180,000 ug/L. When using the combined technology approach (ozone combined with TPE or AS/SVE) hydrocarbon reductions have been more efficient than predicted by stoichiometry (direct reaction of O₂/O₃). Efficient site remediation results have been achieved at ozone to contaminant ratios observed from 1.1:1 to 1.8:1 (ratio of oxidant-to-contaminant) whereas stoichiometry predicts ratios closer to 3:1. The lithology of sites was different, including clean sand, saprolites and weathered schist. Site closure standards for MTBE, BTEX, and TPH are commonly met on sites within one year's time.

Application of Vapor Phase Ozone to Remediate BTEX, MTBE, and EDB Groundwater Plumes

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Advanced Environmental Technologies, LLC performed a multi-depth Ozone injection pilot test on the groundwater at a petroleum impacted site in Quincy, FL, under the Florida Department of Environmental Protection's (FDEP) Petroleum Pre-Approval Program.

The subject facility is located in Quincy, Florida approximately 25 miles west of Tallahassee, FL, has been a gasoline station since at least 1977. This facility dispensed unleaded and leaded gasoline as well as diesel fuel from three 4,000 gallon, and one 6,000 gallon underground storage tanks (USTs). This facility has been in the FDEP's cleanup program for at least 15 years, with the first Contamination Assessment done in 1990, followed by a Remedial Action Plan in 1992, implementation of the groundwater pump & treat system in 1994, additional assessment in 1996-1997, a Remedial Action Plan Modification, for additional groundwater extraction and multiphase wells, in 1998, followed by a vapor extraction pilot test, with the full-scale re-implementation in 2001. The current remedial system was in operation for approximately two years until AET took over as the cleanup consultant in 2002. Prior to 2002, over \$866,000 had already been spent to rehabilitate this site.

Based upon the system performance, existing contamination plume, vapor extraction off-gas concentrations and overall poor physical condition of the remedial system, AET in conjunction with the FDEP decided to perform additional site assessment activities. The most recent vadose zone site assessment data was at least 5-6 years old at the time. This new data indicated that the petroleum impacted groundwater plume was still significantly large with concentrations as high as 55,900 ppb BTEX with a residual petroleum source in the vadose zone with concentrations as high as 629 and 161 mg/kg 26 to 28 and 42 to 44 ft below land surface, respectively.

Using the "post 10 year remediation" data, AET developed a plan to perform an ozone injection pilot test to address the petroleum impacted groundwater at this site. The dual-zone injection well was placed in a location as close to the source area as possible, due to an existing canopy. In addition, the injection well was situated so that existing monitoring and recovery wells could be utilized as observation points at varying distances.

The pilot test setup, equipment, pre, interim and post groundwater sampling event data and analysis will be presented, including illustrations of radius of influence of both DO and ORP, groundwater concentration trends, rate of decay model development and rate of desorption as well as plans for full scale implementation.

Chemical Basis for pH, Eh (Pourbaix) Changes Observed During Low-Mass Air/Oxygen/Ozone Injection for Petroleum Treatment

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Low-mass aqueous reactions during oxidation of petroleum hydrocarbons yield CO₂ and slightly rising pH, now lowering pH. Even microbubble ozone treatment of several chlorinated compounds (PCE, TCE, DCE) with aqueous concentrations up to 2,000 ppb often show increasing alkalinity and pH. Because the addition of ozone produces numerous reactions at the same time, generating both H⁺ and OH⁻, the pH does not change significantly. Measurement of bicarbonate alkalinity while oxidizing on chloroethene or PCP sites can predispose the impending pH change. The addition of CO₂ from both air and end product oxidation reactions yields an equilibrium mixture of bicarbonates and carbonates which moves the groundwater system toward pH 8.

Oxidation states rise from reducing conditions to about 200 mv during remedial operations, substantially less than the 400 mv level likely to promote trivalent (3⁺) chromium conversion to hexavalent (6⁺) chromium. The increase in oxidation potential causes the precipitation of some soluble iron and manganese, coprecipitating other transition metals. The total mass of ferrous iron (Fe²⁺) precipitated, even from 20 ppm initial levels, represents only 1/80,000 of existing soil mass and is not a threat to “plug” the aquifer.

Pay-for-Performance Remediation Technologies - Methods & Case Studies of Science & Economics

Use of Advanced Instrumentation for Field Delivery of Pay-for-Performance In Situ Remediation Projects

Mark Vigneri, Environmental Remediation and Financial Services, LLC, Sea Girt, NJ

BioAug Method of Applying Dehalococcoides Microbes under Pay-for-Performance Contracting

Dave Philbrook, BioAug, LLC, Raleigh, NC

Managing Large Portfolios of Concurrent Pay-for-Performance Projects

Charlie Hursh, SICO Petroleum, Mt. Joy, PA

John Tregidgo, ERFs, Riverdale, NJ

Converting Time and Material Projects to Pay-for-Performance

Jesse Brown, Golder Associates, Inc., Jacksonville, FL

Pay-for-Performance Contracting under the Massachusetts LSP Program

Carl Shapiro, Wheatstone Engineering and Consulting, Inc., Braintree, MA

New Case Studies in Performance Based Technology Substitutions

Ron Adams, ERFs, Ponte Vedra, FL

Use of Advanced Instrumentation for Field Delivery of Pay-for-Performance In Situ Remediation Projects

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Instrumentation for determining the quality of groundwater and the condition of soil has been evolving to support site delineation proposes for decades. The innovations in these areas are directed towards making delineation more accurate. In relation to actual remediation operations, the general theory has been that more accurate delineations produce more efficient remediations. Unfortunately this is not true statement. Correlations between site data and remedial operations are qualitative, not quantitative. Even pilot test data is not transferable to the performance of full scale remediation, unless variables are so limited to allow such.

To address such deficiencies inherent in site data, real-time methods of instrumentation and control are needed to complete soil and groundwater remediations in an efficient manner. To design a remediation method to address unknown variables, a volumetric approach is needed. Using principles from the On-Contact Remediation Process[®] Model (founded in 1998) as a way to manage many simultaneous remediation processes with sets of rules to interconnect physical, chemical and / or biological technologies, instrumentation is a key to real-time control of application of a remedial designs.

This presentation will concentrate on instrumentation used to interconnect many physical technologies including PropagationsSM, ConductivPlanzSM, and Programmable Release Processors (PRPs)SM, LateralsSM and SIPsSM with many types of chemicals and biological remediation materials being injected into the subsurface.

Case studies to be presented include the use of gas analysis matrices, fiber optic detection, and matching insitu chemical modeling with markers. Additionally, a discussion of the first commercial uses of, SignatureSM, a surface grid detection system for simultaneous mapping of subsurface physical devices and the flow of reagents in the subsurface is included.

Concepts from this presentation are a continuation of 2003's Application Theory & Practice of Pay-for-Performance Remediation and 2004's presentation on the three generations of insitu chemical remediation.

Converting Time and Material Projects to Pay-for-Performance

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In May 2000, Golder Associates Inc. installed a multi-phase extraction (MPX) system at a retail petroleum site in Altamonte Springs, Florida to address petroleum impacted soil and groundwater. The MPX system began operating in January, 2001 and operated for 3.5 years at approximately 82 percent operation efficiency. During the first two months of operation, the system removed 115 pounds of petroleum contaminants per day from the vapor phase. The contaminant removal rate declined to approximately 8 pounds per day within 6 months and leveled off at that rate for the next 12 months. During this time period, dramatic reductions in groundwater concentrations occurred across a large portion of the site. The MPX system contaminant removal rates ranged from 1 to 4 pounds per day during the last 18 months of operation with minimal reduction in contaminant concentrations across the site. Prior to the MPX operation, the baseline average BTEX concentration of the four most impacted monitoring wells was 22,275 micrograms per liter ($\mu\text{g/l}$). After 3.5 years of MPX remediation, the groundwater plume was reduced in size from approximately 18,000 square feet to approximately 9,500 square feet and the average BTEX concentration of the same four wells dropped from 22,275 $\mu\text{g/l}$ to 2,490 $\mu\text{g/l}$.

After 3.5 years of MPX operation, reductions in BTEX concentrations were noted in most site wells, with the exception of two monitoring wells located between the existing Underground Storage Tanks (USTs) and dispensers. Golder Associates Inc. completed additional assessment between the USTs and the dispensers in September 2003. A 2 to 4-foot thick layer of clay was identified at a depth of 10 feet below ground surface (bgs) under the dispensers, building canopy, and USTs. Three additional wells were installed under the canopy and a Remedial Action Modification Plan (RAMP) was prepared to address the area of the site not effectively influenced by the MPX system. The RAMP proposed a source removal along with the UST upgrades and in-situ chemical oxidation injections underneath the canopy. Upon approval of the RAMP in June 2004, Golder Associates Inc. began the source removal in October 2004 and the chemical oxidation effort in November 2004. Environmental Remediation and Financial Services, LLC (ERFSS) has completed 8 applications during an 8 month period and the average concentration of BTEX in the area being treated has decreased from 2,770 $\mu\text{g/l}$ to 279 $\mu\text{g/l}$.

Remediation techniques applied at the site include MPX system operation, source removal along with dewatering during UST replacement; and several applications of in-situ chemical oxidation. The paper will include an analysis of contaminant mass removal rates, plume size reduction, and projected versus actual costs to date. Furthermore, the rationale for remedial alternative selection and pay-for-performance contracting will be reviewed for each sequence of the site cleanup.

Pay-for-Performance Contracting Under the Massachusetts LSP Program

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In 1993, the Commonwealth modified the Massachusetts Contingency Plan (MCP) that regulates management of hazardous waste sites, to a privatized system of licensed hazardous waste site decision-makers. LSPs provide these services in Massachusetts to Potentially Responsible Parties (PRPs) at disposal sites with reportable OHM releases.

The MCP provides a well-defined timeline of goals and documentation submittals to DEP of assessment, containment and remediation actions through site closure. It's focal point is achieving timely cleanup of a site's environment. For the PRP and LSP, money is also a key driving force. Pay-for-Performance remediation allows a PRP financing a site cleanup to reach well-defined cleanup performance goals within preset time periods, agreed upon with the LSP during contract negotiation. It also offers assurances which cap the PRP's remediation costs if those milestones are not achieved, where the LSP will modify/step up the technology at no additional cost to the PRP. With this approach, the LSP is held accountable by the PRP for MCP compliance timelines, and agreed-upon performance and cost milestones.

One problem evidenced is that several sites have languished in the system without conducting response actions to achieve MCP site cleanup goals, falling off the regulatory timeline. In 2004, DEP announced an enforcement effort to address these disposal sites. The Pay-for-Performance approach, when combined with in-situ chemical redox remediation and bioremediation polishing technologies, provides the framework of a win-win scenario for the PRP, LSP and Massachusetts DEP. This path clearly sets performance, time and cost goals to achieve site closure within regulatory timelines, without cost surprises. PRPs, whose sites have languished in "trial-and-error" remediation approaches, but now want to achieve site closure in a relatively short time, can use this well-defined approach with clearly defined performance and cost milestones.

New Case Studies in Performance Based Technology Substitutions

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Remediation engineers, scientists, regulators, and site owners are well aware of the asymptotic trends observed for contaminant concentrations as most remediation efforts approach the end of their effective life-span. In fact, it is more typical than not that even well designed remediation systems reach a point when affected area contaminant concentrations have diminished in extent and magnitude; however one or more monitoring points consistently remain above the site cleanup goals. In most cases, continued operation of the remediation system does not produce the desired contaminant removal needed to achieve goals. In the end, the consultant, regulator, and site owner are faced with costs of \$10,000 to \$50,000 or more each year to continue operating and monitoring a system which may take many more years to achieve goals. In-situ treatment of the remaining affected areas can lead to rapid decreases in petroleum compounds, chlorinated solvents, and in some cases, metals.

This presentation will discuss the history and status of multiple sites (petroleum PAP and PBC and chlorinated solvent sites) around the country where this approach has been utilized. In all cases the project goals are being met and several of the sites have been granted SRCOs. Rapid reductions were achieved through the use of complimentary in-situ processes including chemical oxidation and stimulation and maintenance of microbial processes to promote and enhance biodegradation. The in-situ techniques are specifically designed and structured to achieve complete site remediation within the shortest possible time frame by employing cost effective in-situ technologies.

Specifically, the presentation will illustrate the approaches used at petroleum sites (four gas stations and one bulk storage facility in Florida; an airline maintenance hanger in Syracuse; and a plastics plant in Boston) and chlorinated solvent sites (two commercial sites in Florida and one industrial site in New Jersey). In most cases, the existing remediation structures were used or modified for treatment applications to minimize costs. Lastly, these techniques can be applied under pay for performance contracts which caps the total cost and limits the owner's financial risk by paying for results as results are achieved.

Perchlorate: Emerging Issues and Innovative Remedial Approaches

Perchlorate Regulation in the State of Massachusetts

Paul W. Locke, Massachusetts Department of Environmental Protection, Boston, MA

Emerging Science Supporting the 2005 National Research Council Perchlorate Risk Assessment

John P. Gibbs, Kerr-McGee Shared Services LLC, Oklahoma City, OK

Effect of Varying Toxicity Values on Perchlorate Risk Assessment Results

Ishrat S. Chaudhuri, ENSR International, Westford, MA

Julie A.F. Kabel, ENSR International, Westford, MA

Update on DoD Perchlorate Treatment Technology Development

Bryan Harre, Naval Facilities Engineering Service Center, Port Hueneme, CA

Erica Becvar, AFCEE/TDE, Brooks City-Base, TX

Perchlorate Treatment Using Bioreactors: Current Applications and Future Prospects

Paul B. Hatzinger, Shaw Environmental, Inc., Lawrenceville, NJ

A. Paul Togna, Shaw Environmental, Inc., Lawrenceville, NJ

William J. Guarini, Shaw Environmental, Inc., Lawrenceville, NJ

***In Situ* Bioremediation of Perchlorate and 1,1,1-Trichloroethane Using Emulsified Edible Oil Substrate (EOS[®])**

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Perchlorate Regulation in the State of Massachusetts

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In 2001, the first instance of Perchlorate contamination in Massachusetts was identified in groundwater plumes emanating from the Massachusetts Military Reservation on Cape Cod. Since then the Massachusetts Department of Environmental Protection (DEP) has invested significant resources and effort to determine the presence and identify the sources of Perchlorate in drinking water supplies Statewide and to evaluate the health risks of Perchlorate as new information and research becomes available.

In February 2004 DEP issued a drinking water health advisory of 1 µg/L for Perchlorate, consistent with EPA's actions resulting from its January 2002 Perchlorate health assessment document. DEP also initiated the processes to establish a drinking water maximum contaminant limit (MCL) for Perchlorate and hazardous waste cleanup standard. In March 2004, DEP promulgated regulations requiring all public water supplies to test for Perchlorate. Also, in the fall of 2004, DEP promulgated draft revisions to the State's hazardous waste cleanup regulations that included a proposed groundwater cleanup standard of 1 µg/L in areas protected for current or future drinking water use.

DEP and its Science Advisory Committee reviewed the January 2005 National Academy of Sciences Report on Perchlorate and other recent information before proposing a drinking water standard and resubmitting its disposal site cleanup standards in Spring 2005.

This presentation summarizes the road the Commonwealth has taken to regulate perchlorate in both its Drinking Water and Waste Site Cleanup Programs.

Emerging Science Supporting the 2005 National Research Council Perchlorate Risk Assessment

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In sufficient amounts, perchlorate can inhibit iodine uptake by the thyroid, ultimately leading to diminished thyroid function. Recent studies in Europe and the United States have determined that maternal hypothyroidism during pregnancy, even when mild and considered subclinical, may be associated with impairment of normal brain development and intelligence in offspring. Concern about the possibility that iodine uptake inhibition from environmental perchlorate could result in impaired maternal thyroid function during pregnancy and adverse neurodevelopmental effects in the fetus, has led to proposed a proposed reference dose (RfD) as low as 0.00003 mg/kg-day. For 18 months during 2003 and 2004, a committee of the National Research Council (NRC) reviewed the science available in order to assess the risk of perchlorate ingestion. In the committee's January 2005 report, it concluded that the no-observed-adverse-effect level (NOAEL) is 0.4 mg/kg-day and that the no-observed-effect-level (NOEL) is 0.007 mg/kg-day. Based on the NOEL, the committee recommended an RfD of 0.0007 mg/kg-day. Subsequent to the NRC committee deliberations, five new scientific studies have been completed that strongly support the committee's NOAEL and NOEL and support that the recommended RfD is safe for even the most susceptible populations – fetuses of pregnant women with insufficient iodine consumption

Effect of Varying Toxicity Values on Perchlorate Risk Assessment Results

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Perchlorate has been used as a solid rocket propellant and ignitable source in munitions. It is a public health issue of recent interest because it has been found at low levels in the drinking water used by millions of Americans. The main toxicological effect of this chemical is to limit the uptake of iodide by the thyroid gland. This reduction of iodide uptake, in turn, can eventually disrupt thyroid hormones that regulate metabolism and growth. There are various toxicology studies on perchlorate that have been used by Agency and other toxicologists to develop toxicity values that can then be used to calculate safe concentrations of this chemical in soil and water. These include animal toxicology studies, controlled studies in human volunteers, and epidemiological studies. The use of a specific study and interpretation of the results can result in widely differing toxicity estimates, which result in turn in differing safe concentrations. For example, California's public health goal of 6 ppb is based on a human study where adult volunteers were fed daily amounts of perchlorate. In contrast, a recent paper by Strawson et. al. (2004)¹ developed a toxicity value from the same study used by California, which would result in a drinking water goal of 98 ppb. The recent study by the National Academy of Sciences developed a Reference Dose that was 20-fold higher than a previous interim Reference Dose developed by U.S. EPA. Development of site-specific cleanup goals for perchlorate can similarly differ based on which toxicity value is used to develop the cleanup goal. Based on this diversity of toxicological opinion and risk assessment approaches, it is important when conducting a perchlorate risk assessment to consider the full range of toxicity values and understand the uncertainty in these values. This presentation summarizes the pertinent toxicological literature, and discusses the range of toxicity values and uncertainties associated with perchlorate risk assessment.

¹Strawson J., Q. Zhao and M. Dourson. 2004. Reference dose for perchlorate based on thyroid hormone change in pregnant women as the critical effect. *Regulatory Toxicology and Pharmacology*, 39:44-65.

Update on DoD Perchlorate Treatment Technology Development

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Since perchlorate was discovered in water supplies in California, Nevada, and Arizona, much progress has been made in developing treatment methods capable of removing perchlorate from water. Most of the DoD's perchlorate treatment technology efforts have been directed at two technologies: biological treatment and ion exchange. In the biological treatment process, microbes destroy perchlorate by converting the perchlorate ion to oxygen and chloride. In most cases, nutrients must be added to sustain the microbes. In ion exchange the perchlorate ion is replaced by chloride, a chemically similar to the perchlorate ion. Bench-, pilot-, and full-scale studies have demonstrated that ion exchange systems can reliably reduce perchlorate concentrations. This presentation will review the efforts of the DoD to develop treatment technologies for perchlorate over the last ten years and highlight the most recent developments.

Perchlorate Treatment Using Bioreactors: Current Applications and Future Prospects

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Bioremediation is proving to be a versatile and economical approach for treating perchlorate-contaminated water. During the past decade, a variety of different bioreactor designs have been pilot-tested for perchlorate treatment, and seven full-scale systems have been constructed. Five fluidized bed reactor systems (FBRs) currently treat more than 9 million gallons per day of perchlorate-contaminated groundwater, with influent concentrations ranging from < 1 mg/L to greater than 250 mg/L. Perchlorate in the effluent water from each of these systems is consistently below 4 µg/L, the practical quantitation limit for EPA Method 300.0. In addition to groundwater treatment, two continuous stirred tank reactors (CSTRs) are presently removing perchlorate from military and industrial wastewaters at influent concentrations as high as 5,000 mg/L. Future prospects for bioreactors include the treatment of perchlorate-contaminated drinking water and the removal of residual perchlorate from salt brines generated during water treatment by regenerable ion exchange. Field tests have been conducted to evaluate the effectiveness of packed bed reactors (PBRs) and FBRs for treatment of potable water. These tests have resulted in both technologies receiving a preliminary approval for this application from the California Department of Health Services. Membrane bioreactors (MBRs) are being tested in the laboratory for a variety of applications, including drinking water, wastewater, and brine treatment. An overview of the design, operating parameters, and performance of the different bioreactor reactor systems will be presented.

***In Situ* Bioremediation of Perchlorate and 1,1,1-Trichloroethane Using Emulsified Edible Oil Substrate (EOS[®])**

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Studies have shown that microorganisms from a wide variety of aquifers can anaerobically biodegrade perchlorate when supplied with appropriate organic substrates and related amendments. 1,1,1-Trichloroethane (1,1,1-TCA) can also be anaerobically degraded; however, the biological remediation of this compound in actual groundwater plumes is less well documented. Solutions-IES, with funding from the Environmental Security Technology Certification Program (ESTCP), has been evaluating the effectiveness of emulsified edible oil substrate for promoting anaerobic biodegradation of these compounds in a commingled plume at a rocket manufacturing facility in Maryland. The shallow aquifer at the site contains elevated concentrations of perchlorate and 1,1,1-TCA released from a closed lagoon. Based on laboratory studies that compared several potential biodegradable long-term substrates, Solutions-IES selected EOS[®] for the field trial. In October 2003, a 60-foot long permeable reactive biobarrier (PRBB) was created perpendicular to the direction of groundwater flow by injecting approximately 850 pounds of EOS[®] into a 10-foot thick zone. The EOS[®] served as a carbon source for cell growth and an electron donor for energy generation, supporting long-term anaerobic biodegradation of the target contaminants.

Routine performance monitoring demonstrated the effectiveness of the PRBB and the longevity of the EOS[®]. Geochemical parameters confirmed that EOS[®] created conditions favorable for anaerobic biodegradation within and downgradient of the barrier. Perchlorate concentrations entering the barrier at 10,000 µg/L were reduced to BDL within four days of contact. 1,1,1-TCA concentrations (~23,000 µg/L) decreased initially due to sorption to the oil emulsion, but subsequent monitoring showed reductive dechlorination of 1,1,1-TCA to 1,1-dichloroethane and chloroethane with eventual conversion to non-toxic end products. Over one year after EOS[®] injection, the barrier continued to perform well with no evidence of flow bypassing and continuing evidence of residual substrate in the aquifer.

Pesticides

Regulation and Non-Regulation of Pesticides in the Massachusetts Environment

Paul W. Locke, Massachusetts Department of Environmental Protection, Boston, MA

EPA Review of Selected Non-Combustion Technologies for Remediation of Pesticides and Other Persistent Organic Pollutants

Ellen Rubin, U.S.EPA, Arlington, VA

Younus Burhan, Tetra Tech EM, Inc., Reston, VA

Full-Scale Bioremediation of Pesticide-impacted Soil/Sediment at the THAN Superfund Site, Montgomery, Alabama

David Raymond, Adventus Remediation Technologies, Mississauga, ON, Canada

Steven Gable, Adventus Remediation Technologies, Mississauga, ON, Canada

Alan Seech, Adventus Remediation Technologies, Mississauga, ON, Canada

James Mueller, Adventus Americas, Inc., Chicago, IL

Fayaz Lakhwala Adventus Americas, Inc., Chicago, IL

Todd Slater, ATOFINA Chemicals, Inc., Philadelphia, PA

Assessing for the Presence of Pesticides and Polychlorinated Biphenyls Using Passive Soil Gas Sampling

James E. Whetzel, W. L. Gore and Associates, Inc., Elkton, MD

Differential Reactivity of HCH Isomers Towards Nanoscale Zero-valent Iron

Daniel W. Elliott, The Whitman Companies Inc., East Brunswick, NJ

Wei-xian Zhang, Lehigh University, Bethlehem, PA

Steven T. Spear, Lehigh University, Bethlehem, PA

Remediating Chloroacetanilide-Contaminated Water with Dithionite-Reduced Soil and Aquifer Sediments

Hardiljeet K. Boparai, University of Nebraska-Lincoln, Lincoln, NE

Patrick J. Shea, University of Nebraska-Lincoln, Lincoln, NE

Steve D. Comfort, University of Nebraska-Lincoln, Lincoln, NE

Large-Scale Bioremediation of DDT and Toxaphene-Contaminated Soils in an Anaerobic Biocell

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Robert L. Zimmer, Geovation Consultants, Inc., Florida, NY

Sheila M. McGroddy, Geovation Consultants, Inc., Florida, NY

Regulation and Non-Regulation of Pesticides in the Massachusetts Environment

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Under Massachusetts state law, residual levels of pesticides in the environment are not covered by the state waste site cleanup program as long as the pesticide was applied in a manner consistent with its labeling (M.G.L. c21E, §2). The use of pesticides in Massachusetts is regulated by the Pesticide Bureau in the Division of Regulatory and Consumer Services of the Department of Agricultural Resources (<http://mass.gov/agr/pesticides>), so the statutory exemption helps minimize duplicative or overlapping regulation by the two agencies.

The historic use of certain persistent pesticides, such as lead arsenate, has become problematic in recent years as farms and orchards are developed into subdivisions and former railroad lines are converted to bike paths. Residential and recreational uses of these properties increases the potential for exposure to the residual pesticides, which raises questions of safety and liability.

This presentation will discuss the roots and application of the M.G.L. c.21E exemption for pesticides, analyze a recent revision of the law to clarify liability for contamination in railroad rights-of-way and present several case studies addressing the assessment of pesticides-contaminated locations.

EPA Review of Selected Non-Combustion Technologies for Remediation of Pesticides and Other Persistent Organic Pollutants

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The U.S. EPA has an ongoing interest in reviewing technologies that can be used for remediation of pesticides and other persistent organic pollutants (POPs) in contaminated soil. As many as 236 Superfund sites, as well as sites under RCRA, state, and local jurisdictions have pesticide-contaminated soil. The Stockholm Convention identified 12 POPs, including nine pesticides and three industrial chemicals or by-products, and obligated parties to remediate POPs. Site owners and operators, project managers, and other interested parties have expressed concern about the potential environmental and health effects associated with combustion of POPs. Because of these concerns and an ongoing desire to find more cost-effective solutions, environmental professionals are examining the application of non-combustion technologies to remediate POPs in stockpiles and soil. This includes ongoing work by researchers in Europe and Australia, who have been examining a variety of non-combustion technologies.

To address these concerns, EPA's Technology Innovation Program recently completed a review of 13 non-combustion technologies for remediation of pesticides and other POPs. These technologies range from processes that rely on biodegradation of one or more specific pesticide compounds, to thermal energy in a non-combustion environment, to mechanochemical energy. To help project managers and others with identifying specific technologies, EPA has developed a matrix that summarizes available technology-specific information, including capability to handle waste strength, ex situ or in situ application, contaminant treated, cost, pre-treatment needs, power requirements, and configuration. The matrix also indicates whether the technologies have been applied at a full, pilot, or bench scale for the selected contaminants. In addition, EPA has compiled and reviewed recent data from a variety of sites where these technologies have been used to treat pesticides and other POPs. This presentation will summarize the available information including presenting performance information for the case study sites.

Full-Scale Bioremediation of Pesticide-impacted Soil/Sediment at the THAN Superfund Site, Montgomery, Alabama

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Following successful completion of a pilot-scale demonstration in May of 2001, the US EPA selected Adventus Remediation Technologies' DARAMEND® bioremediation for full-scale treatment of pesticide-impacted soils and sediments at the T. H. Agriculture & Nutrition (THAN) Superfund Site (Site) in Montgomery, Alabama. Soils and sediments were excavated from impacted areas of the site including a surface water drainage way, placed in a prepared bed on Site, and subjected to bioremediation using a cycled, anaerobic/aerobic treatment protocol. The soil and sediment, impacted with Toxaphene, DDT, DDD, and DDE, remained in-place following treatment to the remedial objectives.

The remedial goals (i.e., Toxaphene \leq 29 mg/kg, DDT \leq 94 mg/kg, DDD \leq 132 mg/kg, and DDE \leq 94 mg/kg), were reached in all areas of the treatment cell following the application of 3 to 12 treatment cycles. The number of treatment cycles required to reach the remedial goal was primarily dependent on the initial concentrations. Analytical results indicated that mean Toxaphene, DDT, DDD, and DDE concentrations were reduced from 189 mg/kg, 81 mg/kg, 180 mg/kg, and 25 mg/kg to 10 mg/kg, 9 mg/kg, 52 mg/kg, and 6 mg/kg, respectively. This corresponds to removal and destruction efficiencies (RDE) of 95%, 89%, 71%, and 76%.

In some sampling zones initial pesticide concentrations were much higher than the mean concentrations and performance in these zones was correspondingly more effective. For example, Toxaphene, DDT, DDD, and DDE concentrations were reduced from 720 mg/kg, 227 mg/kg, 590 mg/kg, and 65 mg/kg to 10.5 mg/kg, 15 mg/kg, 87 mg/kg, and 8.6 mg/kg, respectively, in heavily impacted regions of the site. This corresponds to RDE's of 99%, 94%, 85%, and 87%

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Assessing Sites for the Presence of Pesticides and Polychlorinated Biphenyls using Passive Soil Gas Sampling

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Volatile organic compounds (VOCs) generally have boiling points below 200°C and vapor pressures greater than 1mm Hg. These compounds are amenable to detection in soil gas using both active and passive sampling methods. For compounds of less volatility, i.e. semi-volatile organic compounds (SVOCs), site assessment using soil gas is limited to time integrated passive collection techniques. Because of the low volatility and therefore, low availability in the soil gas, the range of SVOC compounds detectable by passive soil gas is highly dependent on the design of the collector. The design must employ materials that do not impede vapor migration, but still provide protection of adsorbent materials from liquid water and soil particles.

Organochlorinated pesticides and polychlorinated biphenyls (PCBs), with vapor pressures ranging from $\sim 2 \times 10^{-7}$ to 2×10^{-2} mmHg, are typically considered poor candidates for detection in the soil gas by any means.

However, an advanced passive soil gas collector has been used successfully on several sites to detect pesticides and/or PCBs in the soil gas. Pesticides and PCB congeners up to and including DDT and pentachlorobiphenyl have been observed. This presentation will discuss the passive soil gas collector design and the survey results from pesticide and PCB site assessment programs.

Differential Reactivity of HCH Isomers Towards Nanoscale Zero-valent Iron

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Since 1996, researchers at Lehigh University the efficacy of the nanoscale zero valent iron (nZVI) technology has been tested against a variety of environmental contaminants in both benchscale and field-scale tests. In this study, the target contaminants were four (4) environmentally significant isomers of hexachlorocyclohexane (HCH): alpha-HCH, beta-HCH, gamma-HCH, and delta-HCH. HCH ($C_6H_6Cl_6$) was heavily used as a pesticide in various technical grade and refined formulations around the world from the 1940s into the 1990s. Gamma-HCH, better known as lindane, exhibited most of the pesticidal activity. The HCHs constitute a significant soil contamination issue due to their toxicity and relative recalcitrance to abiotic and biotic degradation mechanisms. The HCHs were also of interest due to their six chlorine substituents, non-planar cyclic structure, and the fact that the majority of ZVI studies reported in the literature involve relatively simple halogenated ethanes and ethenes. In this study, high HCH concentrations ranging from 300-600 mg/L (1-2 mM) were degraded in 95% ethanol by nZVI concentrations of up to 35 g/L (627 mM). The HCH isomers were removed from solution at dramatically different rates. The most rapidly degraded isomer was gamma-HCH followed by alpha, delta, and lastly by beta-HCH. Using a pseudo first-order kinetic model, the half-life of lindane in 95% in the presence of nZVI was approximately 8-24 hours whereas the other isomers were appreciably more stable. The degradation pathway observed involved dihaloelimination of vicinal chlorines to yield the corresponding tetrachlorocyclohexene. The relative reactivity of the HCHs can be correlated to the axial versus equatorial orientation of the chlorine substituents around the ring. With three axial chlorines, lindane was observed to be the most reactive isomer followed by alpha-HCH with two axial chlorines. The delta and beta isomers, with 1 and 0 axial chlorines, respectively, were observed to be dramatically less reactive.

Remediating Chloroacetanilide-Contaminated Water with Dithionite-Reduced Soil and Aquifer Sediments

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The prevalent use of chloroacetanilide herbicides has resulted in non-point contamination of some ground and surface waters. We found that dithionite rapidly dechlorinates these herbicides in water with a stoichiometric release of chloride. Structural and kinetics analyses indicated that the chlorine is replaced by thiosulfate (a product of dithionite decomposition). Pretreatment of aquifer sediments and surface soils with dithionite produced reduced solids that were capable of herbicide dechlorination. In batch experiments, chloroacetanilide herbicides were exposed to dithionite-reduced aquifer sediments and surface soil. Dechlorination kinetics were a function of the dithionite concentration used to reduce the solids and related to the amount of Fe(II) produced. Washing the reduced aquifer sediments removed Fe(II) and resulted in less herbicide transformation. In contrast, the surface soil being rich in clay and iron, effectively degraded alachlor even after washing. Dechlorination also occurred when the washed, dithionite-reduced sediments were amended with Fe(II) (as FeSO₄) at pH 8.5 and continued as long as additional Fe(II) was provided. Fe(II) alone at pH 8.5 could not dechlorinate the herbicides. Comparing citrate-bicarbonate (C-B) and potassium carbonate (K₂CO₃) buffers to maintain high pH, effective degradation of alachlor was observed in the presence of K₂CO₃ while no degradation occurred in C-B buffer. The lack of degradation in C-B buffer is likely due to extraction of Fe(III) oxides by dithionite-citrate-bicarbonate (DCB). The dechlorination of chloroacetanilide herbicides by dithionite and dithionite-reduced sediments and soils indicates a remediation option that could be employed in natural environments when iron-bearing minerals are abundant.

Large-Scale Bioremediation of DDT and Toxaphene-Contaminated Soils in an Anaerobic Biocell

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Organochlorine pesticides such as DDT and toxaphene, along with PCBs, are among the most persistent compounds made by man. Moreover, these contaminants are recalcitrant under most environmental conditions. Whereas anaerobic processes such as reductive dechlorination and dehydrodehalogenation can reduce or eliminate chlorine atoms from DDT and the more chlorinated, higher molecular-weight congeners of toxaphene, recent research suggests that certain metabolites of these “parent” compounds are resistant to further reductive dechlorination even under anaerobic and reducing conditions. For example, DDMu, a metabolite of the DDT-breakdown product DDE, is known to be persistent in marine sediments where anaerobic conditions are prevailing. Toxaphene congeners are chiral in nature and the stereochemistry of certain congeners, particularly those that contain from six to eight chlorine atoms, appears to limit further reductive dechlorination. Accordingly, despite recent advances in anaerobic treatment technologies, the properties of these organochlorine pesticides pose significant challenges to effective treatment and regulatory closure of sites impacted with DDT and toxaphene.

More than 28,000 tons of DDT and toxaphene contaminated soils were excavated, treated and placed in a multi-component anaerobic biocell to facilitate a brownfields-like municipal site redevelopment project in eastern North Carolina. Although several prior years of in-situ treatment yielded up to 80-90% reductions in pesticide levels, these efforts failed to meet the stringent standards for unrestricted use owing to the high toxicity of these pesticides. Accordingly, the anaerobic biocell strategy was employed to mitigate long-term risks to human health and the environment and to expedite the municipal redevelopment project. The treatment process involved the processing of the contaminated soils in a computer-controlled pugmill in which the soils were mixed with different amounts of a patented solid-chemical composition, BioGeoCheMix[®] (“BGC”), depending on the levels of pesticides present in the soils. The BGC material is unique in that it incorporates plant materials and high-surface-area native iron to facilitate anaerobic conditions and reductive dechlorination processes as well as manganese (IV) minerals, such as pyrolusite, to both serve as a sacrificial oxidative catalyst and to facilitate relatively high-energy anaerobic oxidation processes. Recent advances in the BGC technology have incorporated carbon co-substrates designed to help stimulate the anaerobic oxidation of less chlorinated toxaphene congeners and metabolites of DDT in tandem with the reduction of relatively high-energy anaerobic electron acceptors such as nitrate and Mn(IV). Recent data have shown that the application of the BGC-anaerobic reduction/oxidation process to previously treated DDT and toxaphene contaminated soils provided demonstrable further reductions in DDT and its metabolites (such as DDD) and the further reduction of toxaphene concentrations and chlorination levels.

A summary of the design and construction of the anaerobic biocell and treatment process will be presented along with a discussion of the science and data underlying the BGC technology and its application to organochlorine pesticides.

Phytoremediation

Phytoremediation of Arsenic in the Spring Valley Area of Washington, DC

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Grass Phytoremediation: Explosives Uptake and Fate in Decomposing Plant Tissue

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Assessing Plant Derived Organic Matter in PAH Phytoremediation

Samuel T. Gregory, North Carolina State University, Raleigh, NC

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Elizabeth Nichols, North Carolina State University, Raleigh, NC

Elucidating Enzymes Involved in the Degradation of Trichloroethylene in Plants

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Increased Polycyclic Aromatic Hydrocarbon (PAH) Contamination and Plant Type Determine Plant/microbe Interaction in the Rhizosphere

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Exploitation of Endophytic Bacteria to Improve Phytoremediation of Organic Contaminants

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Phytoremediation of Arsenic in the Spring Valley Area of Washington, DC

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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 is being considered as an alternative, in elevated grids of Spring Valley, to minimize destruction of existing trees and reduce restoration costs in these residential areas. In 2004, a field verification study was conducted to evaluate the potential of phytoremediation to address the elevated arsenic soil concentrations. The field verification study consisted of two residential areas and one public access area encompassing 14 study sites. Three species of ferns, *Pteris vittata*, *P. cretica* and *P. multifida*, were planted and grown from May to November. The 2004 activities were successful in reducing arsenic concentrations in the surface soils below target levels in 12 of the 14 study areas. Based on these results, the field activities were expanded in 2005 to include additional sites. The results of the 2005 field demonstration will be presented.

Grass Phytoremediation: Explosives Uptake and Fate in Decomposing Plant Tissue

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The commonly used explosives and propellants, trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and nitroglycerine (NG), are often found in soil and groundwater from military firing ranges. Because of the need for continued training with live ammunition, cleanup of these contaminants may prove expensive. One alternative being considered to manage sites exposed to these contaminants is the use of grasses in phytoremediation. In this study, the uptake of TNT, 2,4-DNT, RDX, and NG in hydroponic studies using three common grasses, yellow nutsedge, yellow foxtail, and common rush, was investigated. Rapid removal from solution by all grasses was observed, with some accumulation of contaminants in the grass tissues. Higher concentrations were observed in killed roots, demonstrating the presence of plant based enzymes actively transforming the uptaken contaminants. Grass with TNT and RDX present in their tissues from previous hydroponic experiments were buried in clean soil to determine the ultimate fate of the contaminants. In twelve days, 97% of the initial TNT and RDX were removed in soil/grass extracts while spiked controls retained high levels of the contaminants. Several of the grass/soil mixtures were soaked in acidic water overnight with shaking to determine the level of leaching possible from the contaminated tissues. Initially, only 18% of RDX could be leached from the plant tissues and after seven days of decomposition that decreased to 7%. No TNT was leached from any of the plant tissues. TNT and RDX were both leached in significant amounts from spiked controls. These studies indicate that TNT, 2,4-DNT, RDX, and NG can be rapidly taken up by several common grasses; that contaminants in plant tissues appear to be removed as the tissues decompose, and that leaching of TNT and RDX is significantly reduced after uptake into grasses and even further as those grasses decompose.

Assessing Plant Derived Organic Matter in PAH Phytoremediation

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Elevated levels of petrogenic PAHs are often found at historical sites of petroleum refinement and use. Knowledge about the impact of plant derived organic matter (PdOM) at such sites is necessary to fully evaluate risk reduction and remediation efficacy by phytoremediation. The purpose of this research is to identify and separate the mechanisms by which PdOM impacts the fate and bioavailability of weathered PAHs. Samples have been collected across successional gradients along a freshwater canal and saltwater marsh where historically high levels of PAHs remain. Sediment samples of both a freshwater and saltwater marsh impacted by creosote contamination are also under investigation.

Alkylated and non-alkylated PAH concentrations (GC/MS SIM) allow the use of chemical fingerprinting techniques to detect contaminant weathering and degradation. Isotopic signatures ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$) of sediment fractions represent another approach to probe the impact of PdOM on PAH bioavailability. Density separations of whole sediment can separate labile carbon pools (light fractions) from more recalcitrant older carbon pools (heavy fractions), with PdOM more likely to appear in lighter density fractions, as evidenced by radiocarbon dating, ($\Delta^{14}\text{C}$ -AMS). Contaminant profiles from bulk sediment, humic fractions, and density fractions all contribute information about the fate of PAHs in soils and sediments with PdOM.

Humic fractions, size fractions, and density fractions of whole sediment have been analyzed for both alkylated and non-alkylated PAH concentrations and isotopic signatures. Fractions from vegetated sites show different PAH distribution profiles than non-vegetated fractions. Preliminary data show that petrogenic and pyrogenic PAH source contamination cycles at different rates among sediment density fractions. Both vegetated and non-vegetated sediments have greater mass amounts of PAHs in lighter density fractions where labile organic carbon is present. Because lighter density fractions may represent more bioavailable carbon pools, these results are important to evaluate PAH bioavailability, degradation, and potential risk to organisms in plant-impacted sediments.

Elucidating Enzymes Involved in the Degradation of Trichloroethylene in Plants

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As the use of phytoremediation for cleanup of halogenated hydrocarbons becomes increasingly widespread, it is imperative to determine the route of metabolism of such chemicals in plants to increase effectiveness and efficiency of degradation. In humans and other organisms, cytochrome P450s are involved in degradation of the common groundwater contaminant trichloroethylene (TCE). Enzymes that have the potential to be involved in TCE degradation in plants include cytochrome P450s, peroxidases, dehalogenases, laccases, and reductases. We have shown that the model plant species, *Arabidopsis thaliana*, is capable of TCE degradation using a sterile technique to expose seedlings to TCE. We are furthering our results by comparing TCE metabolite production in WT *Arabidopsis* to plants that have been modified for certain genetic traits. Analysis of genes whose protein products have sequence similarity to the substrate-binding domain of CYP2E1 may provide insight into whether these genes play a role in plant mediated TCE degradation. We have obtained T-DNA seed lines for 5 probable P450s from *Arabidopsis* that contain sequence homology in 5 conserved residues from the substrate-binding site of human cytochrome P450 2E1 (CYP2E1). These genes are also being over-expressed in *Arabidopsis* and tobacco. CYP2E1 is involved in the rate-limiting step in TCE degradation in mammals. In addition, we are continuing our screening of a tobacco cDNA library using ion chromatography.

Increased Polycyclic Aromatic Hydrocarbon (PAH) Contamination and Plant Type Determine Plant/microbe Interaction in the Rhizosphere

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Although contaminant breakdown by rhizobacteria is a recognized means of phytoremediation, it is yet to be ascertained how rhizodegradation is governed by interaction between the host plant and root-associated bacteria. Our research examines the PAH-degrading bacterial community in the rhizosphere to elucidate trends in the plant/microbe symbiosis under toxic stress conditions. Wheat, lettuce, zucchini, and pumpkin plants were grown in soil from a former manufactured gas plant site. Plant shoot weights at harvest show no effect for increased contamination on pumpkin and zucchini plants, but a negative effect for wheat and lettuce. Bacteria from the plant roots were isolated on plates with PAHs as the sole substrate. Whole genome BOX-PCR fingerprints indicate that change in the community of PAH-degraders corresponds to a rise in contamination level primarily and secondarily to the different plant hosts. These rhizobacteria utilize the aromatic root exudates caffeic acid, cinnamic acid, coumaric acid, naringenin, quercetin, and morin as growth substrates. Probing for genes which encode the enzymes that transform naringenin and quercetin revealed that most bacterial strains possessed flavonol synthase (FLS) but fewer carried quercetinase (*YxaG*). A phytotoxicity test performed on the soils after plant-harvesting indicated that prior plant growth improved germination in the contaminated soil. These results point to unique qualities for pumpkin and zucchini plants in engineered phytoremediation systems.

Exploitation of Endophytic Bacteria to Improve Phytoremediation of Organic Contaminants

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Phytotechnologies are offering efficient tools and environmentally friendly solutions for the cleanup of contaminated sites and water, the 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 recently demonstrated that endophytic bacteria can be efficiently used to improve the phytoremediation of volatile organic contaminants: endophytic bacteria equipped with the appropriate degradation pathway significantly improved the *in planta* degradation of toluene 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, both in the presence and absence of toluene. This work provides a general concept for using horizontal gene transfer to adapt the endophytic microorganisms associated with poplar to deal with the stress imposed by an environmental insult, resulting in the improved phytoremediation of the contaminant.

Remediation

Yakima Valley Spray Facility Cleanup

Richard H. Bassett, Washington State Dept. of Ecology Toxics Cleanup Program, Yakima, WA

Long Term TCE Source Area Remediation using Short Term Emulsified Edible Oil Substrate (EOS[®]) Recirculation.

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Real-Time DNAPL Source Delineation Using the Triad Approach

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Michael J. Maughon, Naval Facilities Engineering Command, North Charleston, SC

Maxie R. Keisler, Naval Facilities Engineering Command, North Charleston, SC

Surgical Implementation of Blast Fractured Bedrock Trench Technology at an Active Chemical Plant

Richard H. Frappa, Geomatrix Consultants, Inc., Amherst, NY

Paul F. Mazierski, Dupont Corporate Remediation Group, Niagara Falls, NY

Craig T. Taylor, URS Corporation, Buffalo, NY

Daniel M. Sheldon, URS Diamond, Niagara Falls, NY

How Clean Can It Get? Critical Review of Mechanisms and Results Achieved Using Thermal Remediation and Where You can Go Wrong

Gorm Heron, TerraTherm, Inc., Bakersfield, CA

Ralph S. Baker, TerraTherm, Inc., Fitchburg, MA

John M. Bierschenk, TerraTherm, Inc., Fitchburg, MA

John C. LaChance, TerraTherm, Inc., Fitchburg, MA

“Low-Quality” Steam Injection To Enhance Conventional In-Situ Remedial Technologies

Daniel Groher, ENSR International, Westford, MA

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Yakima Valley Spray Facility Cleanup

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A pesticide formulator-distributor, Yakima Valley Spray (YVS), operated in Yakima, Washington from 1908 to 1974. A large bulk fuel distributor operated immediately next to YVS during a similar timeframe. A remedial investigation conducted on these properties identified more than sixty contaminants, pesticides, hydrocarbons, volatile organic compounds, and metals that had been released to the soil and groundwater. Nine indicator contaminants would eventually drive the cleanup. The greatest health and environmental threats in soil and groundwater were aldrin, dieldrin, and arsenic.

Site groundwater annually fluctuates from 13 to 21 feet below ground surface. An annual 60 degree direction change in flow occurs too. From an irrigation influence, groundwater fluctuations created a 'smear zone' that contributed contaminants to downgradient receptors. Site cleanup was complicated by contamination under two storage buildings, under two adjacent railroad spurs, an upgradient unknown source of perchloroethylene, a sewer line, buried fuel tanks, and an irrigation canal. A two-year break occurred after the remedial investigation when the site became a Washington State Legislature 'pilot' site.

The Cleanup Action Plan gave the responsible parties options of (1) minimal excavation with long-term bioventing and biosparging, or (2) maximum excavation to low winter groundwater. The parties chose maximum excavation as the cheaper alternative and to expedite facility cleanup.

A consent decree was signed between the ten responsible parties and the State of Washington. Building demolition, temporary track removal, and excavation occurred from January, 2004, to May, 2004. Excavation and transport of about 80,000 tons of contaminated soil to appropriate landfills occurred. Still to be completed are two years of quarterly confirmation samplings and analyses from 17 monitoring wells to determine the success of the source removal. Cleanup cost is estimated at 10-12 million dollars.

Long Term TCE Source Area Remediation using Short Term Emulsified Edible Oil Substrate (EOS[®]) Recirculation.

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Solutions Industrial & Environmental Services, Inc. (Solutions-IES) designed effective treatment approaches using emulsified edible oil substrate (EOS[®]) to remediate trichloroethene (TCE) source areas at two Department of Defense installations. Each site posed unique design challenges and permitting constraints. The Army Environmental Center retained Solutions-IES to treat a 10,000 ft² source area, approximately 15 feet thick, at the former Tarheel Army Missile Plant in Burlington, NC. At this site, the low concentrations of TCE and related contaminants were present in complex saprolite with low well yields and subsurface structures were located nearby. Solutions-IES' ESTCP-funded pilot test at the Naval Weapons Station in Charleston, SC is located in a heavily wooded area with higher contaminant concentrations, a low yielding aquifer and shallow groundwater gradient.

At each site, temporary recirculation systems were used to spread EOS[®] throughout the desired treatment zone. The systems were designed to minimize operation and maintenance needs and were effective in smearing the substrate throughout the subsurface as evidenced by increased levels of total organic carbon in the aquifer. Decreased DO and ORP levels confirmed that anaerobic reducing conditions were quickly established at both sites. Corresponding decreases in TCE were also observed. At the Tarheel Army Missile Plant, TCE concentrations were reduced from 1,690 µg/L to non-detectable levels within 2 months of the EOS[®] injection. Six months post-injection at the Charleston Naval Weapons Station TCE concentrations have been reduced from 18,700 µg/L to 4,300 µg/L. The pilot tests clearly show the effectiveness of EOS[®] for treating TCE-contaminated groundwater in a variety of source area configurations.

Real-Time DNAPL Source Delineation Using the Triad Approach

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A focused, real-time investigation of a dense non-aqueous phase liquid (DNAPL) source zone was conducted at the Solid Waste Management Unit 1 (SWMU1), Naval Air Station Pensacola, Florida. During the 1950's and 60's, SWMU1 received industrial waste from painting and electroplating operations. Chlorinated solvents, including trichloroethene (TCE), were released to the subsurface from drying beds used to dewater sludges generated by wastewater treatment processes. DNAPL is suspected to be present as disconnected residual at the base of the unconfined aquifer at 40 to 44 feet below ground surface. In 1998-99, approximately 10,000 gallons of hydrogen peroxide/iron catalyst solution were injected into the aquifer as part of a source reduction strategy to reduce TCE levels below the default natural attenuation concentrations established by the state regulatory agency. Within two years of hydrogen peroxide injection, TCE concentrations rebounded to initial levels. Based on an evaluation of remedy effectiveness, it appeared that poor remedy performance was due to incomplete characterization of the DNAPL source zone as well as the short-lived nature of the oxidant solution. As part of an on-going optimization study of the SWMU1 groundwater remedy, a focused characterization study was planned using the Triad Approach as guidance. A direct-push rig equipped with a membrane interface probe (MIP) for DNAPL detection and an electrical conductivity detector for soil stratigraphy mapping was used to delineate the zone of DNAPL residual. The number and location of data collection points were decided by a team of scientists and engineers as the investigation progressed based upon the collection of real-time data and a continuously updated conceptual site model. Following the initial MIP survey, a mobile laboratory, capable of producing data of quality equal to that of a fixed-base laboratory, was used to collect confirmation samples during the same mobilization. By combining the use of field analytical techniques with more traditional fixed-based laboratory methods in a single field mobilization, the DNAPL source zone was delineated at considerable cost savings, while still managing data uncertainty and achieving project data quality objectives.

Surgical Implementation of Blast Fractured Bedrock Trench Technology at an Active Chemical Plant

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An Administrative Consent Order (ACO) executed by the New York State Department of Environmental Conservation (NYSDEC) required enhancement of the hydraulic efficiency of the existing Groundwater Remediation System (GWRS) at a large, active chemical plant located in New York State. A technology assessment identified groundwater recovery from blast-enhanced fractured bedrock trenches (BFBTs) as the preferred remedial option to improve control of a chemical plume in approximately 5 acres of the southwestern portion of the Plant. BFBTs have proven to be effective in hydraulically controlling the spread of groundwater contamination, however, technology implementability in a chemical plant setting in close proximity to vibration sensitive processes and equipment owned by a business other than the property owner presented significant technical challenges. A Pilot Scale Technology Demonstration (PSTD) was implemented at the Plant to demonstrate that the technique would not only facilitate hydraulic control of groundwater, but could be implemented safely without impacting Plant equipment or structures.

A significant aspect of the demonstration included an extensive assessment of peak particle velocities (PPV) and ground vibration frequency to assess vibrations produced by blasting. PSTD blast vibration monitoring involved: an assessment of background vibration levels at the Plant, on-site blast vibration level predictions produced during blasting, and real-time monitoring of blast vibrations during the PSTD for comparison to predicted blast vibration levels. Real-time vibration monitoring was used to evaluate design parameters for the blast program. The PSTD was successful and provided information required to implement full scale design for safe, bedrock blasting within 25-feet of sensitive Plant chemical operations and directly beneath high voltage power transmission lines.

The PSTD and full-scale technology implementation produced two, 200-foot long BFBTs. Although originally intended as an enhancement, analysis of hydraulic performance data indicated that higher BFBT pumping rates may actually serve to replace operation and maintenance (O&M) of nearly a dozen conventional pumping wells in the existing GWRS. Benefits of the blast-fractured bedrock trenches include increased mass removal, more efficient formation of continuous hydraulic capture zones, and significantly lower O&M costs compared to the existing GWRS. This work demonstrates the safety and predictability of detonating explosives to create blast-fractured bedrock trenches in sensitive settings, thereby potentially

increasing use of this technology in maintaining cost-effective, long-term hydraulic control at process sensitive industrial operations.

How Clean Can It Get? Critical Review of Mechanisms and Results Achieved Using Thermal Remediation and Where You can Go Wrong

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Recently, results from sites that were heated and treated using thermal remediation have indicated impressive removal rates for dense non-aqueous phase liquid (DNAPL) source zones in soil and groundwater. Results from both a DOE site (Young-Rainey STAR Center), and an industrial facility in the Midwest, have been published, stating mass removal efficiencies in the 99.9 percent range. Soil concentrations below or near non-detect are reported, and groundwater concentrations near or below MCL have been observed inside the original source zones. These results appear almost unrealistic, considering the recalcitrant nature of DNAPLs in the subsurface, long-term diffusion processes, heterogeneity of most source zones, and frequently raised questions about DNAPL capture at thermal sites. Other site reports, particularly from sites where Electrical Resistance Heating was used, have reported much less impressive results, sometimes less than 90% mass removal. As more data is emerging, it is becoming evident that thermal remediation spans a wide range of heating methods, and that applications vary from very robust, effective systems to poorly designed and ineffective systems.

This presentation will review the mechanisms behind thermal remediation critically, focusing on exactly what happens at the pore and micro-scale, as well as larger scale during heating. It will review ways for the contaminants to be contacted, vaporized, transported under various gradients, and show the most proper design for vapor recovery and capture systems. Several typical design flaws will be presented, in an attempt to explain why not all thermal projects have achieved the success made possible by the theory. Finally, a list of typical quality control issues are provided – hopefully leaving the audience with direction for better evaluating thermal remediation proposals and applicability. The authors have worked on approximately 20 field-scale sites where steam enhanced remediation, electrical resistance heating, and thermal conduction heating have been implemented.

“Low-Quality” Steam Injection To Enhance Conventional In-Situ Remedial Technologies

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Conventional remediation technologies such as soil vapor extraction (SVE), multi-phase extraction (MPE), and groundwater pump and treat can be thermally-enhanced to achieve remedial closure objectives that might otherwise be infeasible or too slow. Thermal enhancement can help mobilize light non-aqueous phase liquids (LNAPLs) that are otherwise too viscous to effectively recover; can increase the volatility of target compounds to increase the mass rate of vapor extraction; and can accelerate in-situ biodegradation. Thermal enhancement can be distinguished from thermal remediation by the scale and cost of the heating processes. Full-scale thermal remediation tends to add 100's to 1,000's of kilowatt-hours of energy per cubic yard (KWH/yd³) of soil to increase subsurface temperatures in the treatment volume to greater than 212°F. These high temperatures and aggressive heat input are often required to reach very stringent treatment goals and/or destroy contaminants in-situ, typically in low permeability soil. In contrast, thermally-enhanced remediations tend to require heat inputs of 10 to 100 KWH/yd³ and may only increase subsurface temperatures by 20° to 100°F. The lower energy input for thermally-enhanced remediation often has lower capital and operational costs than full-scale thermal remediation. However, thermal enhancement is most appropriate for a more select range of soil conditions and more flexible remedial objectives.

ENSR has successfully applied low-quality steam (i.e., low temperature and pressure) at three sites with heat input less than 30 BTU/hr/yd³, including: (1) product recovery of No. 6 fuel from a site undergoing re-development in Massachusetts; (2) MPE remediation of chlorinated solvents in groundwater in Illinois; and (3) SVE of toluene and styrene in a former industrial setting in Massachusetts. These remedies will be contrasted with higher heat input full-scale thermal remediation applications.

Remediation Strategies for Contaminated Soils and Sediments

Pathways of Congener-Specific PCB Dechlorination by Palladized Magnesium

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Dechlorination of Persistent Organic Pollutants with Palladized Magnesium: Dioxins and PCNs

Linda Rauch, University of New Hampshire, Durham, NH

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Kevin H. Gardner, University of New Hampshire, Durham, NH

Developments in Bioremediation of Soils and Sediments Polluted with Metals and Radionuclides: 2. Field research on Bioremediation of Metals and Radionuclides

Henry H. Tabak, US EPA, ORD, Cincinnati, OH

Terry C. Hazen, Lawrence Berkeley National Laboratory, Berkeley, CA

Innovative Systems for Dredging, Dewatering or for In-situ Capping of Contaminated Sediments

James T. Olsta, CETCO, Arlington Heights, IL

Jerry Darlington, CETCO, Arlington Heights, IL

Scaling Contaminant Distributions and Contaminant Processes in Sediments

Peter Adriaens, University of Michigan, Ann Arbor, MI

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Issues of Biostimulation, Bioaugmentation and Bioavailability in the Remediation of PAHs in a Coal Tar Soil

Joseph J. Pignatello, Connecticut Agricultural Experiment Station, New Haven, CT

Entombment of Pure-Phase Tar Impacted Sediment in New Bedford Harbor: A Case Study

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Pathways of Congener-Specific PCB Dechlorination by Palladized Magnesium

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PCB contamination in sediments remains a significant problem in many rivers, harbors, and estuarine areas in the US and around the world, and continues to provide PCBs to the food chain despite the long ban on PCB manufacture and use. In this work, rapid degradation of single PCB congeners (BZ 3, 170 and 197) by palladium-coated magnesium (Mg/Pd, 99.9%/0.1% by weight) has been demonstrated in pure solvent systems (10% methanol in distilled water). More than 90% of the initial PCB was removed in 10 to 25 minutes. No degradation byproduct was observed in these experiments. The behavior of biphenyl, the expected degradation byproduct, was also investigated in the same pure solvent system. Rapid removal of biphenyl was observed in these studies (97% removal in 10 minutes). It was hypothesized that biphenyl was volatilized or adsorbed to the Mg/Pd surface. The last two hypotheses are currently under investigation and recent work on closing the mass balance will be presented.

Understanding the fundamentals of the dechlorination pathways of single PCB congeners, including the relative resistance of positional isomers towards degradation, is essential to be able to better predict treatment efficiencies in more complex sediment systems. Preliminary experiments in PCB-contaminated sediments from the Housatonic River, New Bedford Harbor, and Hunter's Point indicate that there is PCB mass reduction occurring by Mg/Pd at a slower rate, over a period of a few days. Contaminant degradation by Mg/Pd is a potential promising technology that could effectively remediate PCB-contaminated sediment to very low levels with an in-situ process.

Dechlorination of Persistent Organic Pollutants with Palladized Magnesium: Dioxins and PCNs

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A significant issue in the field of contaminated sediments is the presence of contamination with persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs or Dioxins), polychlorinated dibenzofurans (PCDFs), and polychlorinated naphthalenes (PCNs). These contaminants pose a serious public health concern as a result of their highly toxic nature. POPs are ubiquitous in the environment on a global scale and have been shown to bioaccumulate in animals.

A great deal of work has been undertaken by researchers studying and developing treatment approaches for PCBs. To date, a lesser degree of effort has focused on some of the other POPs such as Dioxins or PCNs. In particular, PCNs continue to be a little studied group of environmental toxins. Yet these compounds have been found to be equal if not more significant contributors than PCBs to toxicity levels at certain contaminated sites.

Previous work at UNH has shown that PCBs can be successfully dechlorinated by reaction with palladized magnesium. This presentation will focus on recent work investigating the reactivity of palladized magnesium with Dioxins and PCNs in pure solutions as well as in contaminated sediments from the Passaic River.

Developments in Bioremediation of Soils and Sediments Polluted with Metals and Radionuclides: 2. Field research on Bioremediation of Metals and Radionuclides

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The last 15 years have seen an increase in the types of contaminants to which bioremediation is being applied, including solvents, PAHs and PCBs. Now, microbial processes are beginning to be used in the cleanup of radioactive and metallic contaminants of soils and sediments.

Microorganisms can interact with these contaminants and transform them from one chemical form to another by changing their oxidation state through the addition of (reduction) or moving (oxidation) of electrons. In some bioremediation strategies, the solubility of the transformed metal or radionuclide increases, thus increasing the mobility of these contaminants and allowing them to more easily be flushed out from the environment. In other strategies, the transformed metal or radionuclide may precipitate out of the solution, leading to immobilization. Both kinds of transformations present opportunities for bioremediation of metals and radionuclides in the environments - either to immobilize or to accelerate their removal. Metal contamination of soils and sediments is especially problematic because of the strong adsorption of many metals to their particles. Due to the difficulty of desorbing metal contaminants, some traditional remediation methods, simply immobilize metals in contaminated soils, by the addition of cement or chemical fixatives, by capping with asphalt, or by in-situ vitrification. Alternatively, soils are often isolated by excavation and confinement in hazardous waste facilities. Although rapid in effect, both of these options are expensive and destroy soil's future productivity. The success of soil washing and pump-and-treat technologies to remove metals is severely limited by the slow desorption kinetics of adsorbed metals, with the result that additional additives (acids, chelates and reductants) are often used to promote metal transfer to the aqueous phase. These agents improve cost effectiveness but may introduce further harmful chemicals.

A primary strategy of bioremediation is the use of similar metal-immobilizing agents in conjunction with soil washing, with advantage that they pose no known environmental threat themselves. Biopolymers have been discovered that bind metals with high affinity and travel relatively unimpeded through porous medium. Certain microorganisms transform strongly-adsorbing metal species into more soluble forms and plants are being recruited that act as self-contained pump-and-treat systems. Other methods employ enzymatic activities to transform metal species into volatile, less toxic or insoluble forms. Techniques for soil bioremediation are usually designed to be used in-situ, lowering costs; they avoid the use of toxic chemicals, and in nearly all cases, the soil structure and potential for productivity are preserved.

The first review paper, presented at the AEHS 2005 West Coast Conference provided a detailed information on the metal-microbe interactions and the application of these interactions for bioremediation of the metal contaminated soils and sediments. The paper described: (1) microbial processes effecting bioremediation of metals and radionuclides and influencing their

toxicity and transport (metal biotransformation, metal biosorption, metal bioaccumulation and biomining via microbially-generated ligands - degradation and synthesis of organic ligands of toxic heavy metals); and (2) microbial mechanisms involved in bioremediation of metal and radionuclide contaminated soils and sediments (dissimilatory metal reduction, microbial metabolism of iron bacteria, microbial metal leaching, microbial polymers and their use in bioremediation of metal contamination and microbial metal volatilization).

This paper will provide a review of published research on field studies on bioremediation of metal and radionuclide contaminated soils and sediments. The paper will (1) cite examples of field research and cases of field in-situ bioremediation of metal and radionuclide contaminated soils and sediments; (2) discuss the role of phytoremediation in the treatment of metal and radionuclide contaminated soils; and (3) provide information on the use and field-scale application of surfactants in the treatment of metal and radionuclide pollution of soils and sediments. The following metal-microbe interactions that impact bioremediation of metal contamination in soils and that can be applied to field-scale biotreatment will be discussed: (1) biotransformation (bioreduction and biooxidation); (2) bioaccumulation and biosorption; (3) biodegradation of chelators; (4) biosurfactants and biologically-assisted soil washing; (5) volatilization; and (6) biotreatment trains and natural attenuation. The paper will also discuss research on the treatment of metal contaminated soils, wetlands and mine areas with the use of biosolids, by providing information on (1) in-situ soil treatments to reduce phyto- and bioavailability of metals and (2) the use of biosolids to restore metal contaminated mining areas impacted by metal tailings.

Innovative Systems for Dredging, Dewatering or for In-situ Capping of Contaminated Sediments

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Objectives: The environmental remediation community is seeking innovative ways to conduct remediation of contaminated sediments.

Challenge: Traditional dredging practices create challenges in dewatering, finding suitable disposal facilities, as well as, public concern over resuspension of contaminants. In-situ capping (either in place of dredging or for capping residual contaminants) can be limited by concerns regarding navigation, uniform cap placement, biointrusion and geotechnical stability.

Solution: Innovative dewatering, solidification and stabilization practices, can be provided to improve the economics of dredging. A potential solution for many in-situ capping concerns is the use of a reactive material cap. A reactive material cap could greatly reduce the thickness required for the cap compared to conventional sand caps. Various reactive materials (e.g., activated carbon, organoclay, zero valent iron) are used for wastewater and groundwater treatment and may be applicable to in-situ capping. Activated carbon and organoclay effectively adsorb many organics. Zero-valent iron reduces organic solvents into less toxic byproducts.

There are several systems that could be used for in-situ capping with reactive materials. One is a reactive material filled geotextile mat. A reactive material mat would have several advantages over loose placement of reactive materials, including:

- uniform and verifiable mass per area placement of reactive or absorptive material,
- ability to mix reactive or absorptive materials in defined proportions,
- geotextiles provide separation of the reactive material from the contaminated sediment and cover material,
- geotextiles provide a barrier to biointrusion,
- multiaxial strength of the geotextiles provides resistance to uplift and differential settlement,
- and geosynthetic reinforcement provides stability on sloped areas.

Another reactive material system include utilization as of organoclay as a permeable reactive barrier in either a horizontal or vertical configuration to utilize the significant hydrocarbon adsorption capacity.

Results: At the Anacostia River Demonstration Project a coke-filled geotextile mat was successfully constructed and deployed. A barge with crane was used to deploy the material. Other deployment methods have also been used for geosynthetics from shoreline and would be applicable to a reactive material mat.

Scaling Contaminant Distributions and Contaminant Processes in Sediments

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Sediment site managers are often confronted with decisions on sampling density to properly capture spatial variability for site characterization, and with decisions regarding the scale of new technology demonstrations to enable efficacy assessment. Reliable characterization of the spatial distribution of sediment site attributes, such as contaminant concentrations, the impact of microbial activity on contaminants, and microbial characteristics depends on how well sampled values represent all values throughout the entire site. Whereas geostatistical tools have been developed to interpolate the attribute values in space, these do not explicitly take into account the uncertainties associated with the various scales (field cores, columns, or microcosms) at which the data have been collected. A recently developed statistical model (M-Scale) takes into account multiple scales and multiple resolutions to optimize the reliability of sampled data. The model not only serves as a tool to evaluate parameter relationships over different scales by their covariances and data uncertainty, but also makes further use of these covariances and data uncertainty as basis for a precision-optimized estimator. These estimators can then be used to scale laboratory information to the field, and conversely, to use field-derived data for uncertainty-based decision-making for technology demonstrations. Information from each scale will be weighted by the projected similarity to the scales of interest, with adjustments considering the different precision they provide. Unlike conventional geostatistic tools that are based on the point-to-point spatial structures, the multi-scale model introduces a new framework for spatial analysis in which regional values at different scales are anchored by the correlations of each other. Examples will be presented using dioxin distributions, the impact of microbial dechlorination activity on the patterns observed, and microbial abundance interpolations.

Issues of Biostimulation, Bioaugmentation and Bioavailability in the Remediation of PAHs in a Coal Tar Soil

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This presentation will include the results of a lab-scale study of enhanced bioremediation of polycyclic aromatic hydrocarbons (PAHs) in soil from a manufactured gas plant (MGP) site in Connecticut, as well as some results of peripheral studies on sorption reversibility in other soil-contaminant systems. Biodegradation and desorption experiments on the MGP soil were conducted in well-mixed aerobic suspensions containing various additives over a 93-106 day period. Both biotransformation and desorption decreased with PAH ring size, becoming negligible for the six-ring PAHs. Biodegradation by native organisms was strongly accelerated by addition of inorganic nutrients (N, P, K, and trace metals). No further rate enhancement occurred by addition of a site-derived bacterial enrichment culture even though it boosted by ~100-fold the aromatic dioxygenase levels; nor by the addition of chelating agents (citrate or pyrophosphate) even though they were previously found to enhance desorption in killed controls. The strong ability of nutrients to stimulate degradation of the bioavailable PAHs by native cells indicates that their persistence for many decades at this site (and possibly others) is likely due to nutrient-limited natural biodegradation. It also suggests that an effective strategy for their bioremediation could consist simply of adding inorganic nutrients.

Rates of biotransformation of PAHs by biostimulated native organisms outpaced their maximal rates of desorption in sterilized flasks which contained desorption-enhancing chelating agents and an infinite sink polymer adsorbent, Tenax. This indicates that indigenous organisms facilitated desorption. This result contradicts other recent studies including our own which show correlations between physical and micro-biological availabilities of a given compound.

Despite the promising results obtained for this MGP soil, a minor fraction of each PAH, in intact form, remains recalcitrant to biodegradation. Recent work in our group on other soil-chemical systems has shown that organic compounds cause swelling and shrinking of natural organic matter during sorption and desorption. The act of desorption can lead to collapse of pore walls surrounding remaining sorbed molecules, leading to their physical immobilization.

Entombment of Pure-Phase Tar Impacted Sediment in New Bedford Harbor: A Case Study

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This case study involves the assessment and entombment of 10 feet of pure-phase tar currently impacting marine sediments associated with a Manufactured Gas Plant and Tar Processing Facility (“MGP”) in Massachusetts. Lightship Engineering personnel was selected to assess the nature and extent of tar and MGP residuals, conduct hydrogeologic modeling, complete human health and Stage I and II environmental risk characterizations, develop strategies for achieving regulatory closure and, design and implement the selected remedial alternative.

Alternatives to remediate the pure-phase tar in the boat slip included: capping; entombment; dredging; and solidification. Detailed cost and engineering evaluations were conducted to assess the technologic and economic feasibility of each option. Based upon the detailed evaluation, entombment using the Waterloo Barrier[®] system was selected as the best remedial option.

The project team has completed the design of the Waterloo Barrier[®] system and will complete installation in the Spring/Summer of 2005. The Waterloo Barrier[®] sheet piling will minimize the potential for water to migrate into or out of the boat slip. With the Waterloo Barrier[®] in place, boat slip will be filled to grade. A storm water collection system including a geotextile liner, and off-gas collection system including carbon treatment, will be installed within the filled boat slip.

Risk Assessment

Bioavailability Considerations in Risk Management Decision-Making

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Nicholas Basta, The Ohio State University, Columbus, OH

Jeffrey Bryan, Earth Tech, Inc., Bloomington, IN

Veronica Ewald, Earth Tech, Inc., Alexandria, VA

Leta Maclean, Earth Tech, Inc., San Diego, CA

Sarah Medearis, Earth Tech, Inc., Alexandria, VA

Susan Walter, Earth Tech, Inc., Oak Ridge, TN

Clint Zenigami, US Department of the Navy, Pearl Harbor, HI

Initial Risk-based Screening of Potential Brownfield Development Sites

Mary O'Reilly Brophy, New York State Department of Transportation/SUNY School of Public Health, Binghamton, NY

Ronald Brink, Broome County Department of Health, Binghamton, NY

Demystifying Dioxin Data for the Environmental Decision-Maker

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Bioavailability Considerations in Risk Management Decision-Making

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Bioavailability (BA), in a pharmacological context, is a fundamental and well-accepted phenomenon when assessing the therapeutic and toxic effects of a wide variety of chemicals. Despite this acceptance, the routine determination of BA in site-specific risk assessments in support of environmental remediation has been limited.

Using in-vitro methodology, we have determined the BA of arsenic in soil samples collected from a former foundry at the Pearl Harbor Naval Shipyard. The method is designed to simulate mammalian digestive processes and estimates the BA of contaminants detected in an environmental medium. The method, which has been verified with animal testing, is also a precise and cost effective alternative to performing BA tests using laboratory animals.

The foundry data show that the bioavailability of arsenic in soil can range from 20 to 70 percent relative to arsenic in a freely dissolved (i.e., 100% BA) state. In a remedial context, these data suggest that cleanup goals may be up to five times greater than default cleanup goals that do not incorporate site specific BA.

Unless widely and regularly evaluated in the site-specific risk assessment process, risk managers may be at a disadvantage, finding it difficult to incorporate BA routinely in their decision-making process. We suggest that the regular and standardized use of site-specific BA can help facilitate the decision making process; ultimately supporting the regulatory mandate to protect the public health.

Initial Risk-based Screening of Potential Brownfield Development Sites

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Brownfield redevelopment is sustainable only when it is a transparent process protective of public health. The objective the brownfield health risk assessment matrix is to provide a scientifically based, transparent process to evaluate human health risks on proposed redevelopment sites as well as a framework that can be critically evaluated by both environmentalists and the community in general. Public discussion and understanding of current health risk assessment, as well as the risks specific to each brownfield redevelopment site, are essential for an effective brownfield redevelopment program.

The Brownfields Redevelopment Program was started by EPA in 1995 and seeks to use already contaminated sites rather than contaminate even more greenfields. Two of the biggest difficulties are making redevelopment profitable and protecting human health. Traditional human health risk assessment evaluates single chemical exposures and identifies the level below which no adverse effect will occur to the most sensitive subgroups of the population. For cancer causing chemicals the risk must be lower than 1:1,000,000. When brownfield redevelopment sites are associated with high cost, extensive time and unmanageable uncertainty additional greenfield sites will become contaminated and the contamination on current brownfield sites will remain un-remediated.

The citizens' advisory group addressing brownfields in a southern New York county has developed a risk banding matrix to evaluate the uncertainty of the available data, the toxicity of the known or suspected contaminants and the likely exposure routes for each brownfield site in the county. The matrix categorizes sites as high, medium or low risk according to exposure groups. The risk matrix complements the triad approach currently being developed by EPA to identify and manage project decision uncertainties, addresses uncertainty as well as toxicity and has the potential to reduce the cost of traditional health risk assessment at brownfield redevelopment sites.

Demystifying Dioxin Data for the Environmental Decision-Maker

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What is the difference between low resolution and high resolution dioxin results? What are “EDLs” and how do they differ from a sample reporting limit? Do EDLs have uncertainty? If so, what is the source of the uncertainty and are the non-detected results usable for environmental decisions? Do detected dioxin results have uncertainty? Will this uncertainty affect the way the data can be used to make environmental decisions? What is the “TEQ” and how is it derived? These are basic, common questions that an environmental decision-maker might ask in reviewing dioxin results to compare to regulatory standards or to evaluate potential risk to human health. We will answer these questions and give key information concerning dioxin analysis and interpretation of results in terms of potential uncertainty that may bias the resultant data. Topics to be covered will include method issues that may affect bias in results, reporting limit uncertainties (where they come from and why this is a critical issue for data users), and homologues versus specific isomers in terms of toxicity interpretations. Recommendations to reduce dioxin data uncertainty will be given throughout the discussion.

Site Assessment

INL Wireless Sensor Platform

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Newer GPS Technology and its Application to Improved Site Characterization

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Passive Vapor Sampling- Advances in Vapor Concentration Capabilities

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What LSPs Don't Know about Site Characterization and Soil Management

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Michael Flynn, Precision Environmental Management Corporation, Billerica, MA

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Beneficial Use of C&D Recovered Screen Material in Residential Applications: A Case Study

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Dissolved Phase Bedrock Groundwater Contamination: Uniform or Depth-Stratified? A Case Study from Coastal Maine

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The Idaho National Laboratory (INL) is developing a versatile micro-power sensor interface platform for the purpose of periodic, remote sensing of environmental variables such as subsurface moisture, temperature, pressure, contamination, or radiation. The key characteristic of the platform architecture is that all platform components are inactive until energized by a remote power source, thus no internal power source such as a battery is required. Another characteristic is that the platform communicates via short-range telemetry, i.e. no wires need penetrate to the subsurface or through a barrier. Other significant attributes include the potential for a long service life and a compact size that makes it well suited for retrofitting existing structures.

Functionally, the sensor package is “read” by a short-range induction field that both powers/activates the sensor platform and carries sensor information via a response signal superimposed on the field by the embedded microprocessor. Although well suited for the intended application, this approach does have inherent limitations and/or tradeoffs. Those include a limited functional range as defined by the extent of the interrogating induction field and a power budget as defined by the onboard energy storage capacitors. Specific applications require tradeoffs between charge time (measurement cycle time), available power, and working depth. For example, an increase in required power to run sensors will result in either a reduced working depth and/or an increase in charge time.

Although the platform is being developed to address Department of Energy (DOE) long-term stewardship needs, it has the potential to address other monitoring applications where sensors must be buried beneath a surface that must not be penetrated by wires. Examples include applications where above ground sensors or wiring might be damaged by the weather, equipment, or personnel, or in areas where it may be desirable to avoid visual impact or conceal sensors to avoid theft or vandalism.

Newer GPS Technology and its Application to Improved Site Characterization

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This paper presents an innovative method combining global positions systems (GPS), historical aerial photographs and Microstation drafting software to determine the present location of a former potential release area. This is an economic and accurate method that has been proven to be cost effective in determining the correct locations for sampling. By accurately identifying the potential release areas, sampling and assessment are straightforward and streamlined. This approach was used successfully in the case studies described in this paper. The approach used is described below:

- Possible locations of staining/spills are identified on historical photographs;
- Benchmark locations to key the historical photographs are identified;
- The GPS unit utilizes recent field surveys to register the points in the photograph, using drafting and geo-reference software; and
- This manipulated electronic file is then installed in a data-logger within the hand-held GPS unit. The GPS unit is then carried to relative location of the historical aerial photo and in real time; the location of the historical photograph can be charted.

This is a visual field tool for complicated sites. The significance of this approach is that the end user can determine the present location of the former potential spill area depicted on a historical aerial photo in real time. Locations of potential sampling locations can be entered and seen in real time in the field. By using this method, locations of historically identified potential release areas are sampled with great assurances that the sample collections are conducted in the proper location. This method can save money by eliminating the repetitive sampling rounds that traditionally occur at many sites. This method was used successfully for the case studies discussed in this paper. The use of this methodology saved cost and time while at the same time provided sufficient evidence for regulatory concurrence.

Passive Vapor Sampling – Advances in Vapor Concentration Capabilities

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In recent years, vapor concentrations of organic compounds entering buildings, emanating from subsurface contaminant sources, have gained considerable attention from federal and state regulatory agencies. Active sampling techniques are commonly used for this type of site assessment and monitoring.

Passive sampling techniques present an effective alternative to active methods for sampling vapors in the vadose zone, beneath building slabs, in crawlspaces, and in other indoor and outdoor air environments. Most passive techniques are simple to install and operate, require no energy, and have no mechanical parts, and therefore minimal field sampling error.

The sorbent-based, vapor permeable membrane sampler, in particular, has been largely recognized for more than a dozen years as an accurate investigative tool for site assessment. As compared to discrete matrix sampling and active vapor sampling methods, the sampler is known to exhibit a greater sensitivity to a broader range of compounds while minimizing field sampling errors. Recently, methods to report organic vapor data in the parts per trillion range have been developed and applied to this vapor permeable membrane sampler. To provide an accurate estimate of the volume of air the sampler encounters, investigations have been performed to determine the sampler uptake rate.

The presentation will be a status update on the properties of the vapor permeable membrane sampler, along with the research and development of the vapor concentration capabilities and comparable datasets.

What LSPs Don't Know about Site Characterization and Soil Management

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There is a significant difference between site characterization needs to evaluate risks to the public health, welfare and environment under the MCP and evaluating soil conditions relative to future site development and disposal. Many property owners are shocked to discover that the site they thought was "Clean" turns out to be contaminated and in some cases turns out to contain hazardous waste despite having received a Response Action Outcome statement from their LSP. Even relatively sophisticated owners and consultants alike are sometimes caught off guard when the site they thought was adequately characterized for site development needs significant additional testing. The paper presents several commonly made mistakes made by land owners and consultants and LSPs when characterizing a site for future site development purposes. Several examples will be presented illustrating when a soil contaminant may be present which does not pose a risk to the public health, welfare or environment under the MCP but may still be characterized as a hazardous waste. Recommendations for incorporating soil management and disposal needs into the site design program are offered.

Beneficial Use of C&D Recovered Screen Material in Residential Applications: A Case Study

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Florida has established criteria and guidelines to encourage recycling and the use of recycled materials in a manner that protects public health and the environment. Recovered screened material (RSM) generated at a construction and demolition (C&D) debris recovery facility is a recycled material that can be reused in a variety of applications. In order to reuse RSM from a C&D facility, it is necessary to demonstrate that the material poses no significant threat to public health or the environment. The Sun Recycling LLC facilities in Broward and Palm Beach counties are C&D facilities, generating RSM (i.e., soil with wood, concrete, other particles of C&D debris) through mechanical separation using a screen ≤ 0.5 inch. The process generates RSM meeting state requirements for use in industrial, commercial and residential settings. RSM was used on dozens of lots in a residential development in Miramar, Florida to elevate low-lying areas (excluding building pads). In accordance with Broward County Environmental Protection Department (EPD) and Palm Beach County Department of Health (DOH) permits, the Sun facilities perform regular testing of RSM for arsenic. RSM tests showed arsenic concentrations below residential criteria. Quarterly testing did not detect VOCs, SVOCs, or pesticides. RSM was delivered to homesites and mixed with existing on-site soils (e.g., muck). Neighbors of some residents who received RSM raised concerns about contamination. To address concerns, the City of Miramar hired a consultant to collect and analyze samples for arsenic and total recoverable petroleum hydrocarbons (TRPH). Results of that testing indicated arsenic concentrations exceeding residential criteria. Further sampling and analysis of the RSM and local soils in the residential setting were performed by Broward EPD and Sun representatives. Results of arsenic and speciated TRPH analysis performed by the City of Miramar, Broward EPD, and Sun will be discussed. A consensus conclusion of acceptable conditions was reached by all parties.

Dissolved Phase Bedrock Groundwater Contamination: Uniform or Depth-Stratified? A Case Study from Coastal Maine

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Dissolved-phase transport of groundwater contaminants through crystalline bedrock fractures can be highly heterogeneous and challenging to conceptualize. Groundwater flow can be restricted to a discrete subset of connected bedrock fractures. Contaminant persistence may be influenced by matrix diffusion and dead-end fractures, while contaminant transport may not be well correlated with the degree of fracture-zone hydraulic activity. Whole-well sampling assesses the contamination in drinking water wells; however, discrete water sampling from isolated zones is crucial for developing an appropriate conceptual model of contaminant transport.

The case study area in coastal Maine is dominated by fractured volcanic and intrusive bedrock, present at or near the ground surface. Groundwater flow is restricted to fractures or faults within the bedrock. Chlorinated solvents from past operations have been detected in both monitoring and drinking water wells, and historic data collection over the past decade has been appropriately focused on whole-well sampling to ensure receptor protection. Chlorinated solvents have been detected in some whole-well samples at concentrations up to 3,000 micrograms per liter, whereas solvents have not been detected in several nearby locations.

Borehole geophysical surveys indicate that most wells have multiple, discrete hydraulically active zones that exhibit very different flow rates. Thus, the whole-well samples represent an average contaminant condition, combining information from different hydraulically active zones, depth, hydraulic head, orientation, and contaminant concentrations. Isolating and sampling discrete fracture zones with inflatable packers has allowed an assessment of contaminant transport pathways, a refinement of the conceptual site model, and a more direct evaluation of remedial options. An added benefit to the depth-discrete knowledge gained from this case study is the program efficiency and cost savings associated with excluding highly hydraulically active zones that are uncontaminated and focusing on only those zones that contain contamination.

Soil Geochemical Background on a Continental Scale

A Proposed Soil Geochemical Survey of North America

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Landscape Geochemistry on a Continental Scale

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The Geochemical Landscapes California Pilot Study

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Geochemical Modeling of Soil Parent Material Mineralogy

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A Proposed Soil Geochemical Survey of North America

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The U.S. Geological Survey, in collaboration with partners in Canada and Mexico, has initiated the Geochemical Landscapes Project with a long-term goal of a soil geochemical survey of North America. The resulting database will enhance our ability to recognize and quantify changes in soil composition caused by urbanization, industrialization, agriculture, waste disposal, and other human activities. The proposed sample design for the survey consists of a uniform grid of 10,000 sites across the continent. At each site, up to five samples would be collected: 1) the upper five cm; 2) O-horizon (if present); 3) a composite of the uppermost mineral soil; 4) the most representative B horizon; and 5) C-horizon. Analytical protocols include an extensive array of major and trace elements using ICP-AES and ICP-MS following a four-acid extraction to determine total elemental content. This would be supplemented by single-element determinations (Hg, Se, Sb) as well as determinations for total carbon, carbonate carbon, and total sulfur. An estimate of bioaccessibility will be made by a distilled-deionized water extraction and a simulated human gastric fluid extraction followed by ICP-MS. A limited number of organic compounds will be analyzed to study long-range transport of organic pollutants and the distribution of pesticides, PAHs, and their breakdown products. Selected samples will undergo microbiological characterization by a combination of phospholipid fatty acid analysis, BIOLOG analysis, agricultural and human pathogen screens, and enzyme assays.

The project is currently in a pilot phase to test and refine field and laboratory protocols. Sampling has been completed along two transects across the continent. One transect extends from northern Manitoba to the US-Mexico border. The other extends from just north of San Francisco to the Maryland shore. A regional-scale pilot study that is underway in an area of approximately 12,000 square miles in northern California will be completed in 2006.

Landscape Geochemistry on a Continental Scale

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The U.S. Geological Survey, Geological Survey of Canada, and Agriculture and Agri-Food Canada have completed a pilot study to test and refine sampling and analytical protocols for the proposed soil geochemical survey of North America. In 2004, soil samples were collected from 266 sites along two continental transects, one from northern Manitoba, Canada to El Paso, Texas, and a second along the 38th parallel from the Atlantic Ocean to the Pacific Ocean. The transects crossed multiple geologic, climatic, physiographic, land use, soil order, and ecological boundaries. This imposed rigorous field testing of sampling protocols across a broad range of conditions. Each transect was divided into approximately 40 km segments. For each segment, a 1 km wide latitudinal strip was randomly selected; within each strip, the most representative landscape and soil type was chosen as a potential sample site. At one in four sites duplicate samples were collected 10 meters apart to estimate local spatial variability. Samples from each sample site includes: 1) soils collected by horizon (O-, A-, C-horizons, where present) for multi-element four-acid and weak soluble extraction analyses and determination of soil texture, 2) A-horizon samples collected for soil moisture and microbiological characterization, and 3) topsoils collected from 0-5 cm for multi-element chemistry and determination of selected pesticides and other organic compounds. The *in situ* volumes of O- and A-horizon samples were measured so that elements loadings can be calculated. Geochemical results from soil analyses will be integrated in a site-specific descriptive database to identify relations between trace soil constituents and landscape and soil processes across North America.

The Geochemical Landscapes California Pilot Study

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The USGS Geochemical Landscapes project, which has as its long-term goal a soil geochemical survey of North America, is presently in a pilot study phase. The goals are to evaluate sampling and analytical methodologies for a continental-scale study and to explore the utility of regional soil baseline data. One pilot study is a latitudinal transect from Marin County north of San Francisco to the Nevada border in California. We have chemically analyzed nearly 2000 soil samples including 1300 shallow (upper 30 cm) soils collected in 1980 during the National Uranium Resource Evaluation (NURE) Program from El Dorado, Placer, Sutter, Sacramento, Yolo, and Solano Counties. The NURE samples are supplemented by 100 soil profiles from across the entire transect. Comparison of the NURE soil geochemical results with aeroradiometric K, U, and Th data show close agreement, giving us confidence that the NURE soil sampling is representative of surface soil chemistry. Several elements of potential environmental concern, including Cr, Ni, As, and Pb, occur at elevated concentration in the samples. Soils with high contents of Cr (up to 2700 ppm) and Ni (up to 2000 ppm) form both in the foothills of the Sierra Nevada Mountains above Cr and Ni-rich rocks such as serpentinite, and from transported materials in Sacramento Valley alluvial fill. Mineralogical composition and human impacts in soils from these two geologic settings may be important in determining mobilization and toxicity of the metals. Arsenic associated with the Mother Lode gold belt in the Sierra Nevada resulted in the highest soil As concentrations (>80 ppm) in the study area. Elevated Pb concentrations (up to nearly 2000 ppm) are recognized largely in proximity to highways and cities including both Sacramento and Stockton. We are presently conducting studies to determine the mineralogical residence and bioaccessibility of elements in these soil samples.

Geochemical Modeling of Soil Parent Material Mineralogy

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As a contribution to the pilot study for the proposed soil geochemical survey of North America, C-horizon soil samples were collected to investigate the potential for geochemical modeling of soil mineralogy. The samples were collected from 35 sites along the North Dakota - northern Manitoba segment of the continental transect. The samples represent geologically diverse soil parent materials, including glacial lake sediment and till derived from Canadian Shield and Phanerozoic sedimentary bedrock. The silt and clay-sized (<0.063 mm) and the clay-sized (<0.002 mm) fractions were separated by sieving and by wet centrifuge methods, respectively, and analyzed by XRF (fused pellet) and by ICP-OES after aqua regia digestion. Geochemical modeling of soil mineralogy is based on approaches developed by the Geological Survey of Finland. The procedure apportions the chemical elements to mineral groups predicted to be digested by aqua regia digestion and to those decomposed by fusion. The quantitative estimates of mineralogy are based on a simultaneous solution of multiple linear equations using a computer program (MODAN). The purpose of the study is to indicate geochemical differences among grain size fractions, including the <2 mm fraction analyzed for the pilot study, that may be due to mineral partitioning resulting from geological processes. The modeling will provide a basis to interpret soil geochemistry in terms of its mineralogy and potential environmental reactivity.

Tuesday, October 18, 2005

Poster Session- Arsenic

The Source of Arsenic in Bangladesh's Drinking Water

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Arsenic Remediation of Groundwater with Calcium Peroxide Background

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The Source of Arsenic in Bangladesh's Drinking Water

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The life expectancy in Bangladesh during the mid-1960s was only 46 years. Many premature deaths resulted from drinking surface water that was contaminated with bacteria causing diarrhea, cholera, typhoid, and other life-threatening diseases. Aid agencies, the Bangladesh government, and private individuals began installing approximately 10,000,000 tubewells to prevent these deaths by providing access to microbially safe groundwater for drinking. By 1995 Bangladesh had 120,000,000 people, approximately 97% of Bangladeshis drank tubewell water, and the life expectancy had increased to 55 years. Regrettably, this new source of drinking water was not tested for toxic metals. In 1993 chronic arsenic poisoning attributed to groundwater ingestion was first diagnosed. Currently, there are 2 major hypotheses about the source of this arsenic in Bangladesh's tubewell water. According to the first hypothesis, arsenic is initially associated with a poorly soluble pyrite mineral (FeAsS or FeS_2) that is underwater in a reducing environment. This arsenic is released when the pyrite is aerated by lowering the water table during groundwater pumping. According to the second hypothesis, arsenic is released into groundwater by the reductive dissolution of non-pyrite minerals and by the anion exchange of sorbed arsenate or sorbed arsenite. The arsenic, sulfide, sulfate, total sulfur, oxidation-reduction potential, ferrous iron, total iron, manganese, pH, chloride, and phosphate measurements from our 2 national-scale surveys of tubewell water in Bangladesh do not support the "pyrite oxidation" hypothesis. In contrast, these measurements strongly support the "reductive dissolution and anion exchange" hypothesis, which was initially proposed by our team in 1997. An evaluation of these 2 hypotheses using the results from our 2 national-scale surveys will be given.

Arsenic Remediation of Groundwater with Calcium Peroxide Background

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The treatment of arsenic chemistry in the environment involves redox transformations, precipitation reaction and adsorption onto particulates and surfaces. In oxidized environments (ORP > 100mV), As (V) is favored over As(III) and exists primarily as arsenic acids. Under reducing conditions (ORP <100 mV), As (III) is favored, typically as arsenious acids. Oxidation of As (III) to As (V) decreased arsenic toxicity and mobility.

As(V) adsorbs to surfaces more readily than As (III) and additionally can substituted for and incorporate into phosphate-containing minerals. As (V) has a strong affinity for the minerals hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3$) and ferric hydroxide. The strategy for removal of As is to first oxidize As to its +5 state, then remove the As (V) from solution via adsorption and precipitation reactions. Chemical oxidants including Potassium permanganate, calcium peroxide, and calcium hydroxide in concert with ferrous iron were evaluated. The results of the laboratory studies indicated that arsenic removal from groundwater is best facilitated by treatment with 0.55% calcium peroxide and 2000 mg/L Fe (II).

Subsequent to the laboratory tests and prior to the on site pilot test leaching tests were performed on composites of soil and ground water that were treated with the aforementioned treatment. The purpose of these tests is to provide an indication of the stability of the treated soil (i.e. will As and P be re-released from the soils as groundwater migrates through?)

Calcium peroxide and iron have been utilized in a pilot field trial to treat an arsenic plume. The initial results show mitigation of the arsenic in the plume. Results of the pilot test will be presented in this paper

Poster Session – Bioindicators of Environmental Health

Fish: Useful Bioindicators for Evaluation of Contamination in Water Ecosystems

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Fish: Useful Bioindicators for Evaluation of Contamination in Water Ecosystems

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Fish is one of the animal species, which is most often used as an environmental bio-indicator to monitor a level of hydrosphere pollution. The fish were taken during the years 2002 – 2004 from the water reservoirs Smradavka and Korycany located in the south-east part of the Czech Republic. Seven fish species were monitored. Fish tissues were analyzed for both heavy metals (As, Cd, Cu, Ni, Pb, Zn) and PCBs indicator congeners. Atomic absorption spectroscopy was used for heavy metals determination, high resolution gas chromatography with ECD⁶³Ni detection was used for PCBs determination. The levels of particular trace elements ranged as follows ($\mu\text{g}/\text{kg}$ fresh tissue): As 21.6 – 48.0, Cu 126 – 612, Ni 45 – 125, Pb 12.4 – 28.7 and Zn 3700 – 12500. The Cd concentrations were below the limit of determination (0.2). Levels of PCB congeners in fish were variable and did not seem to characterize any particular fish species. The highest values were found for the PCB 153 congener in bream, eel and pike ranging from 12.5 to 22.5 $\mu\text{g}/\text{kg}$ fresh tissue. The lowest concentration in all fish species was found for the PCB 52 congener ranging from 0.12 to 1.30 $\mu\text{g}/\text{kg}$ fresh tissue. The sum of PCB indicator congeners ranged from 9.10 $\mu\text{g}/\text{kg}$ fresh tissue (roach) to 53.9 $\mu\text{g}/\text{kg}$ fresh tissue (bream). The levels of PCB congeners are higher than the background in the Czech Republic (2 – 5 $\mu\text{g}/\text{kg}$ fresh tissue). The overall level of contamination in fish is low and the current limit for residues which is valid in the Czech Republic was not exceeded in any case.

Poster Session - Bioremediation

Biodegradation of Aromatic Compounds by *Halophilic archaea* Isolated from Hypersaline Environments

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Degradation of Hydrocarbons by Bacteria Isolated from Oil-Contaminated Sites

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Degradation of Low and Higher Molecular Weight PAHs by Soil Fungi Under Microaerophilic and Anaerobic Conditions

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Use of Chitosan as an Alternative Material for Immobilization of Microorganism

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Accelerated Bioremediation with Oxygen Release Compound-Advanced (ORC-Advanced™): Evolution of Time-Release Electron Acceptors

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Applications of Hydrogen Release Compound (HRC®) for Accelerated Bioremediation

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Microbial Dechlorination of Polychlorinated Dibenzo-*p*-dioxin/furan Congeners by a *Dehalococcoides* Containing Culture

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Efficacy of Bioremediation with Hydrogen Release Compound (HRC®) as a Replacement for a Pump and Treat System

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Rapid Biological Treatment of Residual DNAPL with Slow Release Electron Donor HRC-X[®]

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Contamination of Soil and Groundwater by Leaking Sewers

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

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Biodegradation of Aromatic Compounds by *Halophilic archaea* Isolated from Hypersaline Environments

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Produced water is salty wastewater that is produced in conjunction with oil or natural gas. For every barrel of oil produced, approximately 10 barrels of brackish or saline water is generated. Presently over 5 billion gallons a day of produced water is generated in the US. The saline content is high and the organic composition is very complex, varying widely in concentration, these constituents include salt (1,000 to 250,000 ppm), hydrocarbons, and, in some cases, heavy metals and trace elements. Thus, the treatment and disposal of produced waters is a challenging task, since the impact and toxicity on soils, vegetation, surface water and shallow ground water is high. The goal of this work was the isolation of halophilic archaea able to degrade hydrocarbons to be used in the treatment of produced water. Six hypersaline sites were tested for the presence of halophilic archaea able to metabolize aromatic compounds: the Uyuni Salt Marsh (Bolivia), the *sabkhas* in the Persian Gulf (Saudi Arabia), the Dead Sea (Israel and Jordan), and the crystallizer ponds in Cahuil (Chile), in Cabo Rojo (Puerto Rico), and in Segipe (Brazil). The strategy used for the enrichment and isolation of halophilic archaea able to grow in aromatic compounds was successful. Twelve strains able to grow in 1,2-benzoanthracene (2 mM) and 44 strains able to grow in p-hydroxybenzoic acid (10 mM) as the sole carbon and energy source were isolated. Strain MM17, isolated from a Dead Sea water sample, showed the best growth and was able to degrade benzoic (10 mM) and p-hydroxybenzoic (10 mM) acids after 200 h of cultivation. Biochemical and genetic analyses of the isolates, together with the analysis of polar lipid profiles, indicate that the strains belong to at least two different genera: *Haloferax* and *Halobacterium*. These strains are now being used on biodegradation studies of hydrocarbons in produced waters.

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Degradation of Hydrocarbons by Bacteria Isolated from Oil-Contaminated Sites

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Crude oil contains mutagenic, carcinogenic, growth inhibitory compounds, which can cause severe damage to aquatic and terrestrial environment. It is estimated that 0.08–0.46% of the total oil production is wasted to the environment, eventually causing pollution to waters and shores. Several petroleum aliphatic and polycyclic aromatic hydrocarbons (PAHs) can act as source of carbon and energy for the growth of microorganisms. (PAHs) are relatively resistant to biodegradation and can therefore accumulate to substantial levels in the environment. Since some of the larger species are carcinogenic, they can present a significant health hazard. Bacterial strains were isolated from soil samples contaminated with petroleum derivatives collected near Paulinia's petroleum refinery in Campinas (SP, Brazil). They were cultivated for 12 days at 30° C and 150 rpm, in a medium containing minerals and 0.05% (final concentration) of one of the following hydrocarbons: tridecane, tetradecane, pristene, hexadecane, phenyldecane, phenanthrene, naphthalene, pyrene and benzo[a]pyrene. The production of biosurfactants, via the determination of emulsification activities and reduction of surface tension, toxicity of the supernatants and also degradation of the hydrocarbons via gas chromatography were determined following growth of the bacteria. A *Bacillus sp* degraded up to 90% of the hydrocarbons present in the medium and toxicity ($CE_{50} = 4.90\%$), which was the second lowest among all the strains tested. It was also able to reduce the surface tension and produce some emulsification activity. A *Enterobacter aerogenes* strain degraded up to 83% of all the hydrocarbons present in growth medium and produced the lowest toxicity ($CE_{50} = 13.10\%$), and was also able to reduce the surface tension of the culture medium. The ability to produce surface active agents, which help the uptake of insoluble substrates, to degrade various aliphatic and aromatic hydrocarbons, suggest that these strains have potential to be applied in bioremediation of petroleum contaminated sites.

We acknowledge financial support from FAPESP-SP, BRAZIL.

Degradation of Low and High Molecular Weight PAHs by Soil Fungi under Microaerophilic and Anaerobic Conditions

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Polycyclic aromatic hydrocarbons (PAHs) are pollutants originated from incomplete combustion of organic matter and fossil fuels or accidental spills during petroleum transportation. These recalcitrant compounds can be carcinogenic and constitute risk for human health. Ligninolytic fungi are natural degraders of lignin, and can also degrade structurally related compounds such as PAHs and other aromatic compounds due to the action of unspecific enzymatic system composed of peroxidases and phenoloxidases, such as Lignin-Peroxidase (LiP), Manganese-Peroxidase (MnP), Laccase (Lac) and Tyrosinase (Tyr). Degradation of PAHs by microorganisms is hindered under low oxygen levels or anaerobic conditions since the absence of oxygen inhibits primary cleavages of the aromatic compounds. In this work the ability of five ligninolytic soil fungi to degrade various molecular weight PAHs (by HPLC), was determined during a 30-day period under microaerophilic and anaerobic conditions. The ligninolytic enzymes produced were also investigated. Naphthalene and phenanthrene (0.5%wt/vol), crysene, perylene, naphthol [2,3-a] pyrene and decacyclene (0.05%wt/vol) were used as carbon sources in a medium containing minerals, vitamins and an oxygen-reducing system (L-cysteine-hydrochloride and resazurin). The inoculated Erlenmeyer flasks were placed into hermetic jars containing Microaerobac® or Anaerobac® plates and incubated at 30°C. Under microaerophilic conditions, laccase activities were more frequent in the medium containing naphthalene and phenanthrene; and LiP activities on decacyclene. The highest values of MnP (11 - 28 U/L.min⁻¹) were detected on perylene. *Aspergillus* sp was able to degrade all the PAHs used (25 - 46.5%). *Achremonium* sp was the best degrader of the low molecular weight (LMW) PAHs: naphthalene (32%) and phenanthrene (20%). *Verticillium* sp showed the greatest degradation of the HMW PAHs: crysene (30%), perylene (25%), naphthol [2,3-a] pyrene (40.5%), and decacyclene (37%). Under anaerobic conditions, maximal laccase activities (0.16 - 0.54 U/L.min⁻¹), were detected on the 30th day for the HMW PAHs. *Trichocladium canadensis* was capable to degrade all PAHs (10 - 22.1%). Strain H2 (an unidentified basidiomycete strain), showed best degradation for naphthalene (19.7%), perylene (17.9%) and naphthol [2,3-a] pyrene (12.4%). These results indicate that ligninolytic soil fungi can degrade PAHs under low oxygenation conditions or in the absence of oxygen, and that their ligninolytic enzymes are produced under such conditions and may be involved in the degradation of PAHs.

Acknowledgment: We thank CNPq (Brazil) for financial support.

Use of Chitosan as an Alternative Material for Immobilization of Microorganism

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Immobilization of organism technique has been used in wastewater treatment for decades to achieve high biomass level, which results in high rate of contaminant degradation. Recently, a similar approach has been proposed for groundwater remediation. The proposed biological permeable barrier uses biocarrier as the reactive material instead of zero valent iron to degrade organic contaminants. While the technique is widely used for environmental issues, traditional materials (e.g., PVA and PEG) are non-biodegradable and require post treatment or disposal after replacement. In particular, replacing the reactive material in permeable barriers is costly and time consuming. Thus, developing an alternative biocarrier, which can be biodegraded and refilled instead of replaced, would be vital to environmental applications, especially for permeable barriers. In this study, *Pseudomonas putida* was encapsulated or immobilized with chitosan which is a naturally existing polymer and the efficiency in degrading phenol and cometabolizing trichloroethene (TCE) were tested. The mechanical strength of the chitosan beads was modified by choosing different crosslinking agents and by adjusting several parameters during the making process. The chitosan beads can sustain for months in column tests without obvious structural breakdown. In batch tests, the acclaimed chitosan beads can remove 99% of phenol at phenol initial concentrations ranging from 100 to 1000 mg/L. Similar tests for cometabolism of trichloroethene showed 50 to 80% removal at TCE initial concentrations ranging from 100 to 1000 µg/L. However, the pH value of the batch systems was found to be critical to the effectiveness of biodegradation. Presumably, the influence of pH is due to the neutralization of surface charge of the beads. Furthermore, the surface structure of the bead can be more porous through proper control of ionic strength and constituents of the bead formation solution. The mass transfer of substrate may be improved by using the chitosan beads of porous surface structure.

Accelerated Bioremediation with Oxygen Release Compound-Advanced (ORC-AdvancedTM): Evolution of Time-Release Electron Acceptors

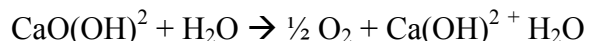
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Oxygen is typically the limiting substrate for microbes capable of aerobically biodegrading contaminants, such as petroleum hydrocarbons, gasoline oxygenates, and certain chlorinated solvent daughter products. Without adequate oxygen, contaminant degradation will either cease or will proceed by a much slower anaerobic rate. Oxygen Release Compound-Advanced (ORC-AdvancedTM) is a state-of-the-art solid oxygen source for stimulating in situ aerobic bioremediation. ORC-Advanced is white powder composed of a proprietary, high oxygen-yielding calcium oxyhydroxide compound. When hydrated, ORC-Advanced is designed to release its full amount of oxygen (17% by weight) consistently over a 12 month period. This process enables aerobic microbes to significantly accelerate rates of bioremediation over longer periods of time.

ORC-Advanced is a proprietary formulation of calcium oxyhydroxide, and, as shown next, releases oxygen and forms simple calcium hydroxide as a by product.



ORC-Advanced has been engineered with Controlled Release Technology (CRTTM), which retards the hydration of the calcium oxyhydroxide crystal and slows the formation oxygen in and its release from the crystal structure. The CRT chemistry prevents premature and rapid release of oxygen that can lead to uncontrolled bubbling and oxygen waste via “blow off” prior to injection into a contaminated aquifer. CRT involves the intercalation (permeation) of phosphate into the crystalline structure of calcium oxyhydroxide.

ORC-Advanced has been tested in the laboratory for oxygen release characteristics and has been injected for aerobic bioremediation at several field sites. This presentation will discuss the chemistry of ORC-Advanced and show laboratory and field results.

Applications of Hydrogen Release Compound (HRC[®]) for Accelerated Bioremediation

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Hydrogen Release Compound (HRC[®]) is a food-grade, polylactate ester that, upon being deposited into an aquifer, slowly releases lactic acid for 12 to 18 months, creating the anaerobic conditions necessary for biodegradation of chlorinated solvents and many other contaminants. Fermentation of lactic acid from HRC by native bacteria produces a series of organic acids and results in the production of molecular hydrogen. Molecular hydrogen is an extremely efficient electron donor for a wide range of reductive biodegradation processes. The material is applied to the aquifer by push-point injection or backfill-auguring and can be applied in grid, barrier, or excavation formats. HRC is typically recommended for treatment of chlorinated solvent contamination found in the dissolved phase or sorbed to saturated soil. However, bioremediation can facilitate removal of residual source or DNAPL material at some sites. In addition to chlorinated solvent biodegradation, HRC has been used for bioremediation of explosives, perchlorate, chlorinated pesticides, and nitrate. HRC has been applied over 600 times since 1997, making it the most widely-used electron donor for accelerating bioremediation. This presentation will give case histories and discussions of lessons learned.

Microbial Dechlorination of Polychlorinated Dibenzo-*p*-dioxin/furan Congeners by a *Dehalococcoides* Containing Culture

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Dehalococcoides ethenogenes strain 195 dechlorinates chloroethenes and a variety of chlorinated aromatic compounds, including 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (1,2,3,4-TeCDD). The ability of *D. ethenogenes* strain 195 to dechlorinate different polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) congeners was investigated. Dechlorination of 1,2,3,4-TeCDD, octachlorodibenzo-*p*-dioxin (OCDD) and 1,2,3,4,7,8-hexachlorodibenzofuran (1,2,3,4,7,8-HxCDF) was examined in a mixed culture containing *D. ethenogenes* strain 195. An individual PCDD/F congener served as a sole electron acceptor in one triplicate bottle set while tetrachloroethene (PCE) and 1,2,3,4-tetrachlorobenzene (TeCB) were added as growth co-substrates along with the PCDD/F congener in another two sets of triplicate bottles. 1,2,3,4-TeCDD was added at 31 μM. OCDD and 1,2,3,4,7,8-HxCDF were added at 5 μM. PCE and TeCB were added at 25 μM. Butyrate (0.1 mM) was added as an electron donor periodically. The mixed culture dechlorinated 1,2,3,4-TeCDD at similar rates both with and without the addition of PCE in original fully-grown cultures and in the first generation transfer bottles which received 10 % v/v inoculum. A pentachlorodibenzofuran congener was detected in all three sets of HxCDF-amended cultures within 1 month. Cultures with TeCB as co-substrate exhibited the most extensive HxCDF dechlorination with production of a tetrachlorodibenzofuran congener within 2 months. No dechlorination products were observed from OCDD within the same time period. The results suggest that PCE co-amendment is not needed to sustain 1,2,3,4-TeCDD dechlorination. Furthermore, *D. ethenogenes* strain 195 could dechlorinate a PCDF congener containing chlorines on both rings. This suggests that this strain may have utility in dechlorinating environmentally relevant PCDD/F congeners.

Efficacy of Bioremediation with Hydrogen Release Compound (HRC®) as a Replacement for a Pump and Treat System

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A pump and treat system was installed in 1985 at a chlorinated ethene contaminated industrial site in California. However, after eleven years of operation, the removal of chlorinated ethenes from groundwater was no longer cost effective. Bioremediation with Hydrogen Release Compound (HRC®) was chosen to replace the pump and treat system, with the intent of cost-effectively accelerating the natural attenuation of the remaining chlorinated ethene contamination.

HRC is a polylactate ester that, upon hydration or microbial cleavage of its ester bonds, slowly releases lactate. Lactate serves as an electron donor and carbon source for microbial reductive biodegradation. HRC is a viscous, amber-colored liquid that is typically injected into a contaminated aquifer using direct push technology or backfill injection via a hollow stem auger. Once in place, HRC creates a plume of lactate and its fermentation products (dissolved hydrogen and other organic acids) downgradient of the injection area and serves to accelerate the anaerobic bioremediation processes that transform chlorinated ethenes to innocuous daughter products, like ethene.

At the California site, tetrachloroethene (PCE) and trichloroethene (TCE) concentrations were reduced by over 97% and 98% respectively in the HRC impacted wells. In a well located in the HRC injection grid, contaminants included TCE, cis-1,2-DCE (dichloroethene), and VC (vinyl chloride). Following the cessation of pumping, concentrations of chlorinated ethenes spiked to elevated levels in this well; however, the subsequent HRC application resulted in the reduction of all chlorinated species. For example, TCE was reduced from 480 ug/L to 4.4 ug/L, which is below the federal TCE MCL of 5 ug/L. Complete reductive dechlorination was achieved, with production of 280 ug/L of ethene. Replacement of the pump and treat system with bioremediation not only resulted in the reduction of contaminant concentrations, but a 75% decrease in annual remediation costs. This presentation will give a detailed site analysis, including product performance results and costs.

Rapid Biological Treatment of Residual DNAPL with Slow Release Electron Donor HRC-X[®]

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The use of in situ bioremediation to stimulate the rapid dissolution, desorption, and biodegradation of residual DNAPL has been demonstrated in the laboratory and in well-documented field studies. Biodegradation of dissolved-phase contaminants increases the partitioning and subsequent biodegradation of residual DNAPL to the aqueous phase by (1) increasing the concentration gradient and driving force for dissolution and desorption and (2) increasing the overall solubility of the DNAPL by production of hydrophilic daughter products.

Specifically, the application of the slow release electron donor substrate, Hydrogen Release Compound-Extended Release (HRC-X[®]), has been successful in remediating high concentrations (>100 mg/L) of chlorinated ethenes, like PCE and TCE in residual DNAPL environments. In situ bioremediation with HRC-X is a low-cost method for residual DNAPL removal and avoids the costly and lengthy assessment associated with defining the exact location of the dispersed residual DNAPL.

HRC-X is a highly concentrated electron donor for bioremediation and has a field longevity of at least 3 years, as verified by field measurements of lactate and its derivative organic acids. Injection of HRC-X directly into the general residual DNAPL area of a contaminated aquifer results in the continuous release of lactic acid and fermentation of the lactic acid to hydrogen in and downgradient of the injection area. Hydrogen from HRC-X is used as an electron donor for reductive dechlorination, which results in dissolution of residual DNAPL and desorption of sorbed contaminants.

This presentation includes a description of HRC-X, as well as the mechanisms by which chlorinated ethene contaminants are dissolved, desorbed, and degraded. Laboratory studies showing the effect of biodegradation on DNAPL longevity and case histories describing successful field applications of HRC-X, including total project costs, will also be presented.

Contamination of Soil and Groundwater by Leaking Sewers

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Many sewers in most European countries are more than 50 years old. Leakages as high as 15 – 25 % of the total amount of sewage in different countries were reported. However, the German soil protection law does not allow to pollute the soil or the underground with any pollutants, including sewage. We investigated the fate of sewage, that trickles from leaky sewers into the unsaturated soil and from there into the groundwater.

Normally, at more than 3 m depth below the surface, there is not much oxygen available for aerobic respiration of sewage compounds. At 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 exceed the 92 – 94 % 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 randomly to some extent 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 biofilm during trickling of sewage. Never-the-less, more microorganisms leave the sandy soil after 125 cm trickling stretch than allowed 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 indigenous soil flora such as pseudomonads or *Streptomyces* 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 are part of a DFG-project, embedded in an ongoing interdisciplinary research group on “Risk potential of sewage from leaky sewers for soil and groundwater” at the University of Karlsruhe, funded by Deutsche Forschungsgemeinschaft and coordinated by me.

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 ubiquitous pollution with tetraalkyllead (TAL) compounds and derivatives. For gasoline production in 1970 in the United States of America 279000 metric tons of organolead were consumed. Another 326000 metric tons of organolead compounds were added worldwide to improve gasoline. Since the 1980's the TAL in gasoline was replaced by methyl-tertiary-butylether (MTBE). In future the MTBE in unleaded gasoline shall be replaced by ethanol.

Whereas an ubiquitous 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 $3.5 \times 10^{-4} \text{ m s}^{-1}$. On average, groundwater saturation starts about 3 m below the soil surface and the flow velocity is about 70 m year^{-1} . No oxygen is found in the groundwater downstream of the industrial site.

Spillage of tetraethyl lead (TEL) and tetramethyl lead (TML) led to severe soil and groundwater contamination at all TEL manufacturing sites and at gasoline distribution stations not only in Germany, but also in other gasoline producing countries. During the regular production process volatile alkyl lead compounds were absorbed from the off-gas of TEL or TML production sites in 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 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 (succeeded by immobilisation of the Pb-ions to PbCO_3 or $\text{Pb}_3\text{PO}_4\text{Cl}$) reduces the environmental risk.

At suitable conditions chemical and microbiological transformation of alkyl lead to inorganic lead may lead to 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, glass columns (volume = 10.2 l) were filled with TEL contaminated soil (~ 300 mg TEL/kg soil and ~ 530 mg oil hydrocarbons/kg soil) from a TEL/TML-manufacturing site and dealkylation activity was monitored. In each of three parallel columns oxygen-saturated water (< 30 mg O₂/L, saturated with pure oxygen) or oxygen-saturated water containing a mineral mix (to supply essential minerals for the microorganisms) was circulated to improve the conditions for the autochthonic 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 respiration 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. Microorganisms survived the alkyllead toxicity and the poor supply with nutrients and a suitable carbon source.

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. From groundwater wells, drilled in flow direction of the groundwater at the downstream end of the industrial area, groundwater, which still contained low levels of tri- and di-alkyllead compounds, was pumped out and re-infiltrated at the upstream end of the area for final purification.

Poster Session- Heavy Metals

Heavy Metal Fractionation in Roof Run-Off In Ile-Ife, Nigeria

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Environmental Cleanup Technology in Industrialized and Transportation Districts of Inorganic Pollutants in Aquatic South Texas

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J.J. Hernandez, Texas A&M International University, Laredo, TX

Characterization, Speciation and Remediation of Lead in Urban Garden Soils

Heather Clark, Wellesley College, Wellesley, MA

Rachel Erdil, Wellesley College, Wellesley, MA

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Establishing Baseline Concentrations of Trace Metals at an Old Landfill

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Justine Cook, The Richard Stockton College of New Jersey, Pomona, NJ

Robert Fromtling, The Richard Stockton College of New Jersey, Pomona, NJ

Tait Chirenje, The Richard Stockton College of New Jersey, Pomona, NJ

Remediation of Heavy Metals Contaminated Sediments by Stabilization/Solidification Technology

Gianluca Intini, Technical University of Bari, Taranto, Italy,

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

David Moreels, Brookhaven National Laboratories, Upton, NY

Safiyh Taghavi, Brookhaven National Laboratories, Upton, NY

Craig Carafola, Brookhaven National Laboratories, Upton, NY

Jeff Fitts, Brookhaven National Laboratories, Upton, NY

Daniel van der Lelie, Brookhaven National Laboratories, Upton, NY

Treatment of Heavy Metals in Stormwater Using Wet Pond and Wetland Mesocosms

Swarna Muthukrishnan, U.S. Environmental Protection Agency, Edison, NJ

Effects of Class B Sewage Sludge Applications on Agricultural Fields in Northwest Ohio

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Lead and Reactive Sulfide Stabilization in Soil: Lessons Learned

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Ronald Richards, Shaw Environmental and Infrastructure, Stoughton, MA

Modeling the Competitive Effect of Phosphate, Sulfate, Silicate and Tungstate on the Adsorption of Molybdate onto Goethite

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Heavy Metal Fractionation in Roof Run-Off In Ile-Ife, Nigeria

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Runoff samples were collected from three different commonly used roofing materials in Ile-Ife, Nigeria. Some water parameters like pH, Temp, TDS, Cl⁻, SO₄²⁻, PO₄²⁻, NO₃⁻ and EC were determined in the samples. Five Heavy metals both as regards total, dissolved and particulate fractions were also analysed. The quantity of these parameters varies with different roofs. In terms of dissolved metals, the concentration (mg l⁻¹) decrease in this order of magnitude Fe>Zn>Cr>Pd>Cd for all the roofs investigated. The tendencies of the roofing materials to leach dissolved metals are arranged as follows: Zn and Cr (metal sheet>asbestos>ceramic); Fe (metal sheet>ceramic>asbestos); Cd (asbestos>metal sheet>ceramic) and Pb (asbestos>ceramic>metal sheet) while those of the particulate metals are: Cd and Pb (asbestos>ceramic>metal sheet); Cr (ceramic>asbestos>metal sheet); Zn (ceramic>metal sheet>asbestos) and Fe (metal sheet>ceramic>asbestos). For all the roofs, both the particulate and dissolved metals except Zn exceed their WHO permissible limits for drinking water. These high levels of the metals may likely result in consumer complaints since some of the metals are not only carcinogenic but may also impact bad taste in water. Direct discharge of the runoff could have toxic effects on natural waters and their local infiltration would rapidly lead to soil contamination. Result of spiking experiments with the runoff samples showed good recoveries for all the metals analysed. Blank determinations were done for background corrections.

Environmental Cleanup Technology in Industrialized and Transportation Districts of Inorganic Pollutants in Aquatic South Texas

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Source pollution by inorganic pollutants is a manifestation of industrialized districts and urbanized areas. Recently we have identified that freshwater sources in the Laredo region of southern Texas is an aspect of the transportation, civil and military defense, tourism and commerce industries that make up the region. Environmental cleanup technology is a field of environmental science and chemistry that is an emergent and dynamic field. The removal of inorganic pollutants such as lead(II), cadmium(II), mercury(II), and silver(I) from aquatic areas and media using silica-based materials are currently being employed. The use of silica-based and clay-based porous composites in the uptake and removal of inorganic particulate matter from freshwater resources such as lakes and rivers which border Mexico will be investigated.

Characterization, Speciation and Remediation of Lead in Urban Garden Soils

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Gardening is an important element of community life and food security in the urban communities of Roxbury and Dorchester, MA that is threatened by extensive lead contamination of area soils. Our lab has formed a partnership with The Food Project, a community organization that promotes sustainable and organic agriculture, and we have been able to form relationships with many local residents to educate members of the community about the health of their soil and the potential risks they face as a result of their interactions with the soil. We have used field portable x-ray fluorescence to test over 500 soil samples and have found that 90% of samples contain concentrations of lead greater than the MA Department of Environmental Protection (MA-DEP) reportable level of 300 $\mu\text{g/g}$ lead in soil. The principle goals of our research are to: 1) characterize the spatial variability of the lead at the neighborhood scale, 2) fingerprint the sources of lead in the gardens, 3) assess the chemical speciation and bioavailability of lead and 4) devise and test a phytoremediation scheme for the area. We are using textural-analytical approaches coupled with trace element ratio analysis and lead isotope analysis to evaluate the mass balance and geochemical characteristics of the lead found in garden soils. Preliminary results indicate that lead concentrations are highest in the finest particle size of soil and that lead is often associated with an identifiable suite of trace elements. Initial observations suggest that point and non-point sources, including lead-based paint chips and particulate matter from leaded gasoline, contribute to the overall soil lead burden. Phytoremediation data is still inconclusive but eight gardens of test crops are currently being planned with sunflowers, collards and mustards as heavy-metal hyperaccumulators. A detailed geochemical assessment of lead in urban garden soils will provide insight into the severity of lead contamination in this high exposure setting and help to design a successful remediation scheme.

Establishing Baseline Concentrations of Trace Metals at an Old Landfill

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Old Buzby Brothers landfill was an active waste disposal site from the late 1950s until the late 1970s—receiving waste from over forty companies and municipalities. Voorhees Township owns approximately 57 acres, which they have decided to develop after remediating the site. Based on data gathered from the site, the township developed an end use plan which includes gardens, an amphitheater, office building, children's play area, bird sanctuary, and open land with trails. The NJDEP, however, has expressed concern regarding the extent of pollution and the possibility of mercury and other trace metal contamination in the Kirkwood-Cohansey aquifer. We will collect soil samples from sites chosen based on the proposed end land use map. These samples will establish baseline concentrations of trace metals and nutrients. Eight onsite sample locations were chosen because their proposed uses have the potential to affect soil quality. Soil samples will be sieved, digested and analyzed for arsenic, copper, chromium, cadmium, selenium, manganese, nickel, and lead using USEPA procedures. Other parameters to be measured include pH, EC and organic carbon. Preliminary testing on site has already detected elevated levels of benzene, mercury, arsenic, and other agents. We expect to find elevated levels nutrients in areas designated for lawns but the distribution of trace elements will depend on the intensity and type of construction activities on the site. Our study will also help NJDEP's concerns on whether the concentrations of some of the aforementioned chemicals are decreasing with time due to natural processes, such as rainfall. Establishing baseline concentrations of trace metals at Buzby Landfill will contribute in assessing the public health risk from the developed areas of the former landfill. Additionally, these values will act as a yardstick against which future changes in soil chemistry can be measured.

Remediation of Heavy Metals Contaminated Sediments by Stabilization/Solidification Technology

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The most widely used procedure for reducing the contamination effects of marine sediments is dredging and disposal of material in controlled dumps. This method is becoming impracticable because it is increasingly difficult to find adequate space. This study was carried out to design an effective treatment method for heavy metals contaminated sediments using stabilization/solidification (S/S) technology. In particular, experimental investigation on laboratory scale has been carried out to highlight the effect of organic pollutants (PAHs) on the hydration kinetics, physico-chemical properties and leaching behaviour of cement-based solidified materials. To better understanding S/S process, both artificially spiked and field samples of Taranto harbour sediments contaminated by heavy metals and PAHs were treated with different kinds of cement and water/cement/sediment ratios. The results of laboratory tests indicated that the treatment of sediment requires an increase of water/cement ratio, due to its remarkable presence of fine fraction. A good immobilization of copper, lead and nickel after only seven days of curing, due to high Ph values (8-9) and percentage of silica (approx. 15% in weight) in harbour sediment, limiting metals leaching from solidified matrix was observed. Moreover the presence of organic compounds implied a negative effect on the cement hydration, retarding setting time. In conclusion the experimental results generally show that cement based stabilization/solidification process is capable of successfully treating marine sediments contaminated by heavy metals and PAHs. With its proven effectiveness in pollutants immobilization this technology is promising for large-scale application.

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

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Uranium (VI) is the most common radionuclide contaminant found within the U.S. nuclear weapon complex at the Oak Ridge Reservation Field Research Center (ORR FRC), which is managed by the U.S. Department of Energy. Nitrate is often a co-contaminant with U(VI) in subsurface environments because of the use of nitric acid in the processing of U(VI) waste. Previous studies of microbial U(VI) reduction in sediments indicate that no net U(VI) reduction occurs until nitrate is reduced. Many Fe(III)-reducing and sulfate-reducing bacteria such as members of the *Geobacteraceae* and *Shewanellae* families possess the ability to reduce nitrate. However these organisms are known to be inhibited by the presence of heavy metals such as nickel, which frequently contaminate these sites. Several nickel resistance determinants have been identified in *Ralstonia eutropha* strains isolated from different biotopes which are heavily polluted with heavy metals. Loci on plasmids isolated from strains *R. eutropha* 31A and *R. eutropha* KTO2 were found to mediate high-level (*ncc*) and low-level (*nre*) nickel resistance. Taghavi *et al.* introduced these Ni resistance markers into mini-Tn5 transposons vectors. These *nre*-based minitransposons were found to have a broad expression range and were successfully used for constructing Ni-resistant transconjugants of bacteria belonging to the families of α -, β -, γ -*Proteobacteria*. In this study the feasibility of applying natural gene transfer to improve the performance of natural bacterial communities concerning uranium reduction under conditions imposed by metal stress is demonstrated, using Ni toxicity and resistance as a model system.

Treatment of Heavy Metals in Stormwater Using Wet Pond and Wetland Mesocosms

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Urban stormwater runoff is a significant source of suspended sediments and associated contaminants, including heavy metals, to receiving waterways. These metals are either dissolved or bound to particulates (coarse - $>75 \mu\text{m}$; fine particulates - $<75 - 1 \mu\text{m}$; colloids - $<1 \mu\text{m}$). Information on the particulate association of heavy metals in stormwater is a critical requirement prior to using pond and wetland best management practices (BMPs) as stormwater treatment controls. Heavy metals in stormwater are primarily removed by sedimentation in structural BMPs, and these sediments may be toxic to benthic invertebrates and aquatic microorganisms. The proposed research will be conducted at U.S. EPA's Urban Watershed Research Facility (UWRF) in Edison, NJ to evaluate the effectiveness of pond and wetland BMP mesocosms to remove heavy metals from stormwater runoff. The runoff draining from roofs and parking lots of the adjacent county college will be investigated. Seven heavy metals (Cu, Zn, Pb, Cr, Fe, Al, and Mn) will be investigated based on results from an earlier screening procedure (August 2004) on stormwater runoff in the same location. The research objectives include: (i) characterizing the association of heavy metals with fine particulates (20 to $0.4 \mu\text{m}$) in stormwater runoff; (ii) evaluating the relative removal of particulate-bound as well as dissolved heavy metals in wet pond and cattail wetland mesocosms; and (iii) investigating the solid-phase chemical associations of heavy metals in cattail wetland sediments by selective sequential extraction procedures and thereby assessing the potential for sediment toxicity and heavy metal bioavailability. The project will commence in March 2005, and two actual rain events per season (winter, spring, summer, and fall) will be sampled in order to determine any seasonal variability in stormwater heavy metal-particulate associations. Wetland sediments will be sampled twice; at the start and after the completion of the stormwater sampling events.

Effects of Class B Sewage Sludge Applications on Agricultural Fields in Northwest Ohio

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Application of sewage sludge, or biosolids, on agricultural fields has been considered by many to be a cost-effective means of waste disposal while simultaneously acting as a cheap, productive fertilizer. However, the effects of such application are not fully known. Our study investigates three main areas of concern regarding this practice in Northwest Ohio: heavy metals, nitrates and total organic carbon. The study is being conducted on an agricultural field in Oregon, Ohio that receives Class B sewage sludge from a nearby sewage treatment facility. Samples were collected at three depths from forty-seven sampling locations throughout the field prior to sludge application and at intervals following application. The effects of application over time, at the different depths and during different seasonal conditions will be evaluated. A control field possessing similar soils and crop rotation activities but no history of sludge application has also been included. Samples are currently being analyzed. Spectral readings have been collected and will be compared with Landsat-7 imagery to assess whether remote sensing can be utilized as a tool with regards to the application of sewage sludge. Results from the first year of the study will be presented. A “sister” study is being conducted by Dr. Robert Vincent at Bowling Green State University for comparison.

Lead and Reactive Sulfide Stabilization in Soil: Lessons Learned

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A Site in greater Boston with a variety of contaminants of concern (including polycyclic aromatic hydrocarbons, mercury, lead and petroleum hydrocarbons) was undergoing redevelopment. To complete construction, large quantities of soil needed to be removed from the site and disposed of or reused in accordance with state and federal regulations. Two contaminants of concern, lead and reactive sulfide, were particularly of concern for on-site stabilization prior to disposal, due to the large cost differential between disposal as a hazardous waste and on-site treatment with off-site disposal subsequent to treatment. The paper details the subcontractor process of on-site soil stabilization for soils that originally had concentrations of TCLP Lead greater than 5 milligrams per liter (mg/L) and reactive sulfide concentrations above 500 milligrams per kilogram (mg/kg). The process of characterization of this site is described, which allowed for soil segregation allowing soil not requiring treatment being transported off-site through a load and go operation and the soil to be stabilized using on-site stockpiling with subsequent treatment in accordance with the Massachusetts Department of Environmental Protection (MADEP) and United States Environmental Protection Agency (EPA) regulations. The treatment process is detailed including an overview of the chemistry of both the lead stabilization and the neutralization of the reactive sulfide and comparison results provided. The paper discusses how the use of on-site stabilization leads to significant cost savings. In addition, lessons learned are described along with recommendations for developing work plans for this type of work.

Modeling the Competitive Effect of Phosphate, Sulfate, Silicate and Tungstate on the Adsorption of Molybdate onto Goethite

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Competitive adsorption amongst anions affects the partitioning and transport of anionic solutes in subsurface and surface waters. To enable the prediction of molybdenum distribution within natural anoxic environments, binary competitive batch sorption experiments were performed using MoO_4^{2-} and goethite suspensions in 0.1M NaCl under anoxic conditions. The competitive anions studied were phosphate, sulfate, silicate and tungstate. The pH range covered was from 3 to 10 and all experiments were performed at 25°C. Molybdate adsorption onto goethite was reversible as shown by the overlapping of sorption and desorption isotherms. The competitive adsorption results showed that the anions which form inner-sphere complexes inhibit the formation of outer-sphere complexes. Tungstate and phosphate strongly competed with molybdate during the adsorption process. Furthermore, tungstate and phosphate show competitive displacement of adsorbed molybdate. The CD-MUSIC (Charge Distribution Multi Site Complexation) model was used to describe the anionic adsorption envelopes and isotherms on goethite. The competitive adsorption envelope predicted by the CD-MUSIC model provided a satisfactory fit for the experimental adsorption data of molybdate over the whole pH range tested. Furthermore, CD-MUSIC prediction of the molybdate adsorption isotherm strongly agrees with the experimental isotherm. Experimental and modeling results strongly suggest that molybdate partition behavior under anoxic conditions strongly depends on the competitive interactions of other anions such as phosphate, silicate and tungstate.

Poster Session- Innovative Technologies

Pilot Scale Application of Heat-Activated Persulfate at a Former Petroleum Underground Storage Tank Area

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Pilot Scale Application of Heat-Activated Persulfate at a Former Petroleum Underground Storage Tank Area

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Thermally activated sodium persulfate was implemented at a pilot scale as the remedial technology at a former petroleum underground storage tank area located in South Carolina. Contamination at the site included BTEX, MTBE and naphthalene. Initial concentrations of the BTEX components were in excess of one ppm, with the MTBE and naphthalene concentrations at 200 ppb. Air sparging was utilized at the site previously, reducing the contaminants to less than 300 ppb for each of the BTEX constituents, and less than 100 ppb for MTBE and naphthalene respectively. However, after two years of air-sparging, persistent concentrations remained, predominantly in the central portion of the plume.

Heat activation of the sodium persulfate was achieved by injecting steam into four points around the surrounding persulfate pilot injection well. The steam injection was not continuous, and was injected approximately eight hours per day for the first three days, followed by eight hours a day for two days one week after the first injection. Approximately ten million BTU's of thermal energy were injected over the total forty-hour injection period. Thermocouple monitoring points positioned in four locations around the injection well indicated subsurface temperature increases, in some cases up to 90 ° C.

Samples were collected seventy-two hours after the steam injection period. The thermally activated persulfate successfully reduced all contaminants to non-detectable levels, or to levels below their regulatory limits. It was also demonstrated that steam injection was a cost effective approach to activating persulfate, with the entire pilot project costs being \$15,000.

Poster Session- Pesticides

In-Situ Bioremediation of Low-Level Dieldrin Impacted Soil

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Fayaz Lakhwala, Adventus Americas, Inc., Chicago, IL

In-Situ Bioremediation of Low-Level Dieldrin Impacted Soil

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In November 2004, Adventus conducted a 2,600-ton *in situ* pilot-scale technology validation project using Adventus' patented DARAMEND technology to remove organochlorine pesticides from impacted soils at a former agricultural site in Florida. The treatment area consisted of two treatment plots identified as North and South, each containing a 1-foot layer of soil with elevated concentrations of dieldrin. Results from the site characterization sampling indicated an average initial soil dieldrin concentration of 45.9 µg/kg in the treatment plots.

Two treatment cycles, each consisting of sequential anoxic and oxic conditions, were applied. These conditions were generated through the application of DARAMEND amendments (0.5 % by weight), which were applied to the soil surface and incorporated to a depth of 1 foot with a tractor-driven deep rotary tiller or disc. After amendment incorporation, water was applied to bring the soil moisture content up to 90% of the soil water-holding capacity. Oxic conditions were then generated through passive drying of the soil and subsequent aeration. These steps were repeated for the second treatment cycle. Each cycle consisted of an eight day anoxic phase, followed by a two day oxic phase.

Soil dieldrin concentrations decreased by 67% (to 15.1 µg/kg) which met the remedial objective within a 2-3 week period at a total project cost of approximately \$12.50/yd³. A third treatment cycle was able to reduce the concentration by a total of 85% to 90%.

Poster Session- Remediation

The Value of Organoclays in Permeable Barriers

George R. Alther, Biomin, Inc., Ferndale, MI

Large-Scale Physical Models of Thermal Remediation of DNAPL Source Zones in Aquifers

Ralph S. Baker, TerraTherm, Inc., Fitchburg, MA

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Gorm Heron, TerraTherm, Inc., Bakersfield, CA

John C. LaChance, TerraTherm, Inc., Fitchburg, MA

Myron Kuhlman, MK Tech Solutions, Inc., Houston, TX

Arne M. Färber, University of Stuttgart, Stuttgart, Germany

Hans-Peter Koschitzky, University of Stuttgart, Stuttgart, Germany

Oliver Trötschler, University of Stuttgart, Stuttgart, Germany

Economic Basis and Application of Thermally-Enhanced Soil Vapor Extraction

John M. Bierschenk, TerraTherm, Inc., Fitchburg, MA

Ralph S. Baker, TerraTherm, Inc., Fitchburg, MA

Uwe Hiester, University of Stuttgart, Stuttgart, Germany

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Successful Remediation at Contaminated Sites with a Very Tight Soil Matrix

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Sorption/Desorption of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzo Furans (PCDDs/PCDFs) in the Presence Of Cyclodextrins

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Carl E. Brown, Environment Canada, Ottawa, Ontario, Canada

Surfactant Injection for the Remediation of Light Non-Aqueous Liquids (LNAPL)

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Ronald Traver, Sovereign Consulting, Inc., Robbinsville, NJ

Darren Scillieri, Sovereign Consulting, Inc., Robbinsville, NJ

HRC[®] Remediation of a PCE Impacted Till Aquifer and Underlying Shallow Bedrock Aquifer

Jonathan K. Child, Fuss & O'Neill, Inc., West Springfield, MA

Timothy J. St. Germain, Fuss & O'Neill, Inc., West Springfield, MA

John B. Hankins, Fuss & O'Neill, Inc., Manchester, CT

Results of the Hydraulic Testing of the Fuel Spill-1 Remedial System Design at Massachusetts Military Reservation

Ronald J. Citterman, CH2M HILL, Otis ANGB, MA

Frank Lewis, CH2M HILL, Englewood, CO

John Glass, CH2M HILL, Herndon, VA

John Schoolfield, Air Force Center for Environmental Excellence, Otis ANGB, MA

Remedial Action Optimization, Marine Corps Mountain Warfare Training Center, Bridgeport, California

Christopher Corey, Shaw Environmental, Inc, Irvine, CA

Christopher S. Seipel, Shaw Environmental, Inc., Irvine, CA

Kathie Beverly, Naval Facilities Engineering Command, Southwest Division, San Diego, CA

Developing an Exit Strategy for Remediation, DFSP Yorktown Fuel Farm, Virginia

Jennifer Davis, NAVFAC Mid-Atlantic, Norfolk, VA

William Hughes, Shaw Environmental, Inc., Virginia Beach, VA

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Ex Situ Treatment of MTBE-Containing Groundwater by an UV/Peroxide System

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Tex Lu, Risk-Based Decisions, Inc., Sacramento, CA

Ian Brown, Risk-Based Decisions, Inc., Sacramento, CA

James C. Powers, Risk-Based Decisions, Inc., Sacramento, CA

Steam Injection Expedites Removal of Viscous NAPL at a Manufacturing Complex

Tim Kemper, Shaw Environmental, Hopkinton, MA

Eric Vining, Shaw Environmental, Hopkinton, MA

Barbara Riley, GE Transportation

Remediation and Restoration of a Sensitive Wetland Located in Western Massachusetts

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Celeste M. Hunt, AMEC Earth and Environmental, Westford, MA

Matt Adkins, CSX Transportation, Inc., Lithia Springs, GA

Multiple Technologies Optimize Remediation of Tetrachloroethylene (PCE) At Former Drycleaning Site in a Residential Neighborhood

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Amyjean Lussier, U. S. Environmental Protection Agency, Boston, MA

Gary J. Creaser, S. W. Cole Engineering, Inc., Bangor, ME

Case Study: Full-Scale Application of Innovative and Standard Remediation Technologies at a Chlorinated Solvent/DNAPL Site

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Design and Implementation of a Remedial Action at the Pownal Tannery Superfund Site

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High-Temperature Burning of Oil Sludges and Oil Contaminated Soils

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Design Considerations for Electrical Safety of Remediation Equipment

Dennis Rentschler, ENSR International, Westford, MA

Keeping the Buses Moving: Remedial Design Constraints at an Active Facility

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A Laboratory Pilot System for the Simulation of Thermal Desorption of Residual Listed Wastes from the Sarex Waste Treatment Process for the Purpose of Waste Delisting

George M. Sawyer, Casie Protank, Inc., Vineland, NJ

**Optimization of Groundwater Remediation Systems and Long-term Monitoring Programs-
A Client's Approach**

Gregory L. Simpson, Textron, Inc., Providence, RI

Remedial Investigation Techniques and Remediation Technologies for a Tidally-Influenced Diesel Plume in the Sub-Arctic

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The Value of Organoclays in Permeable Barriers

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The function of permeable barriers is to 1). allow the groundwater to flow freely through them, and 2). to entrap or destroy chemical contaminants such as metals and organic hydrocarbons. Certain organically modified clays have the ability to act as anion and cation adsorbents, allowing them to remove heavy metals such as Pb and Zn, and anions such as hexavalent chrome, arsenate, and phosphates. They can also remove humic acids, perchlorate and other negatively charged organic compounds.

A neutral type of Oilsorb removes creosote, PNAH's, PCB, dioxene, BTEX and other non-polar organic hydrocarbons of low solubility very effectively.

For good measure, powdered activated carbon can also be included in the barrier mix. Such a design allows for a barrier that retards the movement of organic compounds and metals into the surrounding environment, be that a river or a lake.

This article presents new data on the organoclays capacity for contaminant removal which where obtained in column studies in the laboratory of the University of Virginia.

Large-Scale Physical Models of Thermal Remediation of DNAPL Source Zones 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 will be 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 will be 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 will simulate 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.

Economic Basis and Application of Thermally-Enhanced Soil Vapor Extraction

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The use of thermally enhanced soil vapor extraction (TESVE) has been shown to be more cost effective than unheated soil vapor extraction (SVE) for the remediation of sites contaminated with volatile organic compounds (VOCs). In comparison with “cold” SVE, TESVE increases the vapor pressure of the VOCs due to higher soil temperatures and thus allows much higher contaminant extraction rates to occur, which results in a significant reduction in the time required to complete a site remediation project. In fact, at many operating SVE sites, completion of the remediation would require that soil VOC concentrations be reduced to a specific numeric cleanup standard that may be unachievable due to limitations of the cold SVE technology to treat heterogeneous, layered and/or low-permeability soil.

Experiments from laboratory studies along with field data from 3 sites have been used by VEGAS, the Research Facility for Subsurface Remediation at the University of Stuttgart, Germany, to conduct Life Cycle Assessments (LCA) where TESVE and cold SVE were compared for the purpose of estimating the secondary environmental impacts of such techniques. The results indicate that energy consumption and environmental impacts are favored for TESVE as compared to SVE. These results are discussed as a method to evaluate the cost benefit of TESVE.

Thermal Conduction Heating (TCH) is a method to heat the subsurface at low incremental cost. It is being applied to sites for the purpose of performing thermal enhancement of conventional remediation methods, such as SVE and free-product recovery. One site will be reviewed as a case study. This southern California site has been undergoing high vacuum vapor extraction remediation for a period of more than 6 years. During the years of cold SVE operation the source zone concentrations of VOCs in the saturated clay rich zone, at a depth of 20 to 35 feet below ground surface, have not been reduced. A TESVE system was installed in the spring of 2004, and heat was applied over a period of 12 months. The concept, cost and results from this site will be presented to demonstrate the comparative economics of TESVE and SVE.

Successful Remediation at Contaminated Sites with a Very Tight Soil Matrix

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An innovative three step remediation approach has been developed to successfully treat contaminants at sites with a very tight soil matrix. The first step is to pre-condition low permeability soils using both chemical and mechanical means. The second step is to apply an optimized enhancement of the Traditional Fenton's Reagent chemical oxidation process. Unlike previous applications of Traditional Fenton's Reagent, the new emphasis is on optimization of the "Free Radical Fate and Transport Process and Total Contaminant Mass Desorption". The third step is a bioremediation polishing step applied to treat the remaining desorbed contaminant mass. This break through approach avoids Traditional Fenton's free radical chemical oxidation fate and transport limitations. Fenton's free radicals are typically not applied in very tight soils since they are limited to a shelf life of seconds and minutes.

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 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 very tight soil matrix.

Sorption/Desorption of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzo Furans (PCDDs/PCDFs) in the Presence Of Cyclodextrins

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The goal of this study was to investigate the usefulness of cyclodextrins in the remediation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo furans (PCDDs/PCDFs) in soil and water. Five cyclodextrins having different molecular cavities and active functional groups were selected and evaluated for their ability to include (trap) PCDDs/PCDFs. The inclusion of PCDDs/PCDFs was performed in soil and water. For the soil experiments, cyclodextrins were added to the soil on day one and the concentrations of unbound PCDDs/PCDFs were monitored over a 28-day period. Control experiments were conducted parallel to the testing experiments to assist in the process performance evaluation. The ability of cyclodextrins to remove PCDDs/PCDFs from the contaminated soil was dependent upon the type of cyclodextrin used and constituents of PCDDs/PCDFs. Among the five cyclodextrins investigated, hydroxypropyl- β -cyclodextrin gave the highest removal efficiency for all components of PCDDs/PCDFs. The removal efficiency was 81% at the start (one day after application of cyclodextrins) and then increased to 96% after 28 days. The congeners removal efficiencies ranged from 69% to 96% for 2,3,7,8-TCDD and 1,2,3-TCDD, respectively. The α -cyclodextrin and β -cyclodextrin removed only 45% and 50% of the total PCDDs/PCDFs after 28 days, respectively, whereas hydroxypropyl- β -cyclodextrin and hydroxypropyl- γ -cyclodextrin removed 73% and 80% of the total PCDDs/PCDFs from the contaminated soil, respectively.

Surfactant Injection for the Remediation of Light Non-Aqueous Liquids (LNAPL)

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Sovereign Consulting Inc. (Sovereign) completed a surfactant injection pilot test to remove residual light non-aqueous phase liquid (LNAPL) at an operating retail service station in south-central New Jersey. Sovereign utilized a biodegradable, EPA registered oil spill response chemical surfactant, BIOSOLVE®, produced by Westford Chemical Corporation. The surfactant was mixed on site as a dilute 2% solution, and injected into the area straddling the water table through a grid of 78 closely-spaced Geoprobe™ injections. Prior to the pilot test, a baseline ground-water sampling episode was completed, including the analyses of methylene blue active substances (MBAS). Anionic detergents or surfactants react with methylene blue to form a blue colored complex. The concentration of MBAS in ground water is therefore a measure of the concentration of anionic detergents or surfactants. MBAS was analyzed during the recovery process and during post injection ground-water monitoring. A total of 1,950 gallons (approximately 25 gallons per boring) of surfactant was injected at a rate of 1-3 gallons per minute (gpm). Mobile vacuum-enhance recovery of ground water in the area of the surfactant injection, via existing monitoring wells, was the method of control and recovery of injection fluids and solubilized hydrocarbons from the aquifer matrix. Four days after injection was completed, ground-water monitoring in the injection area identified one monitoring well with approximately 0.49 feet of LNAPL or free product. LNAPL recurrence in the pilot test area for at least a 3-month period following successive recovery events indicate that the surfactant remained in place and “active”. Dissolved-phase benzene, toluene, ethylbenzene, and xylene (BTEX) concentrations increased as high as 840% in monitoring wells closest to the injection area where it was removed.

HRC[®] Remediation of a PCE Impacted Till Aquifer and Underlying Shallow Bedrock Aquifer

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A release of tetrachlorethene (PCE) has been documented in a dense, fine grained till aquifer over an approximate 10,000 square foot area. PCE groundwater concentrations in the unconsolidated aquifer have been detected above 10,000 micrograms per liter (ug/L) with maximum soil impacts located near the bedrock surface. PCE concentrations in the underlying shallow bedrock aquifer (sandstone) exceeded 50,000 ug/L.

In 2001, a bedrock groundwater pump and treat system was installed as a source area control measure to reduce potential off-site migration of PCE and related chlorinated volatile organic compounds (CVOCs) such as trichloroethene (TCE) and cis-1,2-dichloroethene (cis-1,2-DCE). Operation of the system produced only limited influence on groundwater flow potentials and contaminant concentrations.

Supplemental source area remediation was initiated in 2003 using Hydrogen Release Compound (HRC[®]) to enhance in-situ rates of reductive dechlorination within the unconsolidated aquifer. HRC[®] was injected by Geoprobe[®] from the water table to the bedrock surface at rates of 4 to 10 pounds per vertical foot. Within four months, reductions in PCE concentrations were observed throughout the unconsolidated aquifer in conjunction with increasing TCE and cis-1,2-DCE concentrations. Six to nine months following HRC[®] injections, significant reductions in PCE concentrations were observed within the shallow bedrock aquifer. Concurrent iron-fouling issues that were associated with the enhanced bioremediation program resulted in shutdown of the bedrock pump and treat system while the HRC[®] remediation program continued.

A second HRC[®] injection was performed approximately one year following the original injection. Within 14 months of initiating the HRC[®] groundwater remediation program, unconsolidated aquifer PCE concentrations had decreased from >10,000 ug/L to below 50 ug/L and PCE concentrations in the shallow bedrock aquifer had declined from >50,000 ug/L to less than 1,000 ug/L.

Results of the Hydraulic Testing of the Fuel Spill-1 Remedial System Design at Massachusetts Military Reservation

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As a result of historic fuel spills dating back to the 1950s at the Massachusetts Military Reservation (MMR), a plume of ethylene dibromide (EDB)-contaminated groundwater extends over a mile in length southeast of MMR. This plume, designated Fuel Spill-1 (FS-1), is detached from its source area and is currently migrating in a southerly direction terminating at the Quashnet River and surrounding cranberry bogs. The flow of the Quashnet River increases two to three times as a direct result of groundwater discharge to the river and surrounding bog ditches. Groundwater fate and transport modeling was used in the design of groundwater remedial system for the FS-1 plume. Subsequent hydraulic testing of the remedial system has been performed to verify the effectiveness of the system design at meeting the remedial objectives. During hydraulic testing, changes in the groundwater and surface water levels in response to various pumping stresses were monitored. The resulting data provide insights regarding aquifer hydraulic properties, the spatial influence of the remedial pumping, and the nature of groundwater and surface water interactions. The testing data were also used in conjunction with the groundwater fate and transport model to delineate the capture zones of the remedial system's extraction wells, and to compare actual conditions with the predicted conditions of the original wellfield design. Additionally, the hydraulic data were used to optimize the operation of the remedial system and the effectiveness and efficiency of the hydraulic and chemical monitoring network. In this way, the groundwater restoration timeframe is minimized and potential impacts to local ecosystems (i.e., excessive drawdown of groundwater discharging to wetlands) are eliminated.

**Remedial Action Optimization, Marine Corps Mountain Warfare Training Center,
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The U.S. Marine Corps' Mountain Warfare Training Center (MCMWTC), located near the town of Bridgeport, California is a year-round facility located in the eastern Sierra Nevada. The facility supports U.S. Marines Corps mountain warfare and survival training for fleet Marines and reserve troops. MCMWTC has relied on stored fuel products for heating, transportation, heavy equipment, training operations, and emergency generators. Historic releases of these petroleum hydrocarbons have impacted soil and groundwater and are the primary environmental issue at the base.

In 1988, the U.S. Department of the Navy (DON) implemented a comprehensive environmental program at MCMWTC to identify, assess, and implement appropriate remedial actions. The highest priority site on MCMWTC (Installation Restoration Program Site 4) encompasses the base gas station with groundwater impacts into a nearby alpine wetland meadow. Petroleum hydrocarbons were detected in soil and groundwater at concentrations great enough to require active remediation to mitigate the site. In 1998, an active remediation system was installed at the site and has been in continuous operation.

Collaborative efforts have been ongoing between the DON and Shaw Environmental, Inc. to develop and implement appropriate exit strategies for all sites at MCMWTC. In 2004, a Remedial Action Optimization (RAO) Report for IR Program Site 4 was prepared for the DON following the Naval Facilities Engineering Service Center's 2001 interim final guidance document Guidance for Optimizing Remedial Action Operation. The purpose of the RAO report was to review the conceptual site model used to design and implement the remediation processes, review system and cost performance, and make recommendations for future activities at the site. A review of the CSM, operations and cost data, and remedial alternatives identified that significant cost saving could be made at IR Site 4 by modifying the current remediation configuration. The DON has agreed with the results of the evaluation and recommendations given in the report, and has embraced an aggressive approach to move to long-term monitored natural attenuation as the preferred next remedial technology. The DON plans to implement the recommended actions in 2004/2005 to accelerate site closure.

Developing an Exit Strategy for Remediation, DFSP Yorktown Fuel Farm, Virginia

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Recently the focus in accelerating the remediation process at contaminated site is to optimize the process to the reduce cost. There are times when the technology employed to remediate the site is not the most effective in reaching the site closure in the shortest period of time. An exit strategy is a plan to recognize when a change in conditions requires a reevaluation of the remedial technology employed to meet the clean up goals. Conditions that may indicate a change is necessary include decreases in contaminant removal, continuing rebound of contaminant concentrations or free product thicknesses, development of new technologies that would accelerate the rate of contaminant removal or destruction. Approximately 3 million gallons of Naval Special Fuel Oil (NSFO) is present as a free-product plume at the Yorktown Fuel Farm. The NSFO is a very viscous fuel that is present in thicknesses up to 13-feet on the water table. An innovative heat-enhanced recovery system is used to heat the NSFO in the subsurface using horizontal steam circulation wells. The mobilized NSFO is recovered using recovery trenches. Approximately 215,000 gallons of NSFO has been recovered at the site. The clean up goals for the site are to reduce the NSFO thickness to less than 0.01-feet or the asymptotic decline in recovery and 25,000 ppm total petroleum hydrocarbons concentration in soil. Refinement of the exit strategy for this site is predicated upon developing an estimate of the recoverable volume of NSFO at the site using the existing technology. Reviews of available and emerging remedial technologies are conducted to determine if another method can be employed to achieve the established clean-up goals more quickly and economically. Prior to the application of a new technology, it must be first approved by the regulatory agency.

Ex Situ Treatment of MTBE-Containing Groundwater by an UV/Peroxide System

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This paper describes the design, implementation and operating results for an ex situ ultra-violet/hydrogen peroxide (UVP) system to treat MTBE in extracted groundwater. The UVP system is a third stage treatment to reduce the operating and maintenance costs of an existing groundwater pump and treat treatment system that relies on air stripping with a boiler to boost the water temperature, and carbon adsorption. The UVP system is relatively inexpensive and can easily be scaled to cope with different groundwater extraction rates up to 80 gpm by adding UV lamps in series or in parallel at the higher groundwater extraction rates. At an extraction rate of approximately 18-20 gallons per minute (68.4 to 76.0 liters per minute), we were able to achieve 75-85 percent destruction efficiency for MTBE with 60 second exposure to 30 watt UV lamps. The absolute MTBE concentrations in the effluent from the UVP system decreased from an average of 590 µg/L initially to less than 5 µg/L on average currently. Incorporation of this UVP system as a second stage treatment to our groundwater pump and treat/soil vapor extraction system after the air stripper and prior to the carbon polishing vessels significantly increased the usable life of the carbon, requiring no carbon change out in 450 days as compared to carbon change outs every 50 days prior to installation of the UVP system. The UVP system completely resolved the issue of frequent MTBE breakthrough of the carbon that had plagued the remediation system since its inception.

Steam Injection Expedites Removal of Viscous NAPL at a Manufacturing Complex

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This presentation will review an innovative remedial approach to remove viscous Non-Aqueous Phase Liquid (NAPL) from the subsurface below a former manufacturing building complex. This innovative approach injects steam into the vadose and saturated zones within the impacted area to reduce the viscosity of heavy NAPL and expedite its removal through a network of recovery wells. Previous remediation efforts at this location to recover the heavy NAPL using conventional technologies at ambient temperatures were less successful in reducing thicknesses to meet the state's regulatory standards (i.e. less than ½ inch of NAPL measured in monitoring wells). Recent NAPL recovery efforts using steam injection, groundwater depression and down-well NAPL pumps have significantly increased NAPL recovery rates. The steam enhanced NAPL recovery system has recovered 2,500 gallons of NAPL in the first twelve months of system operation and is anticipated to reach the state's regulatory standards for site closure in the future.

Technical aspects of this project that will be presented include:

- Site background and release history
- Remedial objectives and regulatory drivers
- Various remedial alternatives evaluated
- Design considerations for the selected remedy - steam enhanced NAPL recovery system with groundwater depression and treatment, steam migration control and vapor treatment
- Subsurface heat-up time and measurement, including 3-dimensional thermal depictions of site-specific thermocouple data
- NAPL recovery rates and other Critical-to-Quality data
- Lessons learned and key factors for success

Remediation and Restoration of a Sensitive Wetland Located in Western Massachusetts

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A pile of railroad ties, ballast, and debris was identified within the boundaries of a delineated wetland on a property located in Washington, Massachusetts (Site). Additionally, the property was located within an area of critical environmental concern as determined by the Massachusetts Department of Environmental Protection (MADEP). Environmental investigations at the Site indicated elevated concentrations of polycyclic aromatic hydrocarbons (PAHs) within shallow soil in close proximity to the pile. The mound of railroad ties, ballast, and debris was excavated from the Site in September 2003. The excavation resulted in the removal of nearly 1,400 cubic yards of railroad ties, soil, ballast, and debris contained within the pile. Confirmatory soil samples were collected for risk assessment purposes prior to regrading and restoration activities. The restoration plan was approved by the Washington Conservation Commission. Clean topsoil/peat was imported to the Site and regraded to closely correspond with surrounding land surface configurations. A minimum of six inches of topsoil/peat was imported and regraded over the excavated area. After regrading was complete, Site restoration included the planting of the following wetland species: Red Maple, Highbush Blueberry, and Southern Arrowwood. Upon completion of planting, hydroseed was applied to the topsoil/peat to promote vegetative growth. Two different hydroseed mixtures identified as wetland and upland mixtures were applied to the appropriate locations of the regraded area. A Method 3 risk characterization determined that No Significant Risk of harm to human health, safety, public welfare, or the environment existed. This determination was based on the evaluation of the soil, groundwater, surface water, and sediment data collected at the Site and the potential exposure of human and ecological receptors at the Site. The excavation and associated risk assessment resulted in regulatory closure of the Site.

Multiple Technologies Optimize Remediation of Tetrachloroethylene (PCE) At Former Drycleaning Site in a Residential Neighborhood

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The assessment, remediation, and environmental closure of a tetrachloroethylene (PCE) contaminated area associated with a former dry cleaning site located in a residential area in Bangor, Maine was performed using multiple technologies for assessment and remediation. S. W. COLE ENGINEERING, INC. coordinated with adjacent property owners, the Environmental Protection Agency, the Maine Department of Environmental Protection, the City of Bangor and other consultants to implement a site evaluation plan consisting of geophysics, trenching and direct push and conventional drilling. Soil, soil vapor, groundwater and ambient air samples were analyzed by the EPA Mobile Laboratory. Analytical results were evaluated in combination with geological and hydrogeological data and information from previous EPA investigations and investigations by others. Approximately 800 cubic yards of soil were identified to be above the Maine Remedial Action Guidelines.

Confirmation of the conceptual model of unsaturated, contaminated fill, confined by low permeability glacial till resulted in a remediation plan addressing immediate and long term exposure concerns. In situ treatment of saturated contaminated soils was performed by HRC[®] injection. Subslab ventilation systems provided initial and continuing mitigation of household PCE vapor exposures. The unsaturated soils were excavated for off-site disposal (100 to 5,000 mg/kg PCE); segregated for on-site treatment (30 to 100 mg/kg PCE); or treated in-situ using SVE (greater than 1mg/kg PCE).

PCE levels have declined predictably from the initial vapor system concentration level of more than 300,000 $\mu\text{g}/\text{m}^3$ to less than 28,000 $\mu\text{g}/\text{m}^3$ after 3 months of operation. These reductions are consistent with initial projections to meet the soil clean-up guidelines of 3000 $\mu\text{g}/\text{kg}$. Soil clean-up verification sampling in April 2005 will confirm progress toward the closure goal of August 2005.

Case Study: Full-Scale Application of Innovative and Standard Remediation Technologies at a Chlorinated Solvent/DNAPL Site

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Remediation of sites contaminated with high levels of chlorinated volatile organics (CVOCs) in soil and groundwater can be extremely difficult. Achieving remediation goals for soil, groundwater, and indoor air is often complicated by the presence of non-aqueous phase liquids, especially dense non-aqueous phase liquids (DNAPL). For this case study, these common problems were further compounded by the presence of organic silts and peat and the presence of CVOCs near and underneath an occupied building. The subject site is a former manufacturing facility that is now in commercial use. CVOCs were present in soil at concentrations above 5,000 parts per million (ppm) and in groundwater above 100 ppm. DNAPL was found to be present. ENSR developed a pragmatic overall approach and then selected specific technologies to meet the project objectives. ENSR's overall approach to remediation of the site included aggressive treatment of source areas and installation of vapor barriers. Because no single method would work in all areas, ENSR used a variety of remedial technologies. To address the primary source areas, ENSR used excavation, dewatering, and backfilling with zero valent iron. Excavated soil was treated on-site using thermally enhanced vapor extraction. In a secondary source area where soil conditions were more favorable, sparge and vent was used to reduce CVOC levels. Systematic inspection of the floors, sealing of floors, installation of passive vents, and indoor air sampling were used to address potential indoor air issues. Performance and lessons learned from implementation of these technologies will be presented.

Design and Implementation of a Remedial Action at the Pownal Tannery Superfund Site

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The former Pownal Tannery site consists of a 28-acre set of parcels located along the Hoosic River in the village of North Pownal. It was once used as hide tanning and finishing facility which discharged wastes, including solvents, lubricating oils, and tanning wastes to a sludge lagoon complex. M&E and TRC Environmental conducted a remedial investigation and feasibility study to support EPA in developing a record of decision for the site and to serve as the basis of design. The selected remedy that was designed for the 10-acre lagoon complex includes the stabilization and excavation of 55,000 cubic yards of contaminated sludge materials from two of the most hazardous lagoons, consolidation of the sludge over two other lagoons, and capping of the consolidated sludge with a 5.5-acre multi-layer engineered landfill cover system to eliminate multiple human health and environmental risks. Development of the appropriate conceptual design required evaluation of various factors including the volume of material to be landfilled, impacts on the adjacent Hoosic River, and the intended future use of the landfill area. Challenges also included protecting workers and the public from hazardous gases and noxious odors emanating from the contaminated lagoons and constructing the landfill cap in a 100-year flood plain over the stabilized waste. The remediation effort was tailored to restore the natural beauty of the site and open the area for potential reuse as a wastewater treatment facility and for recreational use by the community. The project was completed under a tight schedule and under budget by more than \$1 million.

High-Temperature Burning of Oil Sludges and Oil Contaminated Soils

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The present work is devoted to the solution of quite urgent ecological problem of our days — remediation of oil sludges and oil contaminated soils.

At oil production, transportation and processing the significant amount of oil sludges and contaminated soils, representing serious danger for environment is formed. In Russia about 50-100 mln. tons of oil sludges and oil contaminated soils is formed per one year. The absence of modern technologies of liquidation and utilization of sludges has transformed significant quantity of oil sludge storehouses from means of an environment prevention from petroleum pollution into threat of large-scale contamination of soils, underground and surface waters. The complexity of effective utilization and liquidation of oil sludge wastes is determined by their structure: by petroleum, water, emulsions, mechanical impurities in various proportions. Low average temperature of soils in northern areas of Russia makes biological cleaning low effective application. In the present work the technology of high-temperature burning of oil sludges and oil contaminated soils has been developed. At that technology water, contained in wastes evaporates and the organic substances are decomposed and oxidized, forming nontoxic gaseous products of complete combustion.

The advantages of installations developed on the basis of the given technology: practically complete absence of toxic emissions; safety of servicing; economical operation; quite low cost; reliability and operating longerity of the equipment.

The petroleum contaminated soils are local frequently, and the sites of pollution are considerably removed from each other. Therefore we also made mobile installation for remediation oil sludges, placed in three 20-foot containers with productivity about 100 kg per out.

Design Considerations for Electrical Safety of Remediation Equipment

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Operation and maintenance (O&M) issues, particularly electrical safety requirements, need to be carefully considered when designing remediation systems. The technical backgrounds of individuals, who monitor, troubleshoot and repair remote remediation equipment, differ greatly. Site visits at remediation systems are often staffed by geologists, engineers or environmental scientists and rarely by a licensed electrician. OSHA and NFPA NEC (National Electrical Code) specify electrical work to be performed by a “Qualified Person”. A “Qualified Person” is an individual with not only appropriate technical training and experiences, but also safety training on the hazards involved. Often remediation control designs include display elements and control operators within the same enclosure as the power distribution. This can expose remediation staff to electrical hazards beyond their qualifications. In this case, a qualified electrician would be required to perform simple monitoring, control adjustments or troubleshooting. Alternatively, an electrical design and application which isolates the distributed electrical power from a low voltage controls center can greatly reduce the electrical hazards to all and allow qualified remediation staff to safely perform larger scopes of monitoring or troubleshooting of the control system. Implementing a low-voltage control scheme to a new remediation system should not significantly increase the capital cost. It will be important to specify a low-voltage control scheme in the early stages of the design process and ensure that remediation equipment bids and submittals meet the presented specifications.

Keeping the Buses Moving: Remedial Design Constraints at an Active Facility

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Several feet of floating petroleum product were discovered in groundwater beneath a bus storage and maintenance garage located in the Boston area. The product was found to be migrating along utility lines and impacting nearby structures. The remediation system for the site needed to evaluate and overcome several difficult site constraints in the design. The remedial system selected for the site consisted of a high vacuum dual-phase extraction system, LNAPL recovery, and in-situ bioremediation. The location of the treatment building, extraction wells, piping, trenching, and other remedial equipment/activities was secondary to keeping the bus operations intact. The bus facility processes over 100 buses a day and daily operations including maintenance, bus washing, driver rotation, and bus inspection could not be interrupted during the construction of the remediation system.

The goal of the site remediation is to perform source removal and minimize impacts to existing operations. The remedial design of the system had to overcome several significant design constraints, including:

- Excavation next to multiple bus bays and disturbance of bus parking
- Multiple petroleum product sources
- Location of a treatment building on-site and away from the bus traffic
- Coordination/installation of thousands of feet of conveyance piping
- Odor migration and dust control in the garages
- Explosion proofing of select equipment
- Control of LNAPL migration into a nearby pump station
- Bus traffic and worker protection
- Protection of existing utilities
- Recovery well installation/trenching along multiple utilities at various depths
- Potential impacts to the subway system below the site and
- Small available site footprint with no room for stockpiling of soil or equipment

Remediation was designed to achieve maximum contaminant removal while providing for the least interruption to the busy bus schedule.

A Laboratory Pilot System for the Simulation of Thermal Desorption of Residual Listed Wastes from the Sarex Waste Treatment Process for the Purpose of Waste Delisting

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A laboratory apparatus which conforms to a small scale pilot system for the thermal treatment of residual solids from listed wastes was designed to simulate the thermal desorption process for the achievement of residential cleanup standards or universal cleanup standards on the treated residual solids generated by the SAREX process.

The SAREX process treats listed wastes taken from various facilities by state-of-the-art high speed centrifugation, heating, and chemical treatment to achieve a separation of the waste into three phases—oil, water, and residual solids. The residual solids are slated to be treated by thermal desorption to remove contaminants down to trace levels which conform to residential and/or universal cleanup standards for the purposes of delisting the wastes.

**Optimization of Groundwater Remediation Systems and Long-term Monitoring Programs
– A Client’s Approach**

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Each year, millions of dollars are spent by responsible parties to collect, treat and discharge/dispose of contaminated groundwater and monitor the status of remedial activities. Often, these activities are not subjected to regular value-added evaluations that most other types of projects with a similar magnitude of capital expenditure receive.

To evaluate and optimize its ongoing groundwater remediation projects, Textron, Inc. launched an annual Remediation Optimization initiative in 2002. One of the key components of this initiative is an annual effectiveness report that is completed for each project by Textron’s consultants. By completing this standardized report, the consultant provides the Textron project manager with valuable data regarding the effectiveness and efficiency of the remedial system and monitoring program on a yearly basis and allows site-to-site comparison for benchmarking purposes.

Using the data contained in these reports, Textron is able to compare the effectiveness of remedial systems (including specific system components) and identify costly, under performing systems. Proactive modifications to these under performing systems or alternative approaches can subsequently be evaluated to improve overall system performance. As part of the initiative, Textron’s consultants are also challenged to maintain at least a 90% runtime rate for remedial systems.

The reports also target the overall performance of groundwater monitoring activities by identifying data trends and tracking costs on a detailed basis. Sampling programs have been optimized based on the information provided in the reports. Detailed groundwater monitoring cost tracked across several remediation sites allows Textron to identify inefficient sampling programs and corrective action to be requested.

The Remediation Optimization initiative also challenges consultants on an annual basis to propose more efficient approaches to remedial activities, with performance measured against a 5% annual savings goal. Overall, the initiative has been a success for Textron.

Remedial Investigation Techniques and Remediation Technologies for a Tidally-Influenced Diesel Plume in the Sub-Arctic

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Operations at a former fire-training pit in Kodiak, Alaska have contaminated an area adjacent to a river estuary with fuel (predominantly diesel). Although excavation has removed the primary source, LNAPL is smeared at residual saturation through a 1-meter interval near the water table by tidal fluctuations and groundwater flow across a broad area.

A combination of site characterization techniques was synergistically applied at the site. Continuous-profile electrical resistivity soundings (using an OhmMapper) sought to identify a contaminant signature (low resistivity related to degradation products, or high resistivity associated with continuous free product), but were unsuccessful because of extraordinarily resistive site materials. Laser-induced fluorescence (LIF) profiles were used to help characterize the lateral and vertical extent of contamination and helped determine the placement of monitoring wells. Traditional characterization through soil borings, monitoring wells, and microwells was used in the final phase to definitively delineate the horizontal and vertical extent of contamination.

Site conditions provide challenges that few remedial technologies can meet. Although groundwater moves rapidly through the underlying aquifer, silts in the smear zone may sequester the LNAPL. Rejected technologies include excavation (expensive and intrusive), all types of extraction wells, trenches, or reactive barriers (migration rates too slow), and mobilization via surfactants (unacceptable risk to the estuary). Evaluation of remedial alternatives including enhanced bioremediation and monitored natural attenuation will be discussed. Mixing is a critical challenge for enhanced bioremediation, since the needed amendments must be dispersed throughout the contaminated zone for greatest effect. A one-time treatment could dramatically accelerate biodegradation over the short term along preferential pathways, leaving behind a fragmented patchwork of contamination that should naturally attenuate much more rapidly than had nothing been done.

Poster Session- Sediments

Use of a Bench-scale Treatability Study to Determine Cost-effective Disposal Methods for Contaminated Sediments

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Studies of Trace Metals and Natural Radionuclides in Bottom sediments from Around a Campos Basin Oil Field Offshore Platforms

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Use of a Bench-scale Treatability Study to Determine Cost-effective Disposal Methods for Contaminated Sediments

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Cost-effective disposal is a major concern for sediment remediation projects that require removal of sediments. To meet landfill criteria sediments must pass tests for hazardous waste content, hazardous waste leachability and residual moisture content. A knowledge of these parameters is essential before the cost of the remediation can be estimated. CRA has developed a laboratory treatability study procedure to obtain the required information rapidly. An example of the application of this procedure is a treatability study that was conducted on heavy metal contaminated dredged sediment from a site in Michigan

Three sediment samples were obtained and composited to form a sample that would be representative of site conditions. To be acceptable for disposal at a non-hazardous waste landfill the sediment samples must pass TCLP, stability criteria, and the paint filter test. Sediment leachate data showed that the sediment met only TCLP criteria, therefore stabilization was necessary. Ten polymers were evaluated for their effect on solids settling. A sediment slurry was settled with and without polymer treatment and the supernatant and settled solids were collected. A filter press was used to dewater the settled solids to produce a filter cake, which was tested for water content, TCLP metals, and the paint filter test. The effects of solidification agents on the settled solids were also evaluated. The agents tested were Portland cement, fly ash, and cement kiln dust. The results showed that untreated settled solids did not meet landfill stability requirements. The ability of polymer treatment, solidification and filter cake from dewatering using a filter press to meet the landfill stability requirements will be described. Based on the results of the treatability study a cost-effective technique for sediment treatment and disposal was determined.

Studies of Trace Metals and Natural Radionuclides in Bottom Sediments from around a Campos Basin Oil Field Offshore Platforms

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Offshore oil and gas production can cause a potential impact to the marine environment. Large volumes of aqueous waste are produced during oil and gas production and, normally, these are discharged, following treatment on the platform, to the sea. In this produced water the high concentrations of metals and naturally occurring radioactive materials (NORM) are often found and these contaminants are being introduced or have entered the sediment and water column near production sites. In this work the offshore bottom sediments samples from the Bacia de Campos oil field were analyzed for Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ba, Pb, As, U, ^{226}Ra , ^{228}Ra and ^{210}Pb . The determination of trace metals in sediment samples for total, after microwave digestion, and leachable fraction with 0.5 M of HNO_3 was done by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in TotalQuant mode with ^{115}In and ^{205}Tl as internal standard. Al, Fe and Ba were also determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). ^{226}Ra and ^{228}Ra were determined in surface sediments sampled around the effluent discharges, either their total content by γ -ray spectrometry of ^{214}Bi and ^{228}Ac , respectively, either by gross alpha and beta counting after leaching with EDTA. The total ^{210}Pb activities in sediment samples were determined by γ -ray spectrometry with auto-absorption correction. The results show that there are chemical differences between the areas around the two studied platforms. The results of the principal component analysis (PCA) pointed out a possible preferential deposition of the metals in the Southwest direction. This verification is in agreement with the supposition that the environmental effects would be registered in the Northeast-Southwest alignment due to the action of the Current of Brazil. The sedimentation rate in one studied site was $0.28 \text{ cm}\cdot\text{yr}^{-1}$, what can be attributed to the contribution of particulate material of fluvial origin in this region. In general, the trace metals and radionuclides concentrations in the analyzed sediments are in agreement with the expected values for unpolluted marine sediments.

Wednesday, October 19, 2005

Poster Session- Acid Mine Drainage

Natural Attenuation of Acid Mine Drainage from Microcosms of Davis Mine in Rowe, Massachusetts

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Stabilization of Mine Waste Rock Using Moss

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Natural Attenuation of Acid Mine Drainage from Microcosms of Davis Mine in Rowe, Massachusetts

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Acid mine drainage (AMD) is one of the largest and widespread environmental problems. Conventional methods to prevent and remediate AMD are both time consuming and expensive. Promoting natural attenuation offers a more cost-effective strategy for remediation. Davis Mine in Rowe, Massachusetts is an AMD site where natural attenuation is occurring. Within a few hundred meters from the mine effluent, acidic leachate is neutralized and heavy metal content decreases again. Of the known attenuating processes, microbial reduction of sulfate and iron (III) is believed to be the main contributor of the attenuation of AMD at Davis Mine.

Comparing microcosms of AMD attenuating and generating zones, we can stimulate microbial activity by varying the substrate and nutrients, or incubation temperature. If sulfur related microbial processes are responsible for the natural attenuation, our microcosms should demonstrate a decrease in sulfate concentration and/or an increase in iron (II) concentrations, coinciding with an increase in pH and a decrease in the oxidation-reduction potential (ORP).

Generally, microcosms from the AMD generating zone demonstrated a smaller change in activity than microcosms of the AMD attenuating zone. The pH of the microcosms amended with GNP (glycerol, nitrogen, and phosphorous) increased slightly faster than the unamended microcosms. However, supplying local algae as substrate resulted in a faster increase in pH and a corresponding decrease in ORP. An increase in iron (II) concentration over time suggests that microbial iron reduction is occurring in the microcosms, although at a greater extent in the microcosms of the attenuating zone. Incubation temperature also affected pH and ORP of the microcosms with a faster increase in pH at higher temperatures. Our measurements suggest that not only is natural attenuation occurring within the microcosms of Davis Mine, but also amendment with different substrates and incubation at higher temperatures supports the process of attenuation.

Stabilization of Mine Waste Rock Using Moss

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Moss was found growing on waste rock at the Badger State Mine site northeast of Butte, MT. The waste rock had a high heavy metal content and low pH. The moss, *Mielichhoferia mielichhoferi*, is part of a group of bryophytes known as the "copper mosses," which are known for their ability to grow on metal-laden soil. Propagation of the moss is expected to stabilize the soil, resulting in less runoff and less contamination of surrounding soils. With these benefits, vascular plants may colonize areas where the microbial mats form. The goal of this research is to use *Mielichhoferia mielichhoferi* and two different moisture-retaining agents to stabilize and remediate soil in the arid climate of the Badger State Mine.

Identification of algae and bacteria from the Badger State Mine soil was carried out by microscope examination and 16S rRNA sequencing, respectively. There were six species of algae identified and ten species of bacteria. Three of the algae found are also known to grow in the water of the nearby Berkeley Pit, and have the ability to sequester metals.

Metal analyses were run both on Badger State Mine soil and on moss grown during laboratory experiments. The concentrations in the moss were compared to those in the mine soil to give concentration factors for 10 different metals. Moss grown during the laboratory experiments was found to concentrate silicon, manganese, nickel, copper, zinc, and cadmium. Moss collected at the Badger State Mine was also compared to the mine soil concentrations and found to sequester silicon and copper only.

The main difficulties in propagating moss at this site comes from the aridity of the climate and high metal content of the soil. Consequently, Hydretain(r) polymer and Terra-Sorb hydrogel were used as part of a series of treatments in field and laboratory trials. Both of these substances help to maintain moisture in the soil for a longer period of time after precipitation. Laboratory experiments were created by using petri dishes to mimic the conditions in the field. The number of plants growing and the surface coverage of the petri dishes were then examined.

Little growth was seen during the field experiments, likely due to a lack of precipitation following inoculation at the Badger State Mine. During one field experiment, both the Terra-Sorb hydrogel and Hydretain(r) polymer were applied, and three plots had moss growing when checked later. Two of those plots had also been inoculated with fertilizer to assist with growth. The laboratory test with the Terra-Sorb hydrogel revealed a significant increase in surface coverage when the hydrogel was used as part of the treatment.

This research revealed that there is promise in using moss to help bioremediate mine waste rock in a semi-arid environment. However, future experimentation needs to include improved techniques in inoculation of plots in the field and addition of water after inoculation.

Poster Session- Analysis

Distinguishing Between Multiple Chlorinated Solvent Plumes: A Comprehensive Approach

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Nylon-Mesh Passive Samplers and 1,4-Dioxane: A Case Study in Fractured Rock in Florida

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John C. Alonso, Blasland Bouck and Lee, Inc., Tampa, FL

Analysis of NDMA by Modified Method 1625 utilizing Chemical Ionization and Large Volume Injection

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Arin Jones, Alpha Analytical Labs, Westborough, MA

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Speciation of Metal Ions in Aqueous Systems Using X-ray Photoelectron Spectroscopy

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Four Tips for the Handling of Aqueous Diffusion Samplers

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Analysis of Contaminated Soils and Sediments Using X-ray Tube and Isotope Source Portable XRF Instruments

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Sampling and Analysis of Cranberries in an Area of Plume Discharge

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Distinguishing Between Multiple Chlorinated Solvent Plumes: A Comprehensive Approach

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This paper describes a unique approach to distinguishing between multiple chlorinated volatile organic compound (CVOC) plumes in groundwater. The investigation began with the collection of soil gas samples collected just above groundwater in an area extending some 1,000 feet downgradient from a known source area. The soil gas samples were analyzed for CVOCs. Chemical fingerprinting of perchlorethylene (PCE), trichloroethylene (TCE), cis- and trans-1,2-dichloroethylene (cis- and trans-1,2-DCE) in these samples revealed the presence of at least three distinct CVOCs plumes in groundwater. The data were used to push cone penetrometer tests (CPTs) to 30 feet below ground surface to characterize the subsurface stratigraphy. At each CPT location, a grab groundwater sample was also collected and analyzed for CVOCs. The logs of 296 CPTs were classified by depth as “sand” or “clay”. Sand, sandy silt and silty sand were interpreted as sand while clay and silty clay were interpreted as “clay”. The depths were then converted to elevations above mean sea level using the surface surveyed elevations. A geostatistical analysis was used to create a detailed solid model of the subsurface. The accuracy of the model was quantified and the model used to create fence diagrams and other 3D images of the subsurface. These images revealed the existence of two discrete sand channels which were connected by a sand bridge located precisely at the point where the soil gas fingerprints showed a separation of CVOC plumes. Thus, a geologic basis for the presence of different plumes was established. Finally, chemical analysis of the grab groundwater samples confirmed the existence of multiple CVOCs plumes and revealed that these plumes were separated at specific locations which could be understood by the distinctions in geology and hydrogeology.

Nylon-Mesh Passive Samplers and 1,4-Dioxane: A Case Study in Fractured Rock in Florida

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Passive diffusion samplers provide a potential time-saving and cost-effective sampling alternative to standard sampling procedures, such as low-flow purging and sampling, with the added benefit of limiting the generation of investigation-derived waste in the form of purge water. First generation passive samplers were constructed of polyethylene film filled with laboratory-grade water, and have been proven effective for evaluating concentrations of volatile organic compounds; however, these samplers rely on diffusion across a membrane and are not suitable for other classes of analytes, specifically semi-volatile organic compounds and metals. A new generation of passive samplers using a fine nylon mesh that allows a direct water-to-water interface, has shown a potential application to these other classes of analytes.

The use of 1,4-dioxane as a solvent stabilizer has become an increasing concern at former electronics component manufacturing facilities with soil and groundwater impacts from chlorinated solvents. At one such facility in west-central Florida, a 1,4-dioxane/chlorinated solvent plume is present in the fractured rock aquifer beneath the site.

Rock aquifer monitoring wells present at the site were constructed in the early 1990's, and are generally open-hole wells with a monitoring interval greater than 50 feet, limiting the understanding of the potential vertical distribution of the contaminants in groundwater. A plan to evaluate vertical distribution, using down-hole vertical and horizontal flow measurement and multiple-level sampling with nylon-mesh samplers, was presented to the Florida Department of Environmental Protection, and received approval for implementation.

This paper presents the approach provided to the regulatory agency, and the results of the subsequent study.

Analysis of NDMA by Modified Method 1625 utilizing Chemical Ionization and Large Volume Injection

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In this paper, the authors describe a robust analytical procedure based on a modification of EPA Method 1625. It is a GC/MS analysis utilizing isotope-dilution, chemical ionization and large volume injection. This technique is very powerful, capable of reaching low parts per trillion (PPT) reporting limits.

Speciation of Metal Ions in Aqueous Systems Using X-ray Photoelectron Spectroscopy

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Assessment of bioavailability, mobility and risk of toxic metals in the environment has taken on added proportions in recent years. While the analysis and detection of hazardous metal ions have seen significant gains in the form of lower detection limits and improved sensitivity of analytical measurement techniques, the area of metals speciation analysis has not experienced the depth of development as elemental quantitation methods. Although elemental information provides key parameters for remedial practices and risk assessment exercises, it is now necessary to incorporate other parameters, such as valence state and molecular structure in models to determine treatment feasibility, bioavailability and risk determination. It is thus necessary to preserve the integrity of the chemical state of the matrix containing the metal by minimizing sample preparation and the formation of derivitized products. Results from the application of XPS, a well established surface characterization technique (gives semi-quantitative and qualitative chemical speciation information) are presented on the oxidation states of chromium ions in aqueous media. Aqueous systems containing 1-50 ppm Cr (VI) and Cr (III) singly and as mixtures were analyzed. Binding energy shifts of core level 2p electrons at approximately 579 and 577 eV were identified for Cr (VI) and Cr (III) respectively. Photoelectron peaks identifying Cr (III) and Cr (VI) were also identified in aqueous systems (1 ppm) containing Fe (III), Pb (II) and Zn (II).

Four Tips for the Handling of Aqueous Diffusion Samplers

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Aqueous diffusion bag (ADB) sampling is an innovative method for the collection of volatile organic compound groundwater samples from monitoring wells. This sampling technique offers considerable time and cost savings compared to other sampling methods. An ADB sampler is made of semi-permeable polyethylene membranes filled with de-ionized water. The major advantage of using ADB samplers is that there is no need for onsite sampling equipment, well purging, or disposal of purge liquids, thereby reducing costs and effort.

The ADB sampling technique provides a cost effective and time saving alternative to low-flow sampling in a long-term monitoring program. In order to realize the maximum benefits of ADBs, EA has identified 4 setup and handling tips:

1. For easier deployment, use a weight to counteract the ADB's natural buoyancy. Make sure the weight will not affect other possible sampling parameters (i.e., metals).
2. Assemble ADB setup in a clean, offsite location including the single or multiple bag setups and weight. By creating each well setup prior to mobilizing to the sampling point, labor time in the field can be reduced.
3. Transport ADB setup in pre-cleaned, lay-flat containers from preparation location to sampling point to avoid accidental breakage or cross-contamination. Large "Under the Bed" polyvinyl chloride storage containers with lids have been found to be effective.
4. For long-term use, install dedicated bag setup made of stainless steel wire with bag clips attached at predetermined levels. For each sampling event, the ADBs are clipped onto the wire and lowered into the well. By creating a setup that can be used for multiple events, significant time savings can be realized.

Utilizing ADBs can reduce the total cost of the sampling event by 40-60 percent, the majority of the savings coming from labor. For example, the total time for an event decreased from 12 days to 5 days (1 day to fill and setup bags, 2 days to deploy bags, and 2 days to retrieve bags and collect samples). Following the above 4 tips helped provide the long-term monitoring program with cost and time efficient savings.

Analysis of Contaminated Soils and Sediments Using X-ray Tube and Isotope Source Portable XRF Instruments

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In January of 2005, NITON LLC participated in the Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) of X-ray Fluorescence (XRF) Technologies for Measuring Trace Elements in Soil and Sediment. Two field portable handheld instruments, the XLi 700 Series equipped with Radioactive Isotopes and the XLt 700 Series equipped with Miniaturized X-ray Tube technology, were used to analyze 326 samples from 9 different locations across the continental U.S.A. Thirteen elements: Antimony (Sb), Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Lead (Pb), Mercury (Hg), Nickel (Ni), Selenium (Se), Silver (Ag), Vanadium (V), and Zinc (Zn) with varying concentrations were analyzed on both analyzers. Correlation data obtained from both field portable analyzers, as compared to the reference laboratory, will be presented.

Sampling and Analysis of Cranberries in an Area of Plume Discharge

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Detectable levels of tetrachloroethene (PCE) and trichloroethene (TCE) in surface water samples collected from a network of cranberry bog ditches led to concerns about the marketability of a 57 acre cranberry crop. Low-level detections in surface water resulted from the upwelling and discharge of the Ashumet Valley groundwater plume at the Massachusetts Military Reservation (MMR). Disposal of treated wastewater from the former MMR sewage treatment plant (STP) between 1936 and 1995 and residuals from fire training activities at MMR formed the Ashumet Valley plume. Both the STP and the Fire Training Area are located near the southern boundary of MMR, approximately 4 miles upgradient of the cranberry bogs. To determine whether plume discharge had impacted the marketability of the cranberry crop, a multi-stakeholder group was assembled to develop guidelines for sampling and analyzing cranberries for PCE and TCE. Challenges included: 1) formulating a procedure that provided representative samples; 2) establishing a sample preparation procedure 3) procuring a laboratory that had the required experience, instrumentation, and capacity to meet accelerated data delivery requirements; and 4) a fast-track schedule to gain full stakeholder concurrence prior to the 2004 harvest. For sample analysis, the SW8260B GC/MS Selected Ion Monitoring method was chosen. Advantages in using this method included lower method detection limits (MDL) over standard SW8260 analysis and the ability to target specific compounds. A critical component was the performance of a MDL study for this non-traditional environmental media (i.e., homogenized cranberry fruit) that gained stakeholder approval. The results of the study established MDLs sufficiently low to meet the project data quality objectives. Neither PCE nor TCE were detected above the MDL in any of the cranberry samples. Based on the sampling results, the cranberry crop was considered suitable for market.

Poster Session- Brownfields

A Case Study: In-Situ Soil Pre-Characterization Study and Real-Life Limitations Encountered During Site Development

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A Case Study: In-Situ Soil Pre-Characterization Study and Real-Life Limitations Encountered During Site Development

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A case study presenting the limitations and pitfalls of performing an extensive in-situ sampling program at a complex disposal site is evaluated compared to the actual soil conditions encountered during site development. Development of urban brownfields and contaminated sites for a multitude of land uses both commercial and residential is becoming more common place. The rising value of urban properties and the means to more accurately incorporate the costs of site remediation into site development coupled with legislative changes limiting the liabilities of financial institutions and land developers is bound to continue the trend of accelerated urban redevelopment of brownfields. This case study presents the actual findings encountered during site development compared to the design studies, highlights pitfalls and limitations of the in-situ pre-characterization program and offers potential alternatives for incorporating soil management procedures into site design. The case study involves the construction of a multi-use urban development incorporating retail, transit and residential land uses on a 9 acre lot. The property was contaminated with gasoline and MGP wastes including MtBE, BTEX, Reactive Sulfide and toxic metals.

Poster Session- Chemical Oxidation

KMnO₄ and Hydraulic Fracturing, An Innovative Technology Combination for Passive ISCO Destruction of Chlorinated Compounds

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A Three Year Application of Bulk Quantities of Sodium Permanganate for In-Situ Chemical Oxidation (ISCO) of Chlorinated VOCs

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Lawrence Nesbitt, Shaw Environmental, Inc., Hopkinton, MA

USEPA Superfund Innovative Technology Evaluation (SITE) of Persulfate Oxidation for the Remediation of Chlorinated Solvents

M. Amine Dahmani, University of Connecticut, Storrs, CT

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George E. Hoag, Hoag Environmental Systems, Storrs, CT

Hydraulically Controlled ISCO of TCE and TCA in Groundwater

Chuck Elmendorf, Panther Technologies, Inc., Medford, NJ

Kevin Dyson, Panther Technologies, Inc., Medford, NJ

Peter J. Palko, Panther Technologies, Inc., Medford, NJ

In-situ Remediation of PCE and TCE in Soils Using Sodium Persulfate

Chuck Elmendorf, Panther Technologies, Inc., Medford, NJ

Kevin Dyson, Panther Technologies, Inc., Medford, NJ

Peter J. Palko, Panther Technologies, Inc., Medford, NJ

Aggressive Chemical Oxidation Using Ozone and Hydrogen Peroxide Injection to Address Significant LNAPL Plumes

Cullen Flanders, Groundwater & Environmental Services, Inc., Cranberry Twp, PA

Use of Novel Chemical Oxidation Program to Remediate Petroleum Hydrocarbons at an Active Gasoline Station

Joseph Hayes, Environmental Compliance Services, Richmond, VT

Steven A. Peck, Regenesys, Oceanside, CA

Low-cost Chemical Oxidation at Gasoline Release Sites via Air Hydrogen Peroxide, Ozone and Air Injection (HypeAir)

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Charles B. Whisman, Groundwater & Environmental Services, Inc., Exton, PA

TCE in Fractured Bedrock Groundwater Remediation via Sodium Permanganate Injection and Re-circulation

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The Use of Permanganate for the Oxidation of Pentachlorophenol Part 2

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Short-term “Max-Ox” Ozone, Hydrogen Peroxide, and Air Injection Systems for Aggressive BTEX and MTBE Remediation (Including Fractured/Weathered Bedrock Sites)

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KMnO₄ and Hydraulic Fracturing, An Innovative Technology Combination for Passive ISCO Destruction of Chlorinated Compounds

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The delivery of solid potassium permanganate by hydraulic fracturing offers several benefits over other delivery mechanisms for low permeability media. Fracturing can exploit long recognized fundamental characteristics of solid permanganate – that it is an aggressive and easy to use oxidant, it operates over a wide range of soil conditions and it can persist in the subsurface for long periods of time following placement – to render a nearly ideal single-application, passive remediation program. The advantages follow in at least four categories. First, large quantities of concentrated solid oxidizer can be delivered to the subsurface at one time. This eliminates operation and maintenance costs associated with the operation of injection and extraction pumps and above ground oxidant handling equipment required for permanganate distribution via conventional wells. Second, hydraulic fracturing technology is compatible with and indeed best employed via DPT allowing the creation of source zones of solid oxidizer at discrete depths via one direct push location. This eliminates the costs associated with the installation of permanent injection wells and allows the oxidizer to be positioned vertically in the subsurface to best address varying vertical contaminant distributions which might remain untreated by injection through wells with long screen sections. Third, the radius of influence of hydraulic fractures is vastly greater than that of conventional wells in LPM. This means less injection locations are required than with conventional wells. And fourth, the mechanism of mass transport of oxidizer through the treatment zone can be by diffusion away from the emplaced oxidant source zones, which should encourage the treatment of formation heterogeneities or regions of especially low groundwater flow in the treatment zone. Hydraulic fracture emplaced KMnO₄ for ISCO degradation of chlorinated organic contaminants has been employed on three full scale commercial projects since the fourth quarter of 2003 and on at least one pilot scale project at a DoD site in 2004.

A Three Year Application of Bulk Quantities of Sodium Permanganate for In-Situ Chemical Oxidation (ISCO) of Chlorinated VOCs

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Shaw Environmental, Inc has completed the third year of implement a large, multi-year, *in-situ* chemical oxidation (ISCO) groundwater treatment program at an active manufacturing site located in New England. The program was initiated as part of an effort to reach state cleanup goals and alleviate the need for continued source area hydraulic control. TCE and PCE are the primary contaminants at the site. An ISCO pilot test was conducted in the primary contaminant source area, and based on its initial success a full-scale ISCO system was designed and implemented. The extent of impacts made injection of oxidant a viable alternative due to its potential to more quickly achieve cleanup objectives at a lower cost than implementing a traditional, full-scale groundwater pump and treat technology.

The topographic and geologic conditions vary widely at the site, from low permeability glacial tills with moderate groundwater gradients to highly permeable outwash deposits with low groundwater gradients. Impacts extend into weathered bedrock with an irregular surface profile, and associated varying overburden thicknesses. Sodium permanganate was chosen as the oxidant for its high concentration and suitability for bulk liquid delivery in tanker trucks.

Expanding on the results of the first year of treatment that were presented at the 2003 UMASS Soil, Sediment and Water Conference, this presentation will explain the continuing reductions in contaminant concentrations, over an increasingly larger area, resulting from the second and third year of treatment. The presentation will review the monitoring methods and results, present a general overview of the ongoing success of the program, and a few notable lessons learned.

USEPA Superfund Innovative Technology Evaluation (SITE) of Persulfate Oxidation for the Remediation of Chlorinated Solvents

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This study has been conducted by the Environmental Research Institute (ERI) at the University of Connecticut and the USEPA Superfund Innovative Technology Evaluation (SITE) program to evaluate persulfate-based chemical oxidation technologies developed at ERI. Persulfate oxidation technologies utilize persulfate or a combination of persulfate with a catalyst to destroy contaminants and offer great promise toward economical and permanent solutions for many contaminated sites. These technologies rely on the complete destruction of the contaminants of concern and their breakdown products in soil and groundwater.

A protocol developed by University of Connecticut researchers to assess the efficacy of oxidation technologies at contaminated sites has been used. This protocol, which consists of obtaining data from a treatability study, identified persulfate, Fe(II)-EDTA catalyzed persulfate, and potassium permanganate as oxidation technologies that can be used effectively to treat solvent-contaminated soil and groundwater at a site in Vernon, Connecticut. Based on the treatability report results and additional field data collected at the site, the design for the field implementation of the chemical oxidation remediation was completed and the field application of the persulfate and catalyzed persulfate technologies is being implemented under the USEPA SITE program. Results of this demonstration project obtained thus far are presented here.

Hydraulically Controlled ISCO of TCE and TCA in Groundwater

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A mixed trichloroethene (TCE) and trichloroethane (TCA) contaminant plume was discovered in perched groundwater below a 360,000 square foot building operated by an aerospace manufacturer. Chemical oxidation was evaluated as a cost-effective remedial technology that would aggressively destroy the contaminants and meet the redevelopment schedule for the site. An expedited pre-design investigation (PDI) successfully determined the nature and extent of contaminated media, and provided a sound foundation for the remedial design.

Concentrations of TCE and TCA in the aquifer targeted for treatment ranged from 100 ug/l to 100,000 ug/l. Remediation goals included the rapid destruction of contaminant mass, followed by monitored natural attenuation (MNA). Sodium permanganate (NaMnO_4) was used to treat areas containing only chlorinated ethenes. Chemically activated sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was applied to the mixed TCE/TCA plume. A key element in the success of this application was controlling the movement of chemical oxidants in the aquifer through a series of injection and extraction wells. This ensured physical contact between the oxidants and contaminants, and minimized displacement of the contaminants.

The contaminant plume was in a perched aquifer consisting primarily of coarse to fine sands, underlain by a glacial clay layer. This unique hydrogeology facilitated the injection and hydraulic control of the chemical oxidants.

Our experience with a range of oxidation projects allows us to provide a thoroughly designed program and avoid the trial and error process that is commonly applied today for many ISCO applications. This ISCO application was a remarkable success that ultimately reduced over 95% of the TCE/TCA mass in groundwater and allowed the site to be sold and redeveloped within 18 months. The presentation will highlight the key data requirements for the successful evaluation and implementation of an ISCO treatment program, critical in evaluating and designing and implementing an oxidation technology that is customized for site-specific conditions.

In-situ Remediation of PCE and TCE in Soils Using Sodium Persulfate

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Soils at this former aerospace industrial site contained levels of perchloroethylene (PCE) and trichloroethylene (TCE) at concentrations over 9,500 mg/kg, exceeding risk-based remedial standards set by the New Jersey Department of Environmental Protection (NJDEP). Because the PCE and TCE in soils presented an ongoing source of groundwater contamination, source area remediation in soils was a top remedial priority.

Panther Technologies, Inc. (Panther) implemented an in-situ, chemically activated persulfate technology to remediate 16,000 tons of contaminated soil down to a depth of 25 feet BGS. Two major benefits of this technology included elimination of the contaminants in soils and on-site re-use of the treated soils. Eliminating the source of TCE and PCE in soils has had a significant, positive impact on water quality within only 6 months. Re-use of treated soils on-site saved a significant amount of time and money by eliminating off-site disposal and importation of fill.

Due to heterogeneous soils at the site, including some clay lenses, and the depth interval of the targeted treatment zone (0 to 25 feet below grade), an aggressive remedial technology was required. Panther developed a remedial design incorporating in-situ chemical oxidation (ISCO) and specialized soil mixing equipment to achieve remedial goals. The ISCO and mixing approach developed by Panther was specifically designed to assure sufficient distribution and mixing of the oxidants with the contaminated media, thereby destroying the contaminants in soil.

Persulfate oxidation technology represents an innovative and cost-effective approach to remediation of recalcitrant compounds in soil and groundwater that can be modified for use at a wide range of sites. Delivery and adequate mixing are key elements in the successful application of this technology. The design of this technology can (and in most cases must) be customized to meet the specific characteristics of a given site to assure successful application.

Aggressive Chemical Oxidation Using Ozone and Hydrogen Peroxide Injection to Address Significant LNAPL Plumes

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The presentation will discuss how aggressive chemical oxidation processes using ozone and hydrogen peroxide injection can be utilized to address all phases of contaminants, including non-aqueous phase liquid (NAPL).

The discussion will detail the aggressive processes which assist in breaking down NAPL, including the presence of three oxidation species (ozone, hydrogen peroxide, and hydroxyl radicals), mass-transfer mechanisms, volatilization, and bioremediation. Case study data will be presented where the process was utilized in a significant LNAPL plume to aggressively remediate greater than two feet of weathered gasoline and diesel. The case study also showed significant soil and groundwater remediation, in addition to the LNAPL reduction. Other case study information will be discussed, including utilizing the process on heating oil and diesel releases for higher-chain hydrocarbons.

The presentation will discuss the changes in LNAPL chemical properties during operation and evaluation of the soil/groundwater oxidant demand. Methods to enhance the distribution of oxidants to promote effective remediation will also be evaluated.

Use of Novel Chemical Oxidation Program to Remediate Petroleum Hydrocarbons at an Active Gasoline Station

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A site remediation program was implemented at an active gasoline station located in Barre, Vermont under Vermont's Pay for Performance Program. The remedial design incorporated several technologies including multiphase extraction, ORC® and chemical oxidation to remediate both free phase and dissolved phase gasoline contaminants. The multiphase extraction system operated over a 24 month period and significant reductions in the concentration of gasoline constituents were observed across the site. However, a small area on the site remained above the remedial target levels and chemical oxidation was used to address the residual gasoline contamination. The chemical oxidation process employed at this site was REGENOX™. The REGENOX™ product uses a solid alkaline oxidant that is activated through the action of a proprietary dual catalytic system. The chemical oxidant was applied twice using 8 foot on center spacing across an injection grid. Data were collected to evaluate the performance of the chemical oxidant. Data from both the multiphase and chemical oxidation phases of the program will be presented.

Low-cost Chemical Oxidation at Gasoline Release Sites via air Hydrogen Peroxide, Ozone, and Air Injection (HypeAir)

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Case studies will be presented where BTEX and MTBE impact in soil and groundwater remediated through the combination of short-term hydrogen peroxide and air/ozone injection events. The technology will be presented in detail and case studies will be shown where contaminated soil and groundwater was aggressively remediated through short-term (daily/weekly) remediation solutions. Sites to be discussed include both active and inactive gasoline service stations.

Case studies will be presented where short-term mobile hydrogen peroxide and air/ozone (“HypeAir”) injection systems were utilized to remediate soil and groundwater impacted with BTEX and MTBE at relatively low life-cycle remediation costs (\$15,000 to \$100,000).

The discussion will also explain how the processes have been modified to enhance the radial influence at injection points and to maximize the distribution of the oxidants. The technology to be discussed utilizes numerous aggressive remediation processes together (chemical oxidation with three oxidizing species, mass-transfer from air injection, enhance bioremediation, and soil vapor extraction).

TCE in Fractured Bedrock Groundwater Remediation via Sodium Permanganate Injection and Re-circulation

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In situ chemical oxidation (ISCO) is an emergent remedial technology where organic contaminants are degraded in the subsurface via contact with chemical oxidants. Successful implementation of ISCO has been documented in overburden applications where the delivery mechanism provided sufficient oxidant-contaminant contact. The objective of this pilot study was to field test the application of sodium permanganate solution injection and re-circulation (I&R) for remediation of dissolved trichloroethene (TCE) in fractured bedrock ground water. The study entailed the intermittent injection and re-circulation of a sodium permanganate solution through bedrock fractures expressed in open bedrock boreholes and bedrock monitoring wells. Extracted groundwater was initially dosed with sodium permanganate to create a solution with a 5% concentration that was re-injected back into the fractured bedrock at the contaminant source area. The injected permanganate solution replaced ground water with high concentrations of dissolved TCE (100,000 to 200,000 ug/L), thus allowing continued TCE and permanganate contact via natural advection, dispersion, and diffusion under natural hydraulic gradients. Injected solution was left in the bedrock fracture system until the permanganate was degraded and rebound was observed.

Post I&R groundwater sampling data indicated concentrations of TCE were reduced from between 100,000 to 150,000 ug/L and to below 1 ug/L in the injection well. Concentrations in monitoring wells were reduced from approximately 150,000 ug/L to less than 1 ug/L initially and to between 30,000 and 50,000 ug/L once rebound occurred. Post I&R monitoring did not indicate uncontrolled migration of the permanganate solution. A larger scale source area implementation is currently in progress and is comprised of two additional open bedrock boreholes, injection and extraction manifolds with flow monitoring devices and pressure gauges, and permanganate dosing and injection equipment. Ongoing ISCO implementation and monitoring is projected to occur over the next two years.

The Use of Permanganate for the Oxidation of Pentachlorophenol Part 2

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Pentachlorophenol (PCP), a chlorinated hydrocarbon, has been widely used as an insecticide, pesticide and a wood preservative until 1987 when its use was restricted to certified applicators in the wood preservative industry. PCP is listed in EPA toxicity class II, meaning it is considered moderately toxic. In 1983 the production of PCP was 45 million lbs. According to the EPA, PCP is found at 313 of the 1,585 National Priorities List sites. Potassium permanganate (KMnO₄) has been an effective technology for the oxidation of many organic compounds including chlorinated organics and phenolic compounds.

Preliminary studies have confirmed the ability of permanganate to oxidize PCP in an efficient manner and have been reported previously. It has been shown that the reaction produces two possible intermediates tetrachloro-1,4 benzoquinone or tetrachlorophenol. The goals of this study were: 1) confirm the true nature of the observed intermediate through GC/MS analysis, 2) determine the reaction kinetics of the intermediate with permanganate, and 3) determine the mass balance of the PCP/permanganate reaction by monitoring chloride formation and TOC reduction. Possible reaction mechanisms will be discussed based on confirmed intermediate formation along with final reaction by-products. Data from a recent field evaluation will also be presented.

Short-term “Max-Ox” Ozone, Hydrogen Peroxide, and Air Injection Systems for Aggressive BTEX and MTBE Remediation (Including Fractured/Weathered Bedrock Sites)

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This presentation will explore recent advances in aggressive patent-pending “Max-Ox” chemical oxidation technologies that combine liquid oxidants (such as hydrogen peroxide) and a gas (such as ozone, oxygen, or air) for aggressive injection in soil and groundwater to address significant source reduction in all contaminant phases (adsorbed, dissolved, and LNAPL). Case studies will include remediating thousands of pounds of contaminant mass (such as BTEX, MTBE, and TBA) in soil and groundwater through the injection of ozone, oxygen, air, and hydrogen peroxide.

The technology uses three chemical oxidation species (ozone, hydrogen peroxide, and hydroxyl radicals) aggressively remediating contaminated soil and groundwater. The technology can be applied to varying lithologies and at sites with significant contaminant mass, as case studies will show. Case studies to be presented include recent success stories in weathered/fractured bedrock. The discussion will evaluate the various remedial processes combined into the Max-Ox process, including: chemical oxidation (via three different oxidation species – ozone, hydrogen peroxide, and the hydroxyl radical); enhanced air sparging (scrubbing, mixing, washing effect in addition to mass transfer via air movement); enhanced bioremediation (via increased dissolved oxygen levels outside of injection area); and soil vapor extraction (for off-gas control and unsaturated soil pack).

The discussion will also evaluate different methods available to perform on-site feasibility tests which can be utilized to evaluate the potential effectiveness of in-situ chemical oxidation using ozone and hydrogen peroxide injection. Case study data has indicated that downgradient dissolved MTBE impact can be addressed via aggressive source area remediation and without requiring off-site remediation (due to enhanced bioremediation through elevated dissolved oxygen concentrations).

Poster Session- Environmental Fate

Achievement of a Beneficial Reuse Designation for a Specialized High Volume Byproduct

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Achievement of a Beneficial Reuse Designation for a Specialized High Volume Byproduct

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The State of Florida encourages the recycling and reuse of a variety of materials, assuming that it can be accomplished in a manner that protects public health and the environment. A detailed technical and field evaluation was conducted on behalf of and in cooperation with a major municipal utility, to investigate the reuse potential of large volume byproducts from an electrical generating station which employs circulating fluidized bed (CFB) technology for combustion of coal and petcoke as fuel. In cooperation with FDEP, a 12 month field demonstration was conducted to assess stability, leachability, and runoff from compacted byproduct ("EZBase"). Pads (12 by 50 feet) were constructed of the compacted EZBase material, designed to simulate proposed reuse scenarios. Shallow groundwater monitoring wells were installed immediately adjacent to the pads and were monitored monthly for a variety of constituents, in conjunction with surface water runoff samples collected during rainfall events, and soil samples adjacent to the EZBase pad. Vanadium emerged as a substance of interest in both surface runoff and in soil, but vanadium was not detected in nearby groundwater wells. The groundwater, soil and stormwater runoff data clearly demonstrated that the EZBase byproduct does not pose hazards to the environment, and demonstrated that the environmental fate of analytes in the byproduct is very similar to the other commonly used products in similar applications (e.g., concrete, limerock, asphalt). A variety of potential risk-based reuse scenarios were proposed to the state environmental regulatory agency on the basis of human health and ecological considerations, including soil stabilization in environmental remediation applications, road bed and road surface projects, commercial/industrial site paving projects, and road right-of-way application. Toxicological, risk and engineering questions were satisfactorily addressed and approvals were granted for reuse of the CFB byproduct on a broad scale.

Poster Session- Environmental Forensics

Application of Chemical and Process Forensics for Contaminant Source Identification at the Fuel Storage Facility

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Chemical Heterogeneity Among Marine Bunker Fuels

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Application of Chemical and Process Forensics for Contaminant Source Identification at the Fuel Storage Facility

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Complex inter-related issues of origin, fate and transport of hydrocarbon chemical contaminants are best addressed when site assessment data are integrated with an area's operational and regulatory history. This approach is illustrated in the case study involving a former bulk fuel storage facility. Two major contaminant plumes exist at the site: a NAPL plume at the eastern area and a dissolved phase hydrocarbon plume at the northwestern end of the site. The application of the chemical and process forensics methodology allowed us to determine that the NAPL consisted of a mixture of diesel fuel and gasoline. Chemical characteristics of contaminants revealed that multiple historical releases of hydrocarbon fuels have contributed to the NAPL plume. The dissolved phase plume predominantly consisted of modern formulations of gasoline. The distribution patterns of key hydrocarbon parameters and presence of a boutique oxygenated blending agent points to a specific off-site source of the contamination.

Chemical Heterogeneity Among Marine Bunker Fuels

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Bunker fuel is the term that collectively refers to the family of fuel oils used to power marine vessels. The term ‘bunker’ is derived from the fact that these fuels are stored, or ‘bunkered’, in the ship’s massive fuel tanks and in storage tanks at most ports around the world.

Bunker fuels are produced from ‘leftovers’ from the crude oil refining process. In the past, this primarily included the non-distillable residuum from the atmospheric distillation process. Most refiners now also utilize vacuum distillation that ‘squeezes’ even more desirable, lighter products from atmospheric distillation residuum. The residuum from vacuum distillation, often termed flasher bottoms, is the primary feedstock in the production of modern bunker fuels. As the sophistication of the refining process increases to include additional steps aimed at squeezing more profit from residuums (e.g., visbreaking, coking), the quality of the bunker fuel feedstock is reduced leading to the need to blend other lower boiling residuals (e.g., cat-cracked gas oil) order to achieve bunker fuel specifications. Though considered controversial, it is also not uncommon for low levels of used automotive and marine crankcase lubricating oil to be blended into bunker fuels as a means of disposal.

The specifications of bunker fuels permit refiners considerable latitude in the manufacturing of on-spec bunker fuels. Because no two refineries operate identically, and because bunker fuel blending depends upon the current operating and economic considerations at a given refinery at a given time, the specific nature of the bunker fuels is highly variable. In this poster, we have reviewed the chemical compositional data for a large number of marine bunker fuels that demonstrates their heterogeneous chemical characteristics. The available data includes the general chemical composition and boiling/carbon range distributions as determined by gas chromatography-flame ionization detection (GC/FID) “fingerprinting”, as well as the concentration of parent and alkylated polycyclic aromatic hydrocarbons (PAHs) as determined by modified EPA Method 8270. The objective of compiling these data is to provide that may aid in better predicting the environmental fate and ecological impacts of bunker fuels released into the environment.

Poster Session- Legal Issues

Environmental Insurance: Wave of The Future or Washout?

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Environmental Insurance: Wave of The Future or Washout?

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A number of large insurance companies offer a variety of insurance products, including Pollution Legal Liability insurance to off-set the risk of unknown or unanticipated additional contamination costs and provide financial assurance. Whether this approach to risk transfer will continue to be attractive into the future and how the inevitable claims will be handled remain open questions.

There are a number of sites throughout the nation where environmental insurance has played a part in facilitating settlements or transactions and certain players in the insurance industry aggressively market these services. Is this the wave of the future or just another insurance business opportunity that will generate more litigation than insurance payments? Another source of potential clean-up funding may be historic general liability insurance policies that provide coverage for an “occurrence” that may have resulted in contamination many years ago. Potential policyholders, regulators and environmental professionals of all stripes need to understand the pitfalls inherent in any insurance policy contract as well as what to negotiate for upfront before considering purchasing “environmental” coverage or bringing an insurance company into any settlement or transaction. They also need to know what to consider when trying to obtain Brownfield funding in the form of coverage for environmental liabilities under modern or historic insurance policies. In obtaining “Cost Cap” coverage or other financial assurances going forward, stakeholders may be subject to requirements imposed under contract which they did not anticipate, including more stringent review of what is to be spent and why. In addition, off-site contamination, bankruptcy of PRPs, orphan shares, contamination discovered after remedy implementation or outside of areas of concern originally identified, Remedial Plan modifications and use of unapproved contractors may not be covered.

This presentation will provide information on the recent use of environmental liability insurance at various sites, including the Iron Mountain site in California and several other smaller sites, and then discuss the pros and cons of this emerging approach to facilitating mining site remediation and Brownfield transactions, including tips on things to look out for from an experienced environmental insurance attorney.

Poster Session- Miscellaneous

On the Need for Greater Co-operation Between Academia and Industry in Service Learning

Tait Chirenje, The Richard Stockton College of New Jersey, Pomona, NJ

Community Communications: Powerful and Meaningful Printed Materials

Shannon B. Gleason, ENSR International, Westford, MA

Increasing Sand Strength with Bacteria

Mary J.S. Roth, Lafayette College, Easton, PA

Laurie F. Caslake, Lafayette College, Easton, PA

Blaire L. Banagan, Lafayette College, Easton, PA

On the Need for Greater Co-operation between Academia and Industry in Service Learning

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Apart from bridging the gap between practice and theory, service learning has been shown to: deepen student understanding of course content, increase a sense of social responsibility, and, sharpen students' ability to solve problems creatively and work in a team setting. Service learning has been used successfully in other areas of higher learning. Although private companies in environmental pollution monitoring, remediation and biotechnology have the best settings for service learning, the cooperation of industry and academia is lagging in this area. Most of the cooperation has been in having guest speakers from industry and the exchange of student interns (usually seniors) in specific positions as a recruiting tool by companies. Oftentimes these have already made up their minds about what they want to do in their professional lives, leaving out a majority of students enrolled in lower level classes. Lowerclassmen may be better served by not only hands-on experience, which many professors often incorporate in their curriculum, but real world experience consulting with professionals in their field of work. My classes (Pollution and Regulation, ENVL 3241), and Remediation and Biotechnology (ENVL 4446) have incorporated service learning components that include private companies such as Marathon Engineering (brownfields characterization) and Adams Rehman and Heggan (lake geochemical characterization) with great success. I have also included projects working with local watershed associations, the New Jersey Department of Community Affairs and local municipalities (brownfields), and residents (tracing the source of contamination in their well water). We are currently in negotiations with GeoSyntec, through the town of Voorhees (NJ) to work with them on a reclamation project of an old landfill. Student express gratitude for the chance to experience what professionals in their fields routinely deal with. Federal and State agencies have invested substantially in this area. It is time for private industry to step up.

Community Communications: Powerful and Meaningful Printed Materials

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When a project is complicated by site contamination, stakeholders, agencies, and the public can become concerned or alarmed about potential threats and impacts – both direct and perceived -- to public health and the environment. No matter how sound the technical information and solution, if the community distrusts the information given, the project can languish. Thus, selecting the appropriate community relations strategy, including printed communications materials, for a site is an important factor to consider in the overall project management of a site. This poster provides guidelines for developing powerful and meaningful printed communications materials for sites in communities ranging from low/high concern to low/high trust.

Increasing Sand Strength With Bacteria

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Liquefaction in saturated, loose sand deposits causes a rapid loss of soil strength. Structures built on these types of deposits can suffer catastrophic failure if liquefaction occurs. Engineers use dynamic compaction and vibrocompaction as well as other methods to improve the soil strength. However, these methods are difficult to implement if structures exist on or nearby the site. A proof of concept study has been conducted to determine whether the addition of biofilm-forming bacteria increases the strength of such liquefiable soils. It was hypothesized that the microbes will provide some cohesion between the sand particles thereby increasing their resistance to liquefaction. If the bacteria increase the soil strength, they could be inoculated into soils below existing structures using natural groundwater gradients.

To test the idea, a box model was built that permits liquid flow through a main sand compartment with sampling ports stationed vertically and horizontally. Baseline strength tests using a vane shear device were performed on Ottawa sand pluviated into the box into standing water and on the same sand material pluviated into the box into air. In the second case, water was then added slowly and a low gradient flow established across the sand deposit. The sand deposits were then recreated with *Flavobacterium johnsoniae* added to the standing water for the first case and with the same bacteria introduced up gradient in the second case. After a period of approximately eight days and after confirming the presence and extent of the bacteria in the sand deposit, strength tests were conducted and compared to the baseline results. Increases in strength from 10 to 100 percent were observed indicating that inoculating with bacteria may be a viable way to increase the strength of liquefiable sands.

Poster Session- Modeling

Modeling Zinc and Sodium Chloride Migration in Vadose Zone Soils Beneath Stormwater Infiltration Devices

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Testing New Capabilities for Simulating Free and Dissolved Phase Transport using MT3DMS

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Modeling Zinc and Sodium Chloride Migration in Vadose Zone Soils Beneath Stormwater Infiltration Devices

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Urbanization has been responsible for an increase in the amount of impervious surfaces, leading to an increase in stormwater runoff and a decrease in groundwater recharge. Stormwater runoff contains pollutants, such as nutrients, pathogens, heavy metals, solids, organic compounds, pesticides, and chlorides, which have greatly contributed to the degradation of receiving waters due to surface discharge of stormwater. This has prompted stormwater managers to consider implementing more infiltration practices into their designs. However, past studies have shown that infiltrating stormwater could contaminate the groundwater, and in some cases contamination actually has occurred. Therefore, methods for easily predicting contamination potential need to be developed.

Stormwater pollutants interact with the soils in the unsaturated zone as they migrate towards the groundwater. The specific type of soil and its properties have a profound effect on the movement of water and pollutants. Zinc and sodium chloride were chosen as the pollutants of interest in this research because of their prevalence in stormwater, solubility, and differing migration rates. Through the use of the SESOIL model, factors such as pollutant concentration, rainfall, vadose zone thickness, intrinsic permeability, organic content, and soil pH were evaluated to determine which ones have the greatest influence on pollutant migration in the vadose zone. A factorial analysis (26 full factorial) was used to evaluate the effects of these factors on the maximum penetration depth of zinc and sodium chloride. High and low values for the factors were selected from the literature and the NRCS soils database. The pollutants were treated as separate ions (Zn^{+2} , Na^{+} , Cl^{-}), and the length of each simulation was set at 1 year. Results indicated that rainfall was a common factor controlling Zn^{+2} , Na^{+} , and Cl^{-} migration. Concentration was also influential in Zn^{+2} migration, while intrinsic permeability affected Na^{+} and Cl^{-} .

Testing New Capabilities for Simulating Free and Dissolved Phase Transport using MT3DMS

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The vadose zone free-phase simulation capabilities of the US EPA Hydrocarbon Spill Screening Model (HSSM) were recently linked with the multi-species dissolved-phase contaminant transport simulator MT3DMS. The HSSM simulates a spill release, its one-dimensional migration to the water table, and the development and dissolution of a floating lens of product upon the water table. The linkage enables the analytical treatment of vadose zone transport from multiple spill-type sources to be included in a numerical simulation of dissolved-phase aquifer contamination. The codes were linked by compiling relevant modules of the HSSM as a Dynamic Link Library (DLL), and developing a time-varying source package for MT3DMS referred to as the Hydrocarbon Spill Source Interface Package (HSS Package). We outline the approach adopted for linking the simulation codes, and present a real-world groundwater flow-and-transport simulation in which MT3DMS executes the HSS Package. This simulation illustrates some benefits of the linked simulation approach, in particular the simultaneous calibration of parameters from both models to field data using programs developed to support the use of the HSS Package with PEST.

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Poster Session- Perchlorate

Thermal Treatment of Explosives and Perchlorate in Soil Media

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Perchlorate in Water: A Comparison of Methods 314.0 and 332.0

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Lab and Field Studies of Low Concentrations of Perchlorate in Groundwater

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Ex Situ Treatment of RDX and Perchlorate in Groundwater

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Batch Studies on Perchlorate Reduction by Autotrophic Bacteria Supported on Zero-Valent Iron

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Thermal Treatment of Explosives and Perchlorate in Soil Media

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Thermal desorption is a proven technology for the treatment of explosive compounds in soils. However, the soil scoped for thermal treatment was also found to contain low levels of perchlorate contamination. Thermal desorption has not been applied to perchlorate contaminated soils. This presentation will present the approach taken to modify thermal treatment conditions for explosive contaminated soils to include treatment for perchlorate. Initially, a bench scale study was conducted, at a research laboratory, to determine if thermal desorption was a viable treatment technology for perchlorate contaminated soil. The bench scale study successfully demonstrated the effectiveness of thermal treatment of perchlorate and helped establish baseline treatment conditions. Subsequently, pilot tests were conducted at a full-scale thermal treatment unit using site soil and clean sand spiked with known concentrations of perchlorate. A total of twenty tests were conducted under different combinations of concentration levels and treatment temperatures. These pilot tests allowed field proofing of the bench scale laboratory results and defined the process parameters needed for successful treatment. The pilot tests revealed a reduction in treatment effectiveness at elevated soil concentrations, demonstrating a fixed percentage removal efficiency of perchlorate from soils. During the pilot test period, matrix interferences issues affecting the analysis of perchlorate were investigated and resolved. A proof of performance test was also conducted to establish the air permit compliance for explosive compounds and perchlorate, as well as other air emission constituents. Process parameters continued to be monitored during full scale operations and were continually modified to increase the efficiency of remediation. Approximately 40,000 tons of contaminated soils have been processed at a rate of approximately 750 tons per day. Analytical results from the studies, tests and full scale operations will be presented demonstrating that thermal treatment is highly successful in the removal of explosives and perchlorate from soil.

Perchlorate in Water: A Comparison of Methods 314.0 and 332.0

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Perchlorate is a natural and man-made chemical that has been used as an oxidizer in rocket fuel, munitions and fireworks since the 1950s. It is known to disrupt thyroid function by inhibiting iodine uptake, thereby inhibiting the production of key thyroid hormones. It is very soluble in water and therefore highly mobile. Perchlorate has been detected in drinking water supply wells in several MA communities. In 2004, a drinking water MCL of 1 ppb was proposed by MADEP, consistent with the MCL proposed by EPA in 2002. While the CADHS set a notification limit of 6 ppb, NAS recently concluded that a level equivalent to 20 ppb might be more appropriate. The current accepted method for low level analysis, EPA 314.0, utilizes an Ion Chromatograph fitted with a conductivity detector and a suppressor to reduce interference from background contaminants; however this method encounters problems in the presence of elevated sample conductivity. An alternative method, EPA 332.0, has been developed to address these problems. Method 332.0 utilizes an IC fitted with an MS or MS/MS. The MS technology allows for the detection of perchlorate to sub ppb concentrations even in the presence of high concentrations of interferents. In this paper the authors present method qualification data as well as real world sample data from both methods. Comparison of real world data from samples with high conductivity will demonstrate the capability of Method 332.0 to accurately and precisely quantitate perchlorate at or below the current draft MCLs.

Lab and Field Studies of Low Concentrations of Perchlorate in Groundwater

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Potential remediation processes for explosives and perchlorate-impacted groundwater at military bases are being evaluated on a fast track schedule. Groundwater remediation treatability studies utilizing combined laboratory and field efforts were conducted in 2003 and 2004. The studies focused on *ex situ* remediation of perchlorate using several types of filter media, including granular activated carbon (standard GAC), GAC that has been tailored with a cationic monomer (tailored GAC), type I styrenic ion exchange (IX) resin and nitrate selective IX resin. Historically, military operations at the site have resulted in the groundwater impacts via leaching of propellants, explosives, and pyrotechnic (PEP) compounds. Perchlorate concentrations at the study sites ranged from 0.8 to 5.5 $\mu\text{g/L}$.

Ex-situ treatability studies were conducted with GAC and Tailored GAC on groundwater with concentrations of 0.8 to 1.5 $\mu\text{g/L}$ perchlorate (Study 1) and 1.8 to 5.5 $\mu\text{g/L}$ perchlorate (Study 2). The studies used rapid small-scale column testing (RSSCT) conducted at Pennsylvania State University. RSSCTs conducted per ASTM 6586-00 determined breakthrough behavior of a media via column tests utilizing similitude between media radius sizes.

Ex-situ field scale studies were conducted at selected groundwater monitoring/extraction wells containing 0.8 to 1.5 $\mu\text{g/L}$ perchlorate using standard GAC (Study 3), and containing 1.9 to 3.9 $\mu\text{g/L}$ using type I styrenic IX resin, nitrate selective IX resin, and tailored GAC (Study 4). These studies determined breakthrough behavior under a 3.3 gpm flow rate per treatment vessel with an empty bed contact time of 5 minutes. The objectives for the studies were to demonstrate the ability to remediate groundwater in each operable unit to cleanup goals of less than 1 $\mu\text{g/L}$ perchlorate. These studies were sufficiently robust to provide information to design and implement field-scale applications in the coming year. Results show that IX resins, tailored GAC, and standard GAC are all effective in removing low concentrations of perchlorate from groundwater.

Ex Situ Treatment of RDX and Perchlorate in Groundwater

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Remediation of explosives and perchlorate-impacted groundwater at a military base is being implemented on a fast track schedule, to meet rapid response action (RRA) regulatory requirements under the Safe Drinking Water Act. Historically, operations at the site have resulted in the groundwater impacts via leaching of explosives and propellants. Two RRA groundwater remediation systems were designed, constructed, and installed in 2004 to address these impacts to the sole source aquifer. The systems provide ex situ treatment of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), along with perchlorate, using granular activated carbon (GAC) and nitrate-selective ion exchange resin filter media.

Influent groundwater concentrations at one system are less than 1 µg/L RDX and 2 to 6 µg/L perchlorate, with an influent flow of 100 gallons per minute (gpm). Influent concentrations at the other system are 5 µg/L RDX and 30 to 40 µg/L perchlorate, with an influent flow of 220 gpm. The systems are required to treat the groundwater to 0.25 µg/L RDX and 0.35 µg/L perchlorate. In each system, groundwater is extracted from along the central axis of the groundwater plume and re-injected outside the plume boundary cross-gradient to and deeper than each extraction well.

Several challenging criteria were established for the treatment systems. The design and construction were required to meet the RRA schedule. The systems were required to be mobile treatment systems. They were required to provide flexibility for treatment of multiple contaminants. Specifically, the use of GAC is innovative as it has historically considered ineffective for removal of perchlorate. These special design constraints limited the allowable size of the treatment vessels, which resulted in a shorter empty bed contact time (EBCT) than what is typically used for RDX and perchlorate treatment. This shortened EBCT is feasible due to low levels of RDX, perchlorate, and other geochemical constituents present in groundwater at the site.

Batch Studies on Perchlorate Reduction by Autotrophic Bacteria Supported on 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 degrading bacteria as it does not result in excess biomass growth and can be more cost-effective than organic compounds. As a remediation technology, zero-valent iron (ZVI) in permeable reactive barriers (PRBs) has shown great potential for the effective treatment of halogenated organic compounds, chromate, uranium, and other oxidized elements. Unfortunately, ZVI has been shown to be ineffective in reducing ClO_4^- , in spite of the fact that the reaction is thermodynamically favorable.

In this research, batch experiments were employed to test the feasibility of a novel technology (ZVI-PRM) using zero-valent iron support perchlorate reducing microorganisms (PRM) to remove perchlorate from water. In this process, H_2 released during corrosion of ZVI is used by the PRMs as an energy source and electron donor. Results of batch experiments showed that the kinetics of this new process can be described by Monod equation, with an increase of perchlorate reduction rate with the increase of initial cell density. Neutral pH conditions favored PRM adaptation to the local environment and initiation of perchlorate reduction. Once perchlorate reduction was established, the bioreductive process was insensitive to the increases of pH from near neutral to 9.0. In the presence of nitrate, however, the perchlorate reduction rate was reduced, but not inhibited completely. Additional experiments were conducted to try to enhance the efficiency of this new process by improving the rate of H_2 generation. Unfortunately, pretreatment of ZVI by acid wash and sonication were found not effective in enhancing the efficiency. Neither were the improvements magnificent when the particle size of ZVI was reduced and when Fisher ZVI, which had been reported to be more reactive, were used. In addition, varying the mixing speed from 0 to 200 rpm did not make obvious difference in the rates of perchlorate reduction. Results of these batch experiments suggest that the corrosion of ZVI is most likely a biologically controlled process influenced by the H_2 -utilizing bacteria.

Poster Session- Phytoremediation

Phytoremediation of a Soil Contaminated with HCH

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Accumulation of Heavy Metals by Cucumber and *Brassica juncea* Under Different Cultivation Conditions

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Water Velocity Effects on Heavy Metal Accumulation in Tissues of Hydroponically Grown *Scirpus validus*

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Demonstration of Transient Phytoextraction Agents for Lead Phytoextraction

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Phytoremediation of a Soil Contaminated with HCH

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A chemical industry which produce hexachlorocyclohexane (HCH) used to place its solid waste product in a nearby yard. This industrial plant worked from 1960 to 1978. During this period, this waste product was unloaded in knolls and unevenly spread over the yard. On some occasions it was mechanically spread away. At present time, this contaminated piece of land has an extension of 16 hectares and the HCH concentrations varies from 1 to 2000 mg/Kg of dry soil. On account of economic difficulties it was impossible to carry out a soil remediation, for this reason a forestation was performed in which Eucalyptus dunnii trees were planted. This forestation plan was put into effect in october/november 1997. By now the trees are in an average of 6 meters high. In June 1998, March 2003 and February 2005 efficiency tests were performed for which trees and soils located in places with different concentration of HCH were selected. Lower leaves and log of wood were taken away from these selected plants and analysed in a laboratory, as well as the corresponding soil samples. The growing period of these plants is about 20 years. During this time, a great quantity of HCH from the soil is expected to be bioaccumulated in the trees. We still do not know if the HCH will suffer any kind of transformation inside the woody structure of the three or it will just be stored in the plants. The final destination of these trees is still uncertain but a strong possibility is to incinerate them (sacrifice)

Accumulation of Heavy Metals by Cucumber and *Brassica juncea* Under Different Cultivation Conditions

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Pollution by heavy metals from industries, the storage of polluted wastes, and agricultural fertilizer pose a serious threat to human health. These pollutants may pass into the soil where plant uptake or leaching to groundwater can contaminate the food chain. Phytoremediation is the technique that removed contaminants in environment by plants, and is researched in world, recently. This process, termed evapotranspiration, is responsible for moving contamination into the plant shoots as well. Because contamination is translocated from the roots to the shoots, which are harvested, contamination is removed while leaving the original soil undisturbed. Some plants that are used in phytoextraction strategies are termed "hyperaccumulators", which are plants that achieve a shoot to root metal-concentration ratio greater than one.

Brassica juncea is known as Pb hyperaccumulator well. Cucumber is well used to understand transportation mechanism of heavy metals because the sap of cucumber is easy to collecting. We focused to whether the temperature related to the transportation of heavy metal. Cucumber and *Brassica juncea* were used to this research. These plants were cultivated under hydroponics with Pb (60 to 600 ppm). The cultivation temperature has been changed from 8 degrees to 30 degrees for 96hours. We measured Pb concentration and GSH concentration and protein concentration every 24 hours. Pb concentration was measured by AAS after ashed with microwave system, GSH and protein concentrations were measured after crushing with liquid nitrogen by HPLC. As for the cucumber, at 25 degrees the amount of absorption of lead was the maximum. However as for *Brassica juncea*, at 12 degrees the amount of absorption of lead was the maximum. This result shows that the accumulation time of the heavy metal is different in each plant. And it was shown that GSH and the protein related closely to the accumulation of the heavy metal and the cultivation temperature.

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Water Velocity Effects on Heavy Metal Accumulation in Tissues of Hydroponically Grown *Scirpus validus*

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The uptake of cadmium, copper, lead, and zinc by hydroponically grown *Scirpus validus* was investigated. The roots of the plants were exposed to a continually recycled, nutrient enriched, synthetic stormwater that was dosed with heavy metals to concentrations typically found in urban stormwater runoff. The plants were divided into six groups and the roots of each group were exposed to different but constant water velocities. The heavy metal concentrations in the roots and stems of all plants were determined and compared after three weeks. Metal accumulation in roots was significantly increased for water velocities between 1.3 and 6.0 cm s⁻¹. In a second experiment, the roots of all plants were exposed to a single, constant velocity for approximately 11 weeks. Every two weeks the concentration metals of the roots and stems were determined for a sub-sample of the treated plants. The concentration of metals in the roots plateaued after three weeks indicating that accumulation of metals was dependent upon root growth for the last several weeks of the experiment. At the end of the experiment, however the root concentration for each metal was substantially higher than the roots of control plants. Accumulation of metals in the stem after three weeks appears to be a function of velocity for copper and zinc, but only the long-term accumulation rate of zinc was noticeably increased by increased water velocity. The results suggest that the long-term accumulation by the roots of hydroponic *Scirpus validus* can be increased by increasing water velocity.

Demonstration of Transient Phytoextraction Agents for Lead Phytoextraction

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Phytoextraction of lead from contaminated soils often requires application of chelating agents to enhance the naturally low availability of lead for plant uptake. Soil amendments such as ethylenediamine tetraacetic acid (EDTA) have been used as EDTA forms strong and stable complexes with lead over typical soil pH values. However, the strength of the Pb-EDTA complex restricts its biodegradation, increasing the potential that this complex may migrate, particularly in sandy soils. The objective of this research was to investigate several recently identified soil amendments that biodegrade more rapidly than EDTA and assess whether their complexes with lead would meet the definition of a newly proposed class of agents called transient phytoextraction agents (TPA), that are effective for phytoextraction yet offer low migration risk. Eight amendments (six potential TPAs, EDTA, and deionized water) were tested in twelve lead-contaminated residential soils in a series of batch, column, and growth chamber studies for TPA behavior. Each TPA was assessed based on its effectiveness (i.e., extraction of lead and promotion of lead uptake by the turf grass) and migration control (i.e., soluble lead concentration as function of time following TPA application). Complementary to these studies was a field demonstration conducted at ten homes in Baltimore, Maryland that are known to have lead levels exceeding regulatory guidelines from former lead-based paint use. Plots were established at each home to test the field performance of TPAs compared to EDTA and water to stimulate lead uptake in existing turf grass while minimizing or eliminating the migration of lead below the root zone. Results from all experiments and the field demonstration will be presented.

Poster Session- Radionuclides

Soil Characterization Under an Operating Facility: An Innovative Approach

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Summer Indoor Radon Found to Exceed Winter Indoor Radon

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Measurement Uncertainty of Activated Charcoal and Alpha-Track Indoor Radon Detectors

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Urgent Removal of Uranium-Contaminated Wastewater

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Soil Characterization Under an Operating Facility: An Innovative Approach

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Closure of the Department of Energy's Fernald Site near Cincinnati Ohio involves removal of all above-ground structures by 2006. The preferred approach for the Transfer Tank Area (TTA) Building may involve leaving the building slab in place as a cost-effective alternative. To first consider this option, characterization of the soils immediately under the slab to assess soil contaminant levels against final remediation levels (FRLs) for uranium, thorium, and radium had to be completed. If the soil were found not to meet FRLs, an estimate of the volume of soil requiring on-site disposal was desired to facilitate the closure planning process.

Because vertical drilling through the foundation could not be done due to the presence of large tanks occupying most of the building's floor space and angle drilling could not provide samples at multiple locations immediately beneath the foundation, horizontal directional drilling was deemed to be the only practical alternative for collection of core samples.

A statistically-designed sampling plan for locating the boreholes and discrete sampling points called for collection of sixteen one-foot core samples, four from each of four boreholes at the target depth of ~six inches beneath the foundation (approximately 3.5 feet below ground surface). A Vermeer 16x20 horizontal drilling rig was used to collect the samples from locations as far as 200 feet from four different launching points in clay and silty clay soils. The project was successfully completed in nine days at a cost significantly less than the original estimate, proving the value of this technology for a specific application where site access is a particular challenge. The analytical results indicated that a few sample results (<3%) were slightly above the soil FRLs for two contaminants. The remediation plan for this area is yet to be determined.

Summer Indoor Radon Found to Exceed Winter Indoor Radon

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It has been considered true for many years, probably because of commentary in US-EPA publications for the general public, that winter concentrations of indoor radon are greater than summer concentrations. The higher amount of indoor radon in the winter is attributed to the observation that people normally keep their windows closed during the winter, allowing indoor radon concentrations to rise; the lower amount of in the summer occurs because people often open their windows, allowing outside air (which has very low radon concentrations) to enter. Other US-EPA commentary mention that heavy rainfall causes a temporary increase in indoor radon. It now appears that seasonal rainfall can cause unexpected indoor radon concentrations. In a study of over 1000 homes, where indoor radon concentrations were measured each season over an entire year (a sequence of four three-month measurements), a summer with above normal rainfall had higher indoor radon measurements than the winters before and after this summer. Both winters had less precipitation than the Awet@ summer.

Measurement Uncertainty of Activated Charcoal and Alpha-Track Indoor Radon Detectors

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According to US-EPA protocol, when a home is purchased it should be tested for indoor radon using a short-term (2-7 day) device like a container of activated charcoal, and the indoor radon concentration should be less than 4 pCi/L. When a home is tested because long-term occupancy is likely (e.g., many years), the test is commonly done using a long-term (e.g., 3 month) device like a container of film that can record the tracks produced by alpha tracks generated by radon and its immediate radioactive decay products. For long-term occupancy, the US-EPA recommends that the indoor radon concentration be less than 2 pCi/L. In our study of the indoor radon in over 1000 homes, using both short-term (3 day) activated charcoal detectors and long-term (3 month) alpha-track detectors, we found that at the 70% confidence level, when trying to estimate the average indoor radon over an entire year, an uncertainty of +/- 90% had to be applied to single activated charcoal detectors and +/- 30% to single alpha-track detectors.

Urgent Removal of Uranium-Contaminated Wastewater

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WRS Infrastructure & Environment, Inc. (WRS) was called on by the United States Environmental Protection Agency (USEPA) Region 4 Emergency Response and Removal Branch (ERRB) to perform an emergency removal action at a former uranium processing facility. Wastewater contaminated with depleted uranium and high concentrations of fluoride-chloride / potassium-sodium salts was threatening to overflow from two onsite evaporation ponds, due to fire damage to the overhead shed roof. WRS was tasked by the USEPA to design, construct, and operate a wastewater treatment system to remove approximately 600,000 gallons of this liquid waste.

Working with the USEPA and the Technical Assistance Team, WRS performed bench-scale testing of a proposed treatment process consisting of precipitation of uranium phosphate followed by ion-exchange treatment. The initial bench-scale testing identified that this proposed treatment process was not a feasible treatment option due to resin cost and performance. A second bench-scale test showed that wastewater volume reduction by evaporation followed by concentrated liquid waste solidification would provide an effective, cost-efficient treatment method, allowing disposal of a solid waste greatly reduced in volume from the original wastewater.

WRS designed and constructed an onsite wastewater treatment facility utilizing three industrial evaporators with an aggregate evaporation rate of up to 6.3 gallons per minute and a volume reduction of approximately 89%. The concentrated liquid waste is discharged to a lined roll-off and solidified with a sodium polyacrylate absorbent for disposal. Significant disposal cost and time savings over alternative disposal methods were realized using this approach.

Poster Session- Regulatory

Management of Sites in Sao Paulo State- Brazil

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Management of Sites in São Paulo State - Brazil

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São Paulo State is the most developed and industrialized of Brazilian States, corresponding to almost 40% of internal gross production and more than 30% of exportations of the country. Due to its development, mainly before 1970, when environmental care and sustainability were not a concern, some sites have been contaminated by improper storage, manipulation and disposal of chemicals. These contaminations affected the air, soil, waters, sediments and vegetation.

CETESB, the environmental protection agency of São Paulo, have been taking care of contaminated sites since 1980, when the first cases have been discovered, due its environmental control actions. More recently, with the increment in the number of contaminated sites and the evidence of exposed people, the company have intensified and improved its performance in the management of contaminated sites.

Up to December of 2004, it has been detected 1336 contaminated sites in São Paulo State: 931 (69%) due to fuel storage; 237 (18%) to industrial activity; 92 (7%) to commercial activity; 61 (5%) to waste disposal and 15 (1%) to contingence. The main contaminants are: petrolleum fuels; aromatic solvents, metals, halogenated solvents and PAHs.

To manage contaminated sites, CETESB has developed the following tools: establishment of orientation values for soil and groundwater; announcement of management procedures to be followed by all stakeholders; publishing of a technical manual for contaminated sites management.

The management of contaminated sites is based on a sequence of activities that includes: preliminary evaluation of sites were it has been developed activities that may pollute soil and groundwater; confirmatory investigation of the sites suspected of contamination; detailed investigation and risk assessment of the contaminated sites; definition and project of remediation; execution of remediation, closure and monitoring.

At present, the sites are in the following stages of management: 710 (54%) - detailed investigations in course; 123 (9%) - remedial technology defined; 484 (36%) - remedial actions in course and 19 (1%) - remediation works concluded. Regarding the remedial technologies that are being applied in the sites were remedial actions are taking place we have: Pump and Treat (271 sites); Free phase recovery (205 sites); soil vapor extraction (171 sites); soil/waste removal (124 sites); hydraulic barrier (35 sites); biorremediation (24 sites); monitored natural attenuation (23 sites); chemical oxidation (6 sites).

Efforts are being made in the state to approve a specific law for contaminated sites and to create a financial fun to support remediation action in the sites.

Poster Session- Risk Assessment

Development of a Standardized Approach for Assessing Potential Risks to Amphibians Exposed to Sediment and Soils

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Development of Soils Cleanup Levels and Distribution Functions in the Mexican Framework

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Development of Site-Specific, Ecological PRGs for PCBs and Mercury

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Development of a Standardized Approach for Assessing Potential Risks to Amphibians Exposed to 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. This project was conducted 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, developing standardized laboratory testing techniques, validation of the toxicity testing using spiked sediments, developing amphibian screening values, and preparation of a guidance manual for assessing potential risks to amphibians at Navy facilities. The second phase of work involves refining the test protocol for use with frogs and salamanders, demonstrating and validating use of the amphibian risk assessment protocol at nationwide DoD sites, and achieving ASTM certification. The guidance manual presents a standardized two-tiered risk assessment protocol for evaluating potential risks to amphibians. The Tier I Amphibian Ecological Risk Assessment (ERA) Protocol comprises a screening level ERA. This approach uses readily available information to identify potential amphibian exposure pathways at a site and determine which exposure pathways are potentially complete. Ultimately, the results of the Tier I protocol are used to determine whether or not additional amphibian ERA is warranted. The Tier II Amphibian Ecological Risk Assessment Protocol comprises a refined ERA, and is conducted if recommended at the conclusion of the Tier I assessment. The Tier II protocol approach uses site-specific information to evaluate complete exposure pathways and amphibian ecological resources that are identified through the Tier I screening. For both salamanders and frogs, the refinement, demonstration, and validation phase of work includes additional analysis in the laboratory and the field using two constituents commonly co-located and found at military sites and ranges (lead and copper) and a variety of bioavailability scenarios designed to account for site-specific geochemical and contaminant complexation effects.

Development of Soils Cleanup Levels and Distribution Functions in the Mexican Framework

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The results of probabilistic risk assessment to develop site specific cleanup levels are presented. Characterization of the exposure duration and of the potential Mexican population expose to hydrocarbon contaminated soils is one of the purposes of the study. Sensitive analysis was performed to an exposition model to direct occupational contact exposure to benzene in soil: variables in risk model which contribute most to the variation in estimates of risk conducted field studies. Field investigations focuses on an epidemiological study applied to 350 adults in an urban/rural Mexican community in order to develop empirical distribution functions to address site-specific conditions. Discussion of variability and uncertainties on the main exposure variables developed for Mexican context shows relevant differences with typical default values; arguments on the input variables with point estimates are also discussed. The iterative truncation method was used to identify the concentration at which the risk is acceptable and the maximum concentration that might be left in place. Final discussions about actual remediation goals used in Mexico and alternatives to address concern on uncertainties and variability in Mexican context are presented. This information can be used to guide Mexican research on risk assessment to prioritize resource allocations for additional data collection efforts (e.g., children characterization) and to focus discussions on remediation policy choices.

Development of Site-Specific, Ecological PRGs for PCBs and Mercury

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Ecological PRGs for sediment were developed using site-specific bioaccumulation factors for PCBs and mercury at the former Naval Surface Warfare Center (NSWC) White Oak, Silver Spring, Maryland. The ecological PRGs were developed for remedial efforts associated with a perennial stream that supports a benthic community and a small fish population. Post removal sediment sampling of West Farm Branch after a removal action at an adjacent site indicated high levels of mercury, silver, and PCBs in the sediment at concentrations that exceeded previously developed base-wide risk-based levels. The base-wide levels were developed based on data collected from streams other than Westfarm Branch at the base and so a study was initiated to develop sediment PRGs from composite sediment and fish samples collected from the creek. Black-nose dace were selected as the preferred target species, based on their abundance in previous collection records from the area and their relatively small home range. PRGs developed for the protection of piscivorous wildlife were calculated as the average allowable sediment contaminant concentration over the entire length of Westfarm Branch on the White Oak property using the belted kingfisher and mink as surrogate receptors. PRGs from fish were calculated using tissue residue data from the literature to develop 5th and 50th percentile LOAEL concentrations. A range of PRGs were calculated to be used in risk management decision making.

Poster Session- Risk Based Cleanup

Optimization of Site Closure Through a Risk-Based Approach

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Optimization of Site Closure Through a Risk-Based Approach

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Shaw Environmental, Inc. has assisted many clients in winning regulatory approval to close hazardous waste sites through an optimized approach focused on strategic data collection and evaluation. By recognizing the right amount and type of data sufficient for site characterization, utilizing strategic sample locations, and employing the tools to distinguish site-related concentrations from those that are attributable to natural occurrence, expensive remedial actions have been avoided. Estimated savings are in excess of 50 million dollars.

Use of an experienced multi-discipline team is an important factor in Shaw's success. A team approach during investigation planning assures relevant data collection so that the risk assessments are defensible, without data gaps, and the risk assessment conclusions agree with the site history and site conditions. Up-front agency agreement on data gaps, risk assumptions and remediation goals avoids lengthy discussions and comments during the regulatory agency review and approval process. Electronic compilation of data and ready access to data for all team members across multiple Shaw offices allows the project to draw on talent outside of the local office. Electronic access to data supports nature and extent evaluations, statistical tests, geochemical evaluations, and the risk assessment process. Examples are provided to illustrate application of the tools and results of the analyses.

Poster Session- Site Assessment

An Integrated Geophysical Approach to Environmental Site Investigation

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Using Waterproof, Vapor Permeable Membrane Samplers for Groundwater Sampling Delivering Groundwater Data Without Collecting a Water Sample

Jay W. Hodny, W. L. Gore & Associates, Inc., Elkton, MD

Wayne M. Wells, II, W. L. Gore & Associates, Inc., Elkton, MD

Guidelines for Assessing Disturbed Soils in Urban Wet Areas

Joyce M. Scheyer, USDA Natural Resources Conservation Service, Lincoln, NE

Russell F. Pringle, USDA Natural Resources Conservation Service, Fort Worth, TX

Field Investigation of PAHs in Soils around Nara City in Japan

Ryuji Takeda, Kinki University, Nara, Japan

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Soil Contamination by Polyaromatic Hydrocarbons in Reclaimed Open-cast Mines

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An Integrated Geophysical Approach to Environmental Site Investigation

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The ability to effectively characterize subsurface conditions over large areas is a continuous challenge in environmental site assessment. Often, property owners, consultants, and regulators require non-intrusive methods to develop an understanding of subsurface conditions at a site to determine if more intensive site investigation are needed and gather essential data to develop those programs. Near surface geophysical surveying techniques, particularly ground penetrating radar (GPR) and electromagnetic terrain conductivity (EM) measurements, have the potential to provide data that are highly useful in interpreting subsurface site conditions with respect to potential environmental liabilities. GPR and EM techniques are commonly used jointly to investigate a variety of potential environmental issues including orphan underground storage tanks, conductive contaminant groundwater plumes, buried debris and industrial waste, and subsurface piping and drainage systems. In addition to being used as a preliminary tool, GPR and EM surveying provides complimentary data that aid in refining the interpretation and analyses of other data in an effort to develop a more comprehensive understand of the site. GPR and EM data are frequently used to develop soil boring, groundwater monitoring well, and excavation programs that are essential in developing a more fundamental understanding of the subsurface at environmental sites. This presentation will discuss an integrated geophysical approach utilizing GPR and/or EM to rapidly, non-invasively, and cost-effectively identify subsurface characteristics and features at environmental sites in a variety of field settings. Through the use of case studies, the presentation will demonstrate how integrated GPR and EM survey techniques are commonly used to identify orphan underground storage tanks, buried debris/industrial waste, and other environmental related subsurface site characteristics and how this data can be used to efficiently direct more costly investigative programs.

**Using Waterproof, Vapor Permeable Membrane Samplers for Groundwater Sampling
Delivering Groundwater Data Without Collecting a Water Sample**

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The growing acceptance of passive collectors for non-purge groundwater sampling has led to the development of several diffusion-based devices. The more common ones are generally effective in collecting and reporting non-water soluble volatile organic compounds. However, they can be cumbersome to handle, may require costly field sampling time and can be prone to collection errors and sampling variability. The desire for better field sampling tools, along with a growing need to accurately detect and report water soluble compounds, along with volatile, semi-volatile and heavier compounds, has driven continued research into alternative diffusion-based samplers.

A sorbent-based, passive diffusion sampler constructed of waterproof, vapor permeable membrane was verified by the US EPA ETV program in 2002 for volatile compound monitoring in groundwater applications. Renewed research and development efforts, along with laboratory and field sampling experiments, have demonstrated that this sampler can detect 1,4-dioxane and other water-soluble compounds, along with compounds in the volatile and semi-volatile range. Further, the ability to report the data in units of concentration has been investigated with promising results.

The presentation will discuss the recent sampling results along with the concentration capability development efforts. The objective of the presentation is to demonstrate that accurate and reliable groundwater data can be acquired without collecting a water sample.

Guidelines for Assessing Disturbed Soils in Urban Wet Areas

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Requests for assistance from the field indicate confusion about terms and measurement protocols for soils in urban wet areas. In some instances soil properties that are unique to urban areas and that impact Hydrologic Soil Groups, Hydric Soils, and Drainage Classes need clarification. In other cases, there has been improper use of soil properties for urban wetland and floodplain decision-making. Basic models are often used in simplified form without incorporating the nuances of urban soil interpretations based on internal soil dynamics.

Our objective is to ease the transition of engineers and planners into making soil-based decisions for urban wet areas. We provide a bridge for non-soil scientists to correctly use soil information from different databases. This bridge is based on calculations and diagrams as templates for investigating urban soils. We hope to foster discussion of soil behavioral similarities and differences among urban wet areas.

The properties and measurements for urban soils in this study are drawn from three databases. Measured properties are from the laboratory database. Estimated properties are from the spatial map unit database. Site-specific measurements (such as infiltration or compaction) constitute a third database.

Data for each urban soil are summarized in these diagrams and charts 1) diagram of soil profiles with horizons highlighted that determine internal water flow, 2) diagrams of clay content, very fine sand content, and bulk density changes with depth that affect soil wetness, 3) percent water filled pores and potential water flow calculated between internal soil horizons, 4) effect of compaction and internal layering within the poorly drained “D” hydrologic soil groups, and 5) a chart of key properties of disturbed soils in urban areas that may affect the hydric status of a soil.

Field Investigation of PAHs in Soils around Nara City in Japan

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PAHs are the general term of the compound, having two or more benzene rings. These are discharged from diesel motor gas, tanker accidents, oil emissions by cars, and so on. They float in the atmosphere, and it is considered that they are absorbed in soil as a result of rain.

Generally, compounds that have two and three benzene rings show only toxicity, whereas these having four or more benzene rings show toxicity, carcinogenicity and mutagenicity. Especially, benzo(a)pyrene shown to be an agency of endocrine disrupter. We investigated the action of 16 PAHs specified by the U.S. EPA in soil around Nara city in Japan. Soil was collected from different locations involving traffic and vegetation. Soil from three locations around our university were collected every month for investigating seasonal movement. PAHs were extracted from soil by soxhlet extraction with dichloromethane. They were then analyzed quantitatively by HPLC/UV. We classed PAHs by number of rings, and examined concentration and seasonal movements. All content of 16 PAHs in soils increased in proportion to traffic volume. At the same locations of traffic volume, the gravitation at a location with plant with all content of 16 PAHs in soils was, furthermore, found to have a low concentration. There were different seasonal movements of the 2, 3-ring and 4, 5, 6-ring PAHs. 4, 5, 6-ring PAHs have strong correlation each other ($r > 0.79$), but there were no correlation between 2, 3-ring and 4, 5, 6-ring PAHs. As a result, the traffic volumes are exposition sources of 4, 5, 6-ring PAHs in soils.

Soil Contamination by Polyaromatic Hydrocarbons in Reclaimed Open-cast Mines

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Polyaromatic hydrocarbons (PAHs) rank currently with priority pollutants found in all environmental compartments. Contamination of soil by PAHs was assessed in the revitalized mines. Six sampling sites were chosen within the area of recultivated open-cast mine in the Most region situated in north Bohemia. The strategy of composite samples was used. Sampling was realized twice (April, October) at four from six sample sites. Two sample sites became inaccessible during the second sampling therefore only one sample was taken. Samples were tested for concentrations of PAHs using high resolution liquid chromatography technique with fluorescent detector. Twelve PAHs identified in soil samples included: anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, benzo(a)pyrene, chrysene, dibenzo(ah)anthracene, fluoranthene, naphthalene, phenanthrene and pyrene. Concentrations nearly all particular polycyclic condensed aromatic hydrocarbons were below the limits of determination (0.05 – 0.10 µg/kg in dry matter) even for such analytes which are usually prevailing in soil samples (e.g. anthracene). Concentration of PAHs found in samples from the sampling sites 1 and 2 were higher compared with the other sites. The possible reason could be that these sampling sites are located in the vicinity of decanting plant. The highest concentrations (in µg/kg dry matter) were found for: naphthalene (1.52 – 36.6), fluoranthene (4.28 – 46.5), pyrene (4.9 – 16.0), benzo(b)fluoranthene (1.8 – 15.2), benzo(a)pyrene (1.32 – 9.58), benzo(k)fluoranthene (1.55 – 7.40) and anthracene (3.30 – 5.76). In compliance with valid limits declared by the Ministry of the Environment of the Czech Republic it can be stated that extremely high values were not found in the locality within the scope. The only analyte for which the limit was exceeded was naphthalene at one of the six the sampling sites. Some additional samples must be taken in order to make a reliable decision.

Poster Session- Training Range Issues

A Novel Phosphate Technology for the Sustainable Management of Pb Impacted SAFR Soils

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A Novel Phosphate Technology for the Sustainable Management of Pb Impacted SAFR Soils

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The application of phosphates for the remediation of lead contaminated soil is an established remediation technology. It relies on the ability of lead to precipitate as the highly stable lead apatite (pyromorphite) mineral in the presence of soluble phosphate ions. Many different forms of phosphate have been tested and used in soil lead stabilisation. Examples include aqueous phosphate solutions (e.g. phosphoric acid), phosphate fertilisers (e.g. triple super phosphate), and biogenic or geologic apatites (e.g. bone and rock phosphate).

There is growing interest from regulators concerning the environmental consequences of phosphate leaching during soil lead stabilisation. This can lead to eutrophication of water bodies, which is a problem in much of the United States and Europe. In addition there is awareness that in certain soils soluble phosphate can compete with soil bound arsenate ions, displacing the arsenic into the soil solution and potentially causing off site leaching. Confronted with these issues, Slater (UK) Limited has developed an apatite metal stabilisation product that retains excellent reactivity against lead whilst minimising both the problems of phosphate leaching and oxyanion mobilisation.

Slater (UK) Limited's product has been tested alongside a conventional phosphate stabilisation technology on metal contaminated soils obtained from both urban brownfield sites and military Small Arms Firing Ranges (SAFRs). Tests applied include TCLP, SPLP, BS EN 12457 and SBET. The results reveal that the new product offers excellent lead stabilisation equivalent to that of the standard phosphate material. However in contrast to the standard phosphate product it results in minimal free phosphate release into the soil. It also does not significantly mobilise arsenic in the soil. When applied to SAFR soil, the new product also significantly stabilises antimony. This contrasts with the standard phosphate product which mobilises this toxic metalloid. It is concluded that Slater (UK) Limited's new apatite metal stabilisation product has considerable application in the sustainable remediation of urban brownfield and SAFR impact berm soils.

Poster Session- Vapor Intrusion

Derivation of Soil Screening Values for the Vapor Intrusion Pathway – Is this a Valid Approach?

Lisa Bailey, Menzie-Cura & Associates, Inc., Winchester, MA

Application of the Johnson and Ettinger Vapor Intrusion Model to a Outdoor Trench Scenario

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Derivation of Soil Screening Values for the Vapor Intrusion Pathway – Is this a Valid Approach?

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The EPA Draft Vapor Intrusion Guidance provides risk-based screening values for soil vapor, groundwater, and indoor air. In addition, a number of states provide groundwater and soil vapor screening values that are protective of the vapor intrusion pathway. However, the majority of state and federal soil screening values do not include the indoor air pathway. The Johnson & Ettinger (J&E) soil to indoor air model provides a tool for calculating soil screening values for the indoor air pathway. However, given the uncertainties in predicting partitioning relationships from soil to soil vapor, there is considerable uncertainty associated with the application of this model for predicting indoor air concentrations from soil concentrations. Even with this uncertainty, EPA's 2002 Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites discusses application of the J&E soil model to derive site-specific risk-based soil screening values based on the vapor intrusion pathway; however, the guidance emphasizes that the values should be based on site-specific parameters, and that soil vapor data may be more appropriate for evaluation of the indoor air pathway. Here we present several example sites where both soil and soil vapor data were collected. We present the derivation of soil screening values from the J&E model, and apply these screening values to the soil data sets, calculating risk from modeled indoor air concentrations for the chemicals exceeding the derived soil screening values. We also present risk estimates from indoor air concentrations modeled from soil vapor, first applying soil vapor screening values from EPA's draft vapor intrusion guidance. We compare the risk assessment results from both methods.

Application of the Johnson and Ettinger Vapor Intrusion Model to a Outdoor Trench Scenario

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Construction-related activities are a foreseeable future use at many hazardous waste sites. If volatile chemicals are present in soil or groundwater, construction workers may be exposed to vapors that accumulate in construction trenches dug in soil located in the contaminated area. In order to evaluate potential future risk to construction workers that work in dug trenches, it is important to estimate potential concentrations of volatile chemicals in an outdoor trench. The Johnson and Ettinger (J&E) model is a screening-level model widely used to estimate the transport of contaminant vapors emanating from either subsurface soils or groundwater into indoor spaces located directly above the source of contamination. The J&E model estimates the concentrations of vapors in a building that enter by two mechanisms: diffusion and pressure-driven advection, and through two media: soil and the building foundation. For vapor intrusion into a trench, diffusion through soil is the only mechanism. Assuming that this mechanism is the rate-limiting, the governing equation used by the J&E model to calculate attenuation coefficients for vapors simplifies, such that many of the parameters used by the model drop out of the equation. By selecting appropriate model inputs, the J&E model can be applied to an outdoor trench scenario. We discuss the model parameters that are needed to apply the J&E model to an outdoor trench scenario, and we develop defaults that may be used with the goal of using the J&E model to provide a conservative estimates of air concentrations in a trench for use as a screening tool for risk assessment.