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ABSTRACT BOOK

The 20th Annual International Conference on Soils, Sediments and Water

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University of Massachusetts at Amherst

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Bioremediation of Acid Drainage by Means of a Passive Treatment System

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Acid drainage waters generated in a uranium deposit were treated by means of a pilot-scale passive system consisting of an alkalizing limestone drain, an anoxic barrier for microbial dissimilatory sulphate reduction and an aerobic rock filter for manganese and organics removal, connected in a series. The waters had a pH in the range of about 2.7 – 3.2 and contained radionuclides (uranium, radium), heavy metals (copper, zinc, cadmium, lead, cobalt, nickel, 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 water flow rate through the system varied in the range of about 0.1 – 0.3 l/s. In the alkalizing drain the pH of the waters was increased to values higher than 7 and as a result of this most of the iron was precipitated as hydroxides. A portion of arsenic was also removed mainly by sorption on these hydroxides. The permeable barrier had a volume of 12.5 m^3 and was filled by a mixture of solid biodegradable organic substrates (cow manure, plant compost, hydrolysate of rich-in-cellulose wastes from the paper industry, hay). The barrier was inhabited by a microbial community consisting mainly of sulphate-reducing bacteria and other metabolically interdependent microorganisms. In the barrier the non-ferrous metals were precipitated mainly as the relevant insoluble sulphides, and uranium was precipitated mainly as uraninite (UO_2) as a result of the prior reduction of the hexavalent uranium to the tetravalent form. Radium was removed mainly as a result of its sorption by the solid organic matter present in the barrier. Portions of the other metals were also removed in this way. The effluents from the barrier were enriched in dissolved organic compounds and usually still contained manganese in concentrations higher than the relevant permissible level. These effluents were treated in the rock filter where the Mn^{2+} ions were oxidized by different aerobic heterotrophic bacteria to Mn^{4+}, which were precipitated as MnO_2. The dissolved organic compounds were removed as a result of their oxidation by the heterotrophs inhabiting the filter.

Restoration of Ecosystems and Long-Term Stabilization of Initially Acidic Pit Lakes with a case study at the Gilt Edge Mine Superfund Site, South Dakota

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EPA NRMRL Mine Waste Technology Program and Region VIII Superfund office have jointly conducted an in-situ remediation and restoration technology demonstration and Treatability Study at the Anchor Hill Pit Lake, Gilt Edge Mine Superfund site. The treatability study project has been quite successful to date. The pit lake originally contained 77,000,000 gallons of pH 3 water with elevated heavy metals, sulfate, and nitrate. The Green World Science® patented process for in situ treatment of metals and other contaminants (exclusively licensed to ARCADIS) was implemented to encapsulate metals; create stable long-term water quality and restore a sustainable ecosystem. This technology allows for ecosystem restoration in situ and is substantially more cost-effective than treatment through ex situ water treatment facilities.

Concentrations of dissolved COCs have decreased more than 99%, and aquatic standards (cold water biota under chronic exposure) for heavy metals were attained. Discharge of remediated water from the pit lake to nearby Strawberry Creek began in June 2004. Site stakeholders are considering a site-wide water treatment system whereby acidic waters are collected in the pit from across the site (at a rate of up to 150 gpm), treated in the pit lake in a somewhat “batch” mode, and then subsequently discharging these waters to the creek following a pre-filtration step. This innovative approach, creating a long-term stable ecosystem with low anticipated maintenance requirements for further treatment of acid migration and drainage, has substantial implications on closure strategies for operating and closed pits such as form or may form at mine closures elsewhere throughout the United States.

Results from successful treatment of a uranium mine pit lake in Sweetwater County, WY and a molybdenum mine pit lake in Tonopah, NV will also be presented.

A Geochemical overview of the Berkeley pit-lake, Butte, Montana, USA

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The Berkeley pit-lake contains over 100 billion L of highly acidic (pH 2.6), metal-rich water (Fe ~ 1000 mg/L; Zn ~ 600 mg/L; Cu ~ 150 mg/L). The pit-lake began filling in 1983 when mining of the Butte ore body temporarily ceased, and is still filling at a rate of 7 to10 million L/day. Most of this influent water is deep groundwater draining ~ 10,000 km of subjacent flooded underground mine workings. In the past, an additional source of influent water was the Horseshoe Bend spring (HBS), a large, acidic (pH 3.1) seep discharging near the base of a nearby tailings dam. In 2003, a modern lime treatment facility was built to treat the HBS. The same facility will eventually treat Berkeley pit-lake water when the lake reaches a critical elevation, some 10+ years from now.

Two intriguing aspects of the Berkeley pit-lake are that its water quality is much worse than all known influent waters, and that the chemistry of the pit-lake has shown no improvement with time, whereas the water quality of the subjacent flooded mine workings has improved dramatically with time. In the past 5 years, our research group has combined water quality monitoring, bench-top experiments, and stable isotope investigations to attempt to explain these disparities. The poor water quality of the pit-lake is attributed to a combination of several factors, including: 1) leaching of metal salts from the pit walls as the lake levels rise; 2) evapo-concentration; and 3) subaqueous oxidation of pyrite by dissolved ferric iron. A 4th hypothesis – influx of deep groundwater of poor quality from the direction of the active tailings dam – is also possible, but is difficult to test.

Portions of this study were funded by the U.S. Environmental Protection Agency through its Office of Research and Development under IAG DW89938870-01-0 through the U.S. Department of Energy (DOE) National Energy Technology Laboratory under Contract DE-AC22-96EW96405.

Treatment of Acid Mine Drainage Wastes in a Membrane Bioreactor

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Acid mine drainage (AMD) is a severe pollution problem attributed to past mining activities. AMD is an acidic, metal-bearing wastewater generated by the oxidation of metal sulfides to sulfates by Thiobacillus bacteria in both the active and abandoned mining operations. The wastewaters contain substantial quantities of dissolved solids with the particular pollutants (metal sulfates) dependent upon the mineralization occurring at the mined rock surfaces. The exposure of post-mining residuals to water and air results in a series of chemical and biological oxidation reactions that produce an effluent which is highly acidic and contains high concentrations of various metal sulfates. The metals (metal sulfates) usually encountered and considered of concern for human risk assessment are: arsenic, cadmium, iron, lead, manganese, zinc and copper. These metals as well as sulfate are considerd serious pollutants of the acid mine drainage. The pollution generated by abandoned mining activities in the area of Butte, Montana has resulted in the designation of the Silver Bow Creek-Butte area known as Berkeley Pit, as the largest superfund (National Protection List) site in U.S. This paper reports on bench-scale studies conducted to develop a biotreatment method for acid mine water (AMW) using membrane bioreactor systems to maximize the biological sulfate conversion rate and thus enhance the bioremediation of acid mine water from Berkeley Pit as well as other acidic water pit lakes.

Several biotreatment techniques for the treatment of sulfate by sulfate reducing bacteria (SRB) have been proposed in the past, however few of them have been practically applied to treat sulfate containing AMD. This research deals with development of an innovative polypropylene hollow fiber membrane bioreactor system for the treatment of AMW from the Berkeley Pit Lake using hydrogen consuming SRB biofilms. The advantages of using the membrane bioreactor over the conventional tall liquid phase, gas sparged bioreactor systems are: large microporous membrane surface to the liquid phase; formation of hydrogen sulfide outside the membrane thus preventing mixing with pressurized hydrogen gas inside the membrane; no requirement for gas recycle compressor for hydrogen; membrane surface is suitable for immobilization of active SRB, resulting in formation of biofilms, thus preventing washout problems associated with suspended culture reactors; and lower operating costs in membrane bioreactors, eliminating gas recompression and gas recycle costs. Information will be provided on sulfate reduction rate studies and on biokinetic tests with suspended SRB in anaerobic sludge and sediment source master culture reactors and with SRB biofilms in bench-scale SRB membrane bioreactors. Biokinetic parameters have been deterrnined using biokinetic models for the master culture and membrane bioreactor systems. Data will be presented also on the effect of AMW sulfate loading at 25, 50, 75 and 100 ml/min in scale-up SRB membrane units, under varied temperatures (25, 35 and 40oC), to determine and optimize sulfate conversion for an effective AMD biotreatment. Pilot-scale studies have generated data on the effect of flow rates of AMW (in MGD) and varied inlet sulfate concentrations in the influents on the resultant outlet sulfate concentration in the effluents and on the number of SRB membrane modules needed for the desired sulfate conversion rates i. The pilot-scale data indicate that SRB membrane bioreactor systems can be applied toward field-scale biotreatment (sulfate conversiuon) of AMW from Berkeley Pit Lake as well as from other acidic water pit lakes and for a recovery of high purity metals and a usable water from the AMW wastes.

Use of SRB in a Gravel Bed Reactor for Treatment of Acid Mine Drainage Water

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This paper summarizes work that was performed in response to the need by Noranda Technology Inc. to develop alternative technologies for the treatment of acid-mine drainage being produced at various mine sites in Canada. It is based on the use of sulphate-reducing bacteria entrapped in a submerged gravel bed subjected to AMD. The hydrogen sulphide resulting from the reduction of the sulphate in the AMD binds with dissolved metal ions, producing metal sulphide precipitates in the gravel bed, thus becoming essentially immobilized. This work focussed on the relationship between the activity of the SRB and the physical characteristics of the gravel bed such that a rational design procedure could be followed for scale-up from the laboratory to the field. The laboratory experiments were conducted using plexiglas columns containing gravel beds of various characteristics. The reactors had a working volume of 8 L and the AMD was treated by semicontinuous addition. The scale-up criteria was based on the development of two dimensionless numbers, F_{SRB} and D_{SRB}, that accounted for the volume of AMD entering the bed (V_c), the total surface area of the gravel in the bed (tSA), the interfacial or superficial surface area between the bed and the AMD (sSA) and the void volume in the bed (V_v). A relationship was shown to exist between the proportion of sulphate removed by the SRB to the product of the ratios of V_c/V_v and sSA/tSA (D_{SRB}), while the rate of sulphate removal was related to the product of the inverse ratio, V_v/V_c, and sSA/tSA (F_{SRB}). Based on data from the laboratory-scale gravel bed reactors, the degree of sulphate removal was best with a D_{SRB} value between 0.0075 and 0.015, while the rate of sulphate removal was inversely proportional to the F_{SRB} value.

Algal Bioremediation of the Berkeley Pit Lake System-and an *In Situ* Test Using Limnocorrals

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The Berkeley Pit Lake System is one of the largest contaminated sites in North America and is located near the headwaters of the largest superfund site in the U.S. It is filling at a rate of about 28.7 million liters per day with metal laden, acidic (pH 2.7) water. *Chlorella ellipsoidea* is one of the first autochthonous species of algae from the Berkeley Pit Lake System to be tested for its bioremediative potential. An experimental matrix was designed for this experiment using a completely randomized design (CRD). The matrix was set up with tissue culture flasks having the following treatments: Na_2HPO_4 at 0, 25, 50, 75, 100 mg/l, inoculated vs. no- inoculated with algae (187,500 algae/ml final), and filtered (0.2Fm) vs. non filtered pit water as variables, $NaNO_3$ amount was fixed at53 mg/ml. Three replicates were made of each and the experiment lasted 60 days. The results of this experiment demonstrated significant remediation of most metals. These results will be presented. As a result of the success of these experiments, it is hypothesized that these same principles should work (even better) in the Berkeley Pit Lake system if it is nutrified. In order to more fully test this hypothesis it is important to scale up from imhoff cones to more fully represent the physical and chemical properties of Berkeley Pit Lake System Water for the test. Therefore, the experiment should occur in the Berkeley Pit. This will be possible by using Limnocorrals. These enclosures consist of polyethylene in a cylindrical form (e.g. 1m diameter x 5 m depth) open at the top with camouflaged flotation collars and anchored to the bottom. Limnocorrals have been used for about 40 years for experimental studies in lakes when it is necessary to test biological, physical and chemical properties *in situ* while varying an aspect of the ecosystem on a small scale to determine the outcome (e.g. nutrients, algae) (Cruikshank 1983). Preliminary results of this experiment will also be presented.

The Effect of Drainage Flow and Saturation Conditions on Microbial Pyrite Oxidation in Mine Waste Rock

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Research on microbial iron and sulfur cycling in the mined rock subsurface has focused on biogeochemical reactions at the water-rock interface. A strategy for remediation of acid mine drainage (AMD) sources is initiation of a shift in microbial populations from dominance of iron oxidizing bacteria to iron and sulfur reducing microorganisms by the addition of biodegradable organic matter. However, control of AMD formation by organic carbon addition requires an understanding of the role of hydrologic and transport conditions in biogeochemical iron and sulfur transformation. Experiments were conducted using two 37.8-liter (10 gallon) rock microcosm tanks packed with 0.1 – 10-cm rock particles obtained from a mine waste pile near Leadville, CO resulting in 50% porosity. Filtered deionized water was recirculated through the tanks with a 10-day average hydraulic residence time. One tank was run under saturated conditions and the second was run with trickle flow to achieve 16% saturation. The headspace of both tanks was sparged with air. Production of soluble ferric iron (Fe(III)) and sulfate in the unsaturated tank was significantly higher than in the saturated system, 16 g/L in the unsaturated tank compared with 0.1 g/L in the saturated tank drainage water. Ferrous iron was negligible in the unsaturated tank (< 20 mg/L) whereas it comprised over 75% of the total soluble iron in the saturate tank drainage water, indicating suppression of bacterial iron oxidation. This was consistent with differences in dissolved oxygen, which averaged 4 mg/L in the unsaturated tank compared with 1 mg/L in the saturated tank drainage. The drainage water pH in the unsaturated tank was 1.5, significantly lower than the saturated tank drainage, which had a pH in the range of 2.5 – 3. Results indicate that availability of oxygen is critical to bacterial iron oxidation. Furthermore, significant formation of oxidized iron and sulfate products may occur during periods when drainage flow is minimal. This indicates that methods to inhibit bacterial pyrite oxidation must be effective during periods of unsaturated flow, perhaps even under snow cover.

Analysis

Characterization of Tentatively-Identified Compounds (TICs) and Data Usage Issues

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Avoiding Overestimates of Chlordane and PCBs as Co-Contaminants by Methods 8081/8082

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Analyses by mass spectrometry provide the opportunity to identify a wide range of organic chemicals in environmental samples. Mass spectra for non-target peaks are compared via a computerized search routine against the spectra in the NIST/EPA/NIH database. If a reasonable match is found, the compound is tentatively identified and its concentration estimated. If no match is found, the compound is reported as “Unknown”.

Once TICs are reported, there are no consistent guidelines for how the information should be interpreted and used. For many of these compounds, information regarding fate and transport properties and toxicity is limited or unavailable. A clear understanding of the nature of the TICs and their possible relation to site activities or compounds of concern is necessary before decisions can be made on whether they should be added as target analytes or included in risk evaluations.

One or more TICs have been reported in approximately 70% of the soil and 40% of the water samples collected at the Massachusetts Military Reservation. Over 600 individual chemicals or groups have been reported more than once in soils as TICs. While groundwater samples typically have no or very few TICs detected, over 100 different compounds have been tentatively identified more than once. TICs reported at the site have been categorized by their potential sources. Hydrocarbons and natural plant chemicals account for a high percentage of the TICs; other categories include organics from commonly used products, potential munition constituents and their degradation products, anthropogenic background compounds and analytical artifacts.

TIC data have been used in some instances to modify the analytical program at MMR. The decision to dismiss or incorporate TIC data into human and ecological risk assessments has the potential for overestimating or underestimating total site risk. The potential contribution of TICs on the uncertainty of the risk estimates is discussed.

Avoiding Overestimates of Chlordane and PCBs as Co-Contaminants by Methods 8081/8082

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Analysis of soils and sediments for chlordane and polychlorinated biphenyls (PCBs) by SW-846 Methods 8081/8082 is common. Interest in these persistent organic pollutants (POPs) has increased due to recent risk estimates, focus on POPs bioaccumulation, and application of risk based benchmark screening and action levels. Although the Method 8081/8082 electron capture detector (ECD) offers high sensitivity, the detector's non-specific nature introduces problems of definitive identification and accurate quantitation when multiple compounds of interest or interferences are present. Another difficulty introduced is that the multicomponent species are typically regulated (total PCBs and technical chlordane) although Methods 8081/8082 focus on Aroclors and the alpha and gamma chlordane components of technical chlordane. Recent studies have confirmed that other components and breakdown products of technical chlordane present comparable or higher risk than alpha- and gamma- chlordane.

In a recent Massachusetts military facility preliminary investigation, soil results were reported at or above Region 9 Residential PRGs and/or Massachusetts S-1 criteria by Methods 8081/8082. Data validation identified issues of identification and quantitation inaccuracy where co-contaminants including chlorinated pesticides, technical chlordane, and weathered PCB Aroclors may be present. The nature of the nonspecific detector and quantitation according to Methods 8081/8082 led to uncertain identification and apparent overestimated concentrations. Analytical options were explored to more definitively identify and quantitate chlordane components and PCBs. GC/MS selected-ion-monitoring (SIM) by modified Method 680 was selected for PCB congeners/homologs and major technical chlordane components (alpha-and gamma- chlordane, cis- and trans- nonachlor, and heptachlor) and breakdown products (heptachlor epoxide and oxychlordane). Initial test results confirm that Methods 8081/8082 overestimated concentration and did not provide a complete perspective to evaluate the data. Understanding the method limitations and cost-effective alternatives is necessary before evaluating any site especially where the method bias can inappropriately indicate action based on low risk based screening or action levels.

Arsenic

The Health Effects of Arsenic and Other Toxic Metals in Bangladesh's Drinking Water
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The Health Effects of Arsenic and Other Toxic Metals in Bangladesh's Drinking Water

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The recent transition in Bangladesh from drinking surface water to drinking well water has significantly reduced deaths caused by pathogens. However, death from arsenic in this well water is now affecting large areas of the country. In addition, the finding of young children with melanosis and keratosis, which are typical symptoms of arsenic poisoning in adults, and the observation of an analytical interference for the measurement of iron raised the question of other metals magnifying the toxic effects of arsenic (Sarkar, 1998; Frisbie, Maynard, and Hoque, 1999). In this study, the areal and vertical distribution of arsenic and 29 other inorganic chemicals in well water were determined throughout Bangladesh. This study of 30 analytes per sample suggests the most significant health risk from drinking Bangladesh's well water is chronic arsenic poisoning. The arsenic concentration ranged from <0.0007 to 0.64 mg/L with 48% of samples above the 0.01 mg/L World Health Organization drinking water guideline. Furthermore unsafe levels of manganese, lead, nickel, and chromium in drinking water were discovered in large areas of Bangladesh. Our survey also suggests that well water with unsafe levels of arsenic, manganese, lead, nickel, and chromium may extend beyond Bangladesh's border into the 4 adjacent and densely populated states of India. In addition to the health risks from individual toxins, possible multimetal synergistic and inhibitory effects are evaluated. Antimony was detected in 98% of the samples from this study and magnifies the toxic effects of arsenic. In contrast, selenium and zinc were below our detection limits in large parts of Bangladesh and prevent the toxic effects of arsenic. Our results may allow scientists, policy makers and aid workers to initiate programs to assist the areas most affected by the toxic metals documented by this study.

Comparison of Long Term Availability of As at between a CCA-wood Treatment Site and CCA-treated Wood Test Site

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Contamination of soils by arsenic (As) is of concern due to both its acute and chronic effects on human beings. The form of As, determined by the nature of its source and soil factors, governs its availability and subsequent uptake by both flora and fauna. This study was carried out to determine the long term availability of As at two different sites: (a) a site that used to be a chromated copper arsenate (CCA)-treated wood plant, and (b) a site that has had test plots for the leaching of As, copper (Cu) and chromium (Cr) from CCA-treated wood for more than 50 years. Profile soil samples were collected from various spots at the two sites, digested and analyzed for total As. Soil samples were also fractionated and different species of As were determined. Preliminary results showed that As concentrations and speciation at the two sites were different. The CCA-treatment site had at least an order of magnitude higher As concentrations than the treated wood site, possibly due to the direct leaking of the somewhat concentrated treating solution from the plant into the surrounding soils. Concentrations at the treated wood test site reflected that lower concentrations of As had leached from the wood and even lower concentrations were retained be the soil. Only relatively available As leached out of the wood, and therefore was not readily sorbed by the soil, at the treated wood test site. On the other hand, As persisted at the CCA-treatment site for a very long time because large concentrations were released, and they consisted of many different forms (not just the available form). The implications from these results are that the chemical forms of the released As and soil properties are important in determining its fractionation and eventual bioavailability.

Effects of Different Extraction and Analysis Techniques on the Determination of Arsenic Species in Soils

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Speciation data is usually accepted only by some regulators but there seems to be no set laws or regulations on this matter. The lack of species-specific regulations is mostly due to the absence of methods that can reliably measure the analytes of interest at the regulatory levels. The most common method for the extraction of As species from soils and sediments is the use of phosphate-based solutions. In this method, a 0.1 M phosphoric acid solution is used to extract As(III) and a 0.1 M Sodium phosphate solution for As(V) and methylated arsenic species. After extraction, the first extract is analyzed for As(III), while the second is analyzed for total inorganic arsenic and methylated arsenic species by hydride generation - cryo-trapping – atomic absorption spectrometry (HG-CT-AAS) which provides detection limits below 0.001 mg/Kg. It is very important to use a method that can differentiate between As(III), As(V) and organic arsenic species in the extracts instead of total inorganic As analysis. Time after time, we have seen that other As species are also extracted in each step that can not be distinguished from the target species by total inorganic arsenic analyses. For instance, during extraction of As(III), we have seen that 8 times more As(V) was extracted in addition to various other organo-arsenic species. This means that if total inorganic arsenic was determined instead of As(III), a false and significantly high concentration for As(III) would be obtained. This could cause costly wrong decisions in risk assessment, treatment and remediation studies. Another alternative to HG-CT-AAS is using ion chromatography coupled to an ICP-MS (IC-ICP-MS). This technique can determine each As species in a single run and allows determination of arsenosugars that are present in fish tissue. Various cases will be presented where the use of different analytical techniques resulted in unreliable data.

Phytofiltration of Arsenic: Demonstration of Laboratory and Field Flowthrough Systems

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The national standard for arsenic in drinking water has recently been lowered by the U.S. Environmental Protection Agency from 50 to 10 µg/L, with small drinking water systems carrying the majority of the burden for complying with this new limit. Chinese brake fern (*Pteris vittata)*, recently discovered to naturally hyperaccumulate arsenic in soil, was grown under hydroponic conditions to determine whether this fern could be used to remove arsenic from drinking water supplies to levels that meet this new limit. During the optimization of this technology through a series of batch experiments, the effect of source water quality (e.g., pH, dissolved ions, arsenic oxidation state), *Pteris* species, as well as growth and operating conditions on the efficiency of arsenic uptake were investigated. Currently, two flowthrough systems have been developed, with one system at Edenspace for continual testing of performance parameters (e.g., flow rate, influent arsenic concentration, quantity of clean water produced, residence time) and the other system deployed in Albuquerque, New Mexico to test performance of the system under actual site conditions. The test at Albuquerque focused on using the system as a polishing step to remove arsenic from low levels near the 10 µg/L standard. Under low flow rates (< 500 gallons per day), the system was capable of consistently achieving arsenic concentrations of less than 2 µg/L in the effluent. Performance of both systems under varying operating conditions will be presented, illustrating their potential use at small drinking water systems.

Understanding the Causes and the Permanent Solution of the Groundwater Arsenic Poisoning in Bangladesh

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The groundwater arsenic poisoning in Bangladesh is the largest disaster in the history of human civilization. More than 100 million people have been drinking arsenic poison water on a daily basis. A large number of scientists believe that the groundwater arsenic poisoning in Bangladesh is a natural disaster that the poisoning has been present for thousands of years, and that oxyhydroxide reduction is the main mechanism for the mobilization of arsenic into groundwater. However, historical ground water use data from the dug wells and the tube wells, historical medical data, arsenic toxicological data, hydrological, hydrogeological and geochemical parameters reject the reduction hypothesis and suggest that the groundwater arsenic poisoning in Bangladesh is a recent, man-made disaster and that oxidation is probably the principal mechanism for releasing arsenic into groundwater.

The oxidation of arsenic bearing minerals present in the Bengal delta sediments is responsible for the release of arsenic oxides in solution to the ground water. The subsequent migration of this arsenic contaminated groundwater through these deltaic sediments is the principal causes of arsenic poisoning in Bangladesh.

Arsenic bearing minerals of several kinds are present in deltaic environments rich in organic matter. Available sources for arsenic are the ocean, coal beds in India and mountains to the north. Minerals formed in these reducing-environments below the groundwater table would be stable unless they were exposed to oxidizing-environments. If the groundwater table were lowered by increased irrigation during the dry season or by pumping deep tube wells and irrigation wells drilled below the zone of fluctuation exposing the sediments to the oxygen of the atmosphere, then these arsenic rich minerals would oxidize thus releasing arsenic.

Increased irrigation did become necessary during India's 30 years of unilateral diversion of river water from the Ganges, Tista and 28+ common rivers of Bangladesh and India. This cut the normal flow of the 30+ rivers during the dry season. If the oxidation of arsenic bearing minerals is the cause of arsenic release to the groundwater due to a lowered water table then the solution to the arsenic problem is to restore the natural river flow of the Ganges, Tista and other common rivers of Bangladesh and India. This would restore the groundwater level to a level that existed in Bangladesh prior to the construction and commission of Farakka Barrage in 1975.

Other man made environmental disasters created by the Farakka, Tista and other barrages/dams constructed in the common rivers of Bangladesh and India would also be solved if these barrages were removed and a normal flow restored. The river beds could then be dredged and groundwater produced at a safe yield rate. A comprehensive plan not only for water supplies but associated waste disposal should be worked out for all of Bangladesh. Individual units within the plan could then be developed on the bases of need and tied into the overall plan as it develops.

The Nexus Between Groundwater Modeling, Pit Lake Arsenic Geochemistry and Ecological Risk in the Getchell Main Pit, Nevada, U.S.A.

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The proliferation of mine pits that intersect the groundwater table has engendered interest in the environmental consequences of the lakes that form after cessation of dewatering activities. Due to naturally occurring arsenic mineralization, the Getchell area has ambient groundwater-As up to 1 mg/L. To simulate post-closure groundwater inflows, MODFLOW-SURFACT was calibrated to head data collected during formation of an earlier pit lake at the site, and to dewatering data collected during later development of the underground workings. Predictive simulations show that the pit lake will be a terminal water body recovering to within 99% of the pre-mining water level within 100 years after termination of dewatering.

To predict pit lake chemistry, wall rock characteristic of the Ultimate Pit Surface (UPS) was leached in humidity cells to develop Chemical Release Functions (CRFs) describing temporal UPS leaching. The groundwater flows through the UPS (from MODFLOW-SURFACT) were coupled with the oxidized thickness of the exposed UPS and the CRFs for each lithological unit to compute pit lake water quality. The juvenile Getchell Main Pit lake (after 5 years) is predicted to be a calcium sulfate, pH 7.8 water body containing 920 mg/L TDS and 0.6 mg/L As. Evaporation and later inflows result in a mature pit lake (at 100 years) with a pH of 7.9, 1580 mg/L TDS and 0.9 mg/L As. The predicted pit lake chemistry was consistent with the pre-dewatering pit lake chemistry.

The pit lake chemistry was used as input to an ecological risk assessment for the for 8 indicator species; the mallard duck, cliff swallow, golden eagle, little brown bat, spotted sandpiper, deer mouse, mule deer and cattle. Receptor exposure scenarios for the mature pit lake demonstrated that As dose concentrations were driven primarily by food ingestion for the receptor species, except for the sandpiper (a shore bird) where sediment ingestion was the driver. However, because As does not bioaccumulate substantially in the food chain it did not translate into an unacceptable dose.

Bioindicators of Environmental Health: Concepts and Applications

Use of Bioindicators for Site Monitoring Requirements
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Immunological Alterations as Bioindicators of Environmental Health
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Jessica Duffy, New York University School of Medicine, Tuxedo, NY
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Erik Carlson, New York University School of Medicine, Tuxedo, NY

Field Bioindicators in Reptiles and Amphibians
John Schaffer, Tetra Tech, Morris Plains, NJ

Selenium as a Bioindicator of Susceptibility to Mercury Toxicity: The “Tonic to Target” Paradigm Shift
Nicholas V. C. Ralston, Energy and Environmental Research Center, Grand Forks, ND
Laura J. Raymond, Energy and Environmental Research Center, Grand Forks, ND

Genomic Indicators of Environmental Health
Rebecca D. Klaper, University of Wisconsin-Milwaukee, Milwaukee, WI

Biological Indicators for Freshwater Flow in the Tampa Bay Estuary and Tidal Rivers.
David Wade, Janicki Environmental, Inc., St. Petersburg, FL
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Use of Bioindicators for Site Monitoring Requirements

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The use of bioindicators for monitoring site conditions has a long history starting with the use of canaries by miners to monitor carbon monoxide levels in mines. In the early 1970s bioindicators emerged as formal monitoring tools for soil, water and air pollution, e.g. use of invertebrates and fish to monitor the quality of streams as recommended by Clean Water Act monitoring programs. Specifically, bioindicators have been used investigators to characterized site conditions for research project and as formalized monitoring tools for regulatory monitoring requirements or recommendations. This paper will review the use of bioindicators of soil, water and air quality conditions as part of site regulatory site monitoring requirements and recommendations. An analysis of past and current trends in the use of bioindicators for site monitoring will be presented. The use of bioinidicators both nationally and internationally will be discussed.

Immunological Alterations as Bioindicators of Environmental Health

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Fish represent a sensitive target for the toxic effects of most aquatic pollutants. Because of the sensitivity of the immune response to environmental toxicants, and its importance for maintaining host resistance against disease, chemical-induced immune dysfunction can be predictive of the toxicological hazards/risks associated with pollutant exposure. The previous establishment of highly sensitive immune assays to enumerate these alterations has culminated in a well-characterized battery of endpoints that can be used successfully to predict biological impact and adverse health outcomes in exposed populations. Studies in this laboratory using a a variety of laboratory-reared and feral fish species (i.e., Japanese medaka, bluegill, tomcod, smallmouth bass, flounder and trout) have demonstrated that immune parameters such as antibody-forming cell numbers, lymphoproliferation, host resistance against infectious pathogens and oxygen radical production can be used successfully to assess the immunotoxicity of common aquatic pollutants such as metals (i.e., cadmium, nickel and seleniium), polycyclic (i.e., benzo[a]pyrene [BaP]), and halogenated (polychlorinated biphenyls [PCB]) aromatic hydrocarbons, pesticides (i.e., permethrin and malathion), as well as complex environmental mixtures (i.e., contaminated groundwater). For example, smallmouth bass recovered from a PCB-contaminated site demonstrated a suppressed ability to phagocytose foreign agents, while medaka exposed to environmentally-relevant levels of malathion in the laboratory demonstrated reduced resistance against infection with bacterial pathogens and a compromised ability to produce antibodies. Such sensitivities also have major applications in efficacy-testing programs including those following remediation. Information on host immunocompetence generated from such programs could aid in management decisions regarding the effectiveness of any remedial activities, and the rates of recovery of affected sites. It could be assumed that changes in directions indicating decreased exposure/effects of affected sites precede an improvement in the ecological health of the environment. Thus, assays that measure immune dysfunction can serve as rapid indicators of the direction of change in the toxic exposure and effects at a particular monitoring site. Funded by USACEHR Contract No. DAMD 17-99-9011 and Hudson River Foundation Graduate Fellowship.

Field Bioindicators in Reptiles and Amphibians

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Ecological risk assessments have long focused on assessing exposure and characterizing risks to higher vertebrates such as birds and mammals based upon the historical and current toxicological studies being conducted in field and laboratory populations. Fish too, have also received considerable attention given their importance in the food chain and to human consumption. Reptiles and amphibians have not received as much attention and field based investigations for population health remains limited. An increasing toxicological literature base and renewed interest in these vertebrate groups as indicator species within the food chain has resulted in a greater need for field based studies to determine the relative health of these species in contaminated environments. In an attempt to assess the utility of field based observations, a screening checklist that parallels those used for external fish necropsy was developed. A field checklist allows for consistent recording of health and overall condition using field based observations for individuals of the species collected. The checklist primarily focuses on aquatic reptile species as a majority of contaminated sites have aquatic habitats with contaminated surface water and sediments. The primary group focused upon was the freshwater chelonians, which are long lived, and thus prone to prolonged exposure to bioaccumulating contaminants in local food chains.

Selenium as a Bioindicator of Susceptibility to Mercury Toxicity: The “Tonic to Target” Paradigm Shift

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Measuring the amount of mercury present in the environment or food sources may provide an inadequate reflection of potential health risks if the protective effect of selenium is not also considered. Selenide has an extremely high affinity for mercury (k_d 10^{-45}). As a result, Hg-Se complexes readily form, especially in intracellular reducing environments. This interaction has also been assumed to have a physiological “protective” effect whereby supplemental Se prevents negative effects in animals fed otherwise toxic amounts of Hg. Likewise, numerous studies indicate that the Se naturally present in foods, such as fish and seafood, provides this physiological protection against Hg toxicity. However, rather than being a protective “tonic”, selenium may instead be the “target” of Hg toxicity, whereby Hg sequesters Se. Studies have shown Hg exposure reduces the activity of enzymes that require the primary amino acid, selenocysteine, at their active site. The additional Se may simply support continued Se-dependent enzyme synthesis. Similarly, Se addition to aquatic ecosystems has been found to enhance Hg retirement and reduce Hg bioaccumulation through Hg-Se formation. Since Se suspended in the water column will be in an oxidized state that is unlikely to bind Hg, the mechanism of Hg-Se formation appears likely to be biologically mediated. The Hg-Se interaction is apparent throughout the mercury cycle, influencing its transport, biogeochemical exposure, bioavailability, toxicological consequences and remediation. Further research is necessary to understand the molecular mechanisms responsible for Se’s protective effects against Hg toxicity and identify populations which may be protected or at greater risk.

Genomic Indicators of Environmental Health

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Traditional biological indicators to measure environmental health require destructive sampling, rely on population and community level responses, and are retrospective in their assessment in that they attempt to link current declines in populations to past measurements of stressors. In addition it is difficult to separate the exposure and effects of the multiple factors to which an organism may be exposed in the environment. Genomic technologies are beginning to offer a method to overcome these obstacles in risk assessment. By measuring changes in gene expression (the production of mRNA or proteins) of hundreds of genes at a time, genomics can provide a fingerprint for each stressor, measure effects at low levels of exposure, and identify changes in physiology before a larger physical response is detected. As an example, fathead minnows that were fed methyl mercury contaminated diet were analyzed for changes in gene expression to liver and gonad tissues. At very low levels of mercury contamination changes in the expression of genes associated with reproduction, nervous system function, and immune response were observed. A companion study found a decrease in overall fitness of females and a change in hormone levels of male fish with increasing exposure. Linking molecular, hormonal and fitness level responses will ultimately be necessary to initially validate molecular indicators as biomarkers. However, once validated these measurements will provide a sensitive, rapid way to test for exposure and possible fitness effects within a population. Genomics may also provide a way to link the response of multiple species in the environment. Other projects using genomics of native species, from sturgeon to Daphnia will be discussed.

Biological Indicators for Freshwater Flow in the Tampa Bay Estuary and Tidal Rivers

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A suite of new biological indicators has been developed to identify and quantify biological indicators for freshwater flow in the Tampa Bay Estuary and tidal rivers. The development of these indicators was funded by Tampa Bay Water, the Tampa Bay Estuary Program, and the Gulf of Mexico Program. These indicators include:

- A benthic salinity index to estimate antecedent salinity conditions for a location based on benthic community structure;
- Statistical models relating fish populations to freshwater flow; and
- Artificial neural network models of the relationships between biological communities and freshwater inflow.

These biological indicators were developed to support environmental managers who are charged with the dual responsibility of balancing the development and utilization of freshwater resources with the protection of environmental conditions and minimization of impacts to living resources within the Tampa Bay Estuary and its tributaries.

The bay and its major tributaries are gaining increasing importance as a water supply source. Withdrawals and consumptive use from tributaries will reduce freshwater flow in the system, however, the critical question remains regarding what quantifiable effect these reductions in freshwater flow will have on the hydrology and ecology of the river and estuary. These indicators were developed to support the efforts to address these important questions.

Salinity is often the most influential factor in determining habitat potential for benthic biota in coastal areas. Freshwater inflow to estuaries affects the salinity regime and subsequently, the habitat potential of these areas. Modifications to freshwater flow, in terms of volume or timing, can alter salinity and biological communities in unwanted ways. Benthic macrofauna and fishes are often used as indicators of habitat quality, often reflecting pollution or other causes of degradation. The specific objective of these projects was to develop new empirically based indicators of salinity effects and the resulting biotic community structure. The overall approach was to develop statistical tools with the following key characteristics:1) based on Tampa Bay specific monitoring data, 2) based on monitoring programs that will continue in the future (e.g., same collection gear, same taxonomic methods), 3) empirically-based using an unbiased approach, 4) adjusted for significant confounding influences (e.g., silt/clay composition), 5) validated with an independent set of observations, 6) biologically meaningful, and 7) scaleable (i.e., applicable to station, bay segment, bay-wide uses). A comprehensive benthos, pollutants, and water quality database was developed to integrate the data from several concurrent monitoring programs and develop a very large suite of derived biological metrics.

Results of these analyses indicated that developing several segment specific indicators would be more useful than developing a single indicator. Indicators were developed for four river segments (Alafia River, Hillsborough River, Palm River, and McKay Bay) based on relationships between flow, ambient bottom salinity and biological communities.

Bioremediation

Bioremediation of Dual Contaminant Mixtures: TCE and RDX
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A Kinetic Model of Reductive TNT Transformation by *Escherichia coli* Resting Cells
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Combined Anaerobic Oxidation and Reductive Dechlorination for Optimizing Bioremediation of CVOCs: Theoretical and Practical Considerations
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Evaluation of Biological Treatment Options for N-Nitrosodimethylamine (NDMA) in Groundwater
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Sheryl Streger, Shaw Environmental, Inc., Lawrenceville, NJ
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Treatment of Vinyl Chloride Contaminated Groundwater at a Landfill Site: Comparison of Biosparging and iSOC™ Bioremediation Systems for Plume Cut-off
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Treatment of PCP-Contaminated Soil Using an Engineered Ex Situ Biopile Process at a Superfund Site
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A Comprehensive Performance Analysis of Hydrogen Release Compound (HRC®): Lessons Learned and Future Directions.
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Bioremediation of Dual Contaminant Mixtures: TCE and RDX

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High explosives and chlorinated solvents are common soil and groundwater contaminants at numerous military facilities worldwide. One such site is the former Nebraska Ordnance Plant (Mead, NE), which has areas of contaminated groundwater with both trichloroethylene (TCE) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazocine). Contaminated groundwater is currently extracted and treated using ex-situ adsorption to granular activated carbon (GAC). Bioremediation of this contaminant mixture is a potential alternative for treating groundwater at the site, as numerous studies have found that these contaminants are amenable to biological transformation under reducing conditions. In the present study, two cultures are being tested for biodegradation potential: anaerobic digester sludge from a municipal wastewater treatment plant, and a facultative culture enriched from solids backwashed from GAC contactors exposed to TCE- and RDX-contaminated groundwater. With no prior exposure to RDX, both cultures biodegraded RDX in single-component tests under anaerobic conditions. RDX concentrations decreased rapidly with evidence for transient production of nitroso-RDX metabolites. The culture enriched from the backwash solids degraded RDX at a much faster rate than the anaerobic sewage sludge. Unacclimated anaerobic sludge did not transform TCE during initial 10-day batch tests. Both cultures are currently being grown in the presence of TCE, and additional tests will determine if the acclimated cultures can biodegrade TCE and mixtures of TCE and RDX. Successful biodegradation of this contaminant mixture will yield a new remedial option that can reduce the required time and costs for remediating this contaminant mixture.

A Kinetic Model of Reductive TNT Transformation by *Escherichia coli* Resting Cells

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TNT biotransformation via nitro-reduction may be harnessed for bioremediation of hazardous waste sites. However, these transformations have been poorly understood or modeled. Traditional Michaelis-Menten model does not describe the nitro-reduction kinetics due to product toxicity and reducing power limitation experienced by cells. In this paper, TNT transformation by *Escherichia coli* was monitored and a kinetic model for TNT depletion was developed and experimentally calibrated. Using resting cells of aerobically pregrown *Escherichia coli*, 2,4,6-trinitrotoluene (TNT) was transformed via hydroxylaminodinitrotoluenes (2HADNT, 4HADNT, with 4HADNT as the dominant isomer) to 2,4-diamino-6-nitrotoluene (24DA6NT) as final product. Factors controlling the TNT transformation were quantified, including enzyme concentration, substrate concentration, and exogenous reducing power concentration. At higher cell densities, or by supplying glycerol as exogenous reducing power source, the rate and extent of TNT reduction increased revealing the importance of enzyme concentration and reducing power. Product toxicity (resulting from toxicity of TNT transformation intermediates) was quantified. A comprehensive model incorporating reducing power limitation, product toxicity, substrate inhibition, as well as substrate limitation adequately described the experimental observations.

Combined Anaerobic Oxidation and Reductive Dechlorination for Optimizing Bioremediation of CVOCs: Theoretical and Practical Considerations

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In-situ anaerobic bioremediation has become a preferred remedy for ground-water contaminated with chlorinated solvents (CVOCs). Most anaerobic bioremediation programs for CVOCs have focused on driving classical reductive dechlorination via the addition of carbon substrates (electron donors), bioaugmentation with *Dehalococcoides* cultures or both. Relatively few examples of anaerobic oxidation processes have been demonstrated for CVOCs, either alone or in combination with reductive dechlorination. Anaerobic oxidation processes coupled to the microbial reduction of electron acceptors such as nitrate, Mn(IV), Fe(III), and sulfate under anaerobic conditions may offer alternate catabolic pathways for CVOCs that may compliment reductive dechlorination. For example, reductive dechlorination may proceed rapidly for highly chlorinated compounds such as PCE, TCE and 1,1,1-TCA and help activate these compounds for further degradation, whereas anaerobic oxidation processes may be more effective for less-chlorinated intermediates such as cDCE and vinyl chloride. In addition, combined anaerobic oxidation-reduction treatment may help accelerate bioremediation by (a) improving electron flow and regenerating oxidants and reductants; (b) enhancing the biological removal of intermediates and byproducts of substrate-enhanced anaerobic treatment; and (c) promoting a broader array of catabolic processes than can directly or indirectly attack CVOCs and their daughter products. Accordingly, the combination of anaerobic reduction and oxidation processes should provide means for improving and optimizing the anaerobic bioremediation of CVOCs, particularly for source areas of contamination. Sites with large amounts of non-aqueous-phase contamination, (i.e., those that may require long-term treatment), may particularly benefit from this approach. Practical considerations for the assessment and implementation of combined anaerobic oxidation-reduction programs will be discussed, and data from ongoing anaerobic bioremediation programs will be presented to illustrate the efficacy and potential of this approach for CVOC source-area remediation.

Evaluation of Biological Treatment Options for N-Nitrosodimethylamine (NDMA) in Groundwater

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N-Nitrosodimethylamine (NDMA) is a potent carcinogen and an emerging groundwater contaminant. The origin of NDMA in groundwater and drinking water includes industrial, agricultural, water treatment, and military sources. The objective of this project was to evaluate possible bioremediation strategies for treating NDMA-contaminated groundwater. Our initial studies revealed that the propane-oxidizing strain *Rhodococcus ruber* ENV425 cometabolically degraded NDMA. The toluene-oxidizing strains, *Pseudomonas mendocina* KR1 and *Pseudomonas* sp. ENVPC5, each of which contains toluene-4-monoxygenase (T4MO) were also observed to degrade NDMA. In addition, rapid removal of NDMA was achieved using a *P. putida* strain containing cloned T4MO, further demonstrating the role of T4MO in NDMA degradation. To evaluate the potential for *ex situ* biological treatment of NDMA, a chemostat was seeded with *P. mendocina* KR1 and continuously fed toluene (~ 2 g/day) as a primary substrate. After establishing the culture at a dilution rate of 0.02 hr^{-1}, NDMA was fed to the reactor at concentrations ranging from 25 to 250 g/L, to represent typical groundwater concentrations. Strain KR1 consistently degraded NDMA to below 0.2 g/L during the 4-month study. In addition to the reactor studies, the potential for *in situ* treatment of NDMA was examined using groundwater samples from a contaminated site in California. The addition of toluene, propane, and methane to microcosms prepared with these samples was not effective for stimulating indigenous organisms to cometabolize NDMA. However, appreciable losses of NDMA was observed in groundwater augmented with *R. ruber* ENV425 in the presence or absence of propane as a cosubstrate. The results from this research provide a firm basis for the development of *in situ* and *ex situ* biological approaches for NDMA remediation.

Treatment of Vinyl Chloride Contaminated Groundwater at a Landfill Site: Comparison of Biosparging and iSOC™ Bioremediation Systems for Plume Cut-off

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Persistent vinyl chloride plumes resulting from incomplete reductive dechlorination of chlorinated solvents in groundwater downgradient of landfill and dry cleaner sites often present significant risk to drinking water resources and potentially to indoor air quality. A groundwater remediation program designed to treat a large deep vinyl chloride plume (85 ft below the water table) was implemented in June 2003 downgradient of a former landfill site in Massachusetts. Response actions selected for the site include a system for vinyl chloride hot spot treatment by direct aerobic biostimulation using biosparging and iSOC™ (*in-situ* Submerged Oxygen Curtain) technology. iSOC™ is an *in situ* bioremediation/natural attenuation enhancement substrate delivery system. The iSOC™ unit provides a large surface area for delivery of oxygen by mass transfer from the gas phase to the dissolved phase in groundwater without sparging.

Initial performance monitoring results have indicated that oxygen delivery is effectively stimulating aerobic bacteria and reducing vinyl chloride concentrations. Dissolved oxygen has increased from less than 1 mg/L to 11 mg/L in the biosparging treatment zone. Dissolved oxygen concentrations as high as 130 mg/L have been achieved in iSOC™ treatment wells and the concentration of vinyl chloride within the active iSOC™ treatment zone has been reduced to 3 to 4 ug/L from a baseline concentration of 10 to 15 ug/L. The presentation will include an evaluation of treatment zones developed by the biosparging and iSOC™ systems, system performance, and the design, development, and optimization of aerobic treatment zones for plume cut-off.

Treatment of PCP-Contaminated Soil Using an Engineered Ex Situ Biopile Process at a Superfund Site

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Releases of creosote and pentachlorophenol (PCP) at a New Brighton, Minnesota wood treatment facility, resulted in widespread soil and groundwater contamination. Site investigations lead to the facility's inclusion on the National Priorities List (NPL), and the Minnesota Pollution Control Agency was designated lead regulatory agency. Biological treatment was the preferred remedy for 18,000 yd^3 of contaminated soil, and Biogenie was contracted to design, construct and operate an *ex situ* Biopile to achieve the remedial objectives. Most project owners and remedial managers perceive the Biopile process as a passive remediation technology, not fully appreciating the scientific and engineering expertise required to design and operate an effective Biopile. This paper highlights the "behind the scenes" efforts of the scientific and engineering team responsible for the Biopile project, and specifically how those efforts achieved difficult remedial objectives within a treatment performance guarantee contract.

The New Brighton project required that an *ex situ* Biopile be used to achieve site reuse criteria of 10 mg/kg PCP and 5 mg/kg cPAHs, with a schedule dictating operation during winter months reaching -22°C. Biopile operating parameters were developed during laboratory Treatability Studies (TS) designed to optimize the biodegradation capacity of indigenous microorganisms. Specific operational parameters were also devised to manage soil containing a fair proportion of highly impacted woodchips. An engineering team applied the TS results during scale-up Biopile design and the project team mobilized to the site for construction. Once operational the cleanup objectives were met within 18 to 38 weeks, depending on initial PCP concentrations which were up to 350 mg/kg. Average PCP reduction rates achieved 95% for soils and 76% for soils containing wood chips.

With appropriate design and operating parameters, the engineered *ex situ* Biopile process enabled more than 96% of the total volume of soil to be successfully treated and backfilled on site, thus significantly reducing overall project costs.

A Comprehensive Performance Analysis of Hydrogen Release Compound (HRC®): Lessons Learned and Future Directions.

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Since 1999, Hydrogen Release Compound (HRC®) has been a commercially-available product for engineered bioremediation of anaerobically biodegradable contaminants. 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 anaerobic bioremediation processes.

In this review of HRC field application results, we summarize application types, contaminants treated, site types, application locations, injection methods, site lithology and hydrology, and concentration ranges of geochemical species. The source of this information is a database of 474 HRC field applications, a series of 66 HRC publications (many by independent authors), and 10 detailed site case histories that are available electronically. We will also address the overarching issue of incomplete dechlorination and discuss how the cause of incomplete dechlorination can be “diagnosed” and a remedy implemented.

First and foremost, the hidden mass input from desorption of soil-phase contaminants and dissolution of residual DNAPL should be considered significant factors in an apparent slow down of dechlorination. Additionally, competing electron acceptors such as ferric iron can have a significant effect on the rate of dechlorination. For sites with these behaviors, we recommend, “more time and more electrons.” On the other hand, if sufficient electron donor is present, but phylogenetic DNA tests show that the appropriate microbial community is not present in sufficient numbers, bioaugmentation with a dechlorinating inoculum is an appropriate remedy. Site examples with monitoring data will be used to support these conclusions.

Environmental Biotechnology

Monitoring Bioremediation by Analyzing In Situ Gene Expression

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Case Study Applications of BioTraps for Streamlining Remedial Program

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Quantitative Detection of and Augmentation with Reductive Dechlorinators

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Functional and Taxonomic Microarrays for Profiling Natural Microbial Populations Involved in Bioremediation

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Kinetics and Microbial Ecology of Perchlorate-Reducing Bacteria: Implications for Remediation

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Preliminary Knowledge Base of the Association between Molecular Techniques and Other Site Parameters for Better Evaluating Reductive Dechlorination Potential

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Monitoring Bioremediation by *in situ* Gene Expression Analysis

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Investigations into the mechanisms for dissimilatory Fe(III) reduction in subsurface environments may be greatly simplified by the fact that microorganisms in the *Geobacteraceae* are the predominant Fe(III)-reducing microorganisms in a diversity of subsurface environments in which Fe(III) reduction is important. The finding that *Geobacteraceae* can account for ca. 40-90 % of the total microbial community under Fe(III)-reducing conditions in some subsurface environments suggests that subsurface Fe(III)-reducing communities may provide the type of low-diversity community that is most amenable to environmental expression studies. In this study, the ability to monitor the *in situ* metabolic state of the microbial community via mRNA analysis was evaluated with mRNA extracted from 3 different subsurface Fe(III)-reducing subsurface environments where *Geobacteraceae* predominate: 1) a U(VI) contaminated field site in Rifle, CO that was supplemented with acetate to stimulate U(VI) and Fe(III) reduction,; 2) the Fe(III)-reduction zone of a petroleum contaminated aquifer at a USGS Groundwater Toxics Site in Bemidji, Minnesota: and 3) a runoff recharge pool from a highway in Plymouth, MA that has been exposed to calcium magnesium acetate (CMA) as the primary road deicing agent every winter for the past 7 years. *In situ* gene expression studies were first carried out on three genes that are unique to micro-organisms within the *Geobacteraceae*; *nifD*, which encodes the dinitrogenase gene involved in nitrogen fixation, citrate synthase, a key enzyme in *Geobacteraceae* central metabolism that is distinct from other prokaryotes, and *ompB*, a gene with homology to previously described multicopper oxidases, that is thought to be involved in the reduction of insoluble Fe(III)-oxides. *nifD* was selected because it has been suggested that there might be a need for nitrogen fixation in acetate-amended or petroleum-contaminated subsurface sediments where the influx of organic carbon into these otherwise nutrient-poor subsurface environments can result in a limitation of fixed nitrogen relative to the availability of carbon substrates. Analysis of levels of *nifD* mRNA in sediments collected from the petroleum-contaminated site did, in fact, demonstrate that *Geobacteraceae* were expressing nitrogen fixation genes. Expression of *nifD* was repressed when ammonium was added to the sediments. A diversity of *Geobacteraceae* citrate synthase, *ompB*, *recA*, and *nifD* genes have also been identified in all three subsurface environments and their levels of expression have been monitored. In addition, BAC and small insert libraries from genomic DNA extracted from these sites are currently being assembled in order to identify other significant genes that are unique to the *Geobacteraceae* for future *in situ* gene expression studies. These results demonstrate that monitoring the *in situ* metabolic state of the microbial community as well as estimating rates of metabolism is feasible via mRNA analysis. This will help move bioremediation from a primarily empirical practice to more of a science.

Innovative Methods for Evaluating the Feasibility of Bioremediation and Natural Attenuation

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Recently, the utilization of biotechnology in contaminated site investigation and remediation has exploded. Applications of biotechnology that previously were used only in high-end genetic laboratories and universities are now being applied to the environmental cleanup industry – with excellent results and many opportunities for continued advancements. These new tools allow the environmental practitioner to evaluate site aquifer conditions in a more efficient, more accurate, and less costly manner than conventional aquifer characterization techniques.

Previously, when environmental practitioners were interested in evaluating the potential for biodegradation in an aquifer few choices existed beyond utilization of conventional aquifer characterization techniques, evaluation of natural attenuation geochemical datasets, and performance of laboratory biodegradation microcosms. Today, several new sampling and analytical tools exist that have the potential to revolutionize how biofeasibility evaluations are performed. This paper presents some of these new tools, case study data from sites where these tools were implemented, and summarizes where the state of the science is heading.

One of the tools to be discussed is the “Bio-Trap” sampling device, also known as a down-well microcosm. The Bio-Traps contain “BioSep® beads that absorb organics and provide a porous surface that allows for the rapid development of bio-films. The Bio-Traps can either be installed “non-baited” to assess baseline biological conditions in the aquifer or can be impregnated with a variety of electron donors or acceptors to assess microbial response.

The bio-films are extracted from the traps at a specialty laboratory where a variety of analyses are performed, including: DNA (both PCR and DGGE), functional gene identification, phospholipid fatty acids (PLFA) and other genetic biomarkers.

Site-specific results for use of Bio-Traps for biofeasibility studies on chlorinated solvent, BTEX, and MTBE sites will be discussed. Data from the down-well microcosms (BioTraps) will be compared with laboratory biodegradation microcosms performed with site soils and groundwater. Utilization of Compound Specific Isotope Analysis (CSIA) will also be discussed.

Quantitative Detection of and Bioaugmentation with Reductive Dechlorinators

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With the recent discovery that the microorganisms responsible for the complete biodegradation of chlorinated solvents may not be present at all sites, bioaugmentation with mixed cultures capable of degrading a wide range of contaminants is now being successfully used at a variety of sites to increase the rate of reductive dechlorination and reduce the time that it takes to obtain site closure. By using a "differential diagnosis" approach, bioaugmentation can be used to close sites which may have otherwise not achieved complete reductive dechlorination within a reasonable timeframe. Regenesis's Bio-Dechlor INOCULUM^{TM} product, an enriched natural microbial consortium containing various species of dechlorinating microorganisms, has now been applied at fourteen sites located within eight states. Bio-Dechlor INOCULUM^{TM} includes *Dehalococcoides* strain BAV-1, an organism that can complete the final stages of chlorinated ethene degradation from the dichloroethene step through to ethene. The BAV-1 strain is unique because it can metabolically degrade chloroethene (vinyl chloride) to ethene. This is considered to be a superior feature relative to all other known strains that can only degrade vinyl chloride co-metabolically. The difference is that the BAV-1 strain will derive energy from the degradation process whereas organisms that perform the task co-metabolically cannot.

Real Time Polymerase Chain Reaction (RT-PCR) is a technique in which the number of organisms in a sample can be determined by measuring the amount fluorescence of produced during the PCR reaction. Available commercially as Bio-Dechlor CENSUS^{SM}, this technique is now being used not only to determine if the necessary microorganisms are present within the aquifer in the appropriate numbers and if the addition of external organisms is required, but also to track the changes induced in the microbial community by the addition of a carbon source or the addition of organisms. Recent advances in this technology have now allowed us to target functional genes, or gene sequences that are specific to organisms able to perform the desired reductive dechlorination tasks, as opposed to only genes on the 16S rRNA sequence that are common to all organisms with this phylogenic group. DNA-based methods such as Denaturing Gradient Gel Electrophoresis (DGGE) and lipid analyses such as Phospholipid Fatty Acid analysis (PLFA) can also be used to observe the effects of bioaugmentation or biostimulation on the microbial community as a whole, often more quickly than the effects of the application can be observed through VOC analysis only. The integration of these techniques and others into existing monitoring programs gives us a greater understanding of what is occurring within the subsurface and allows us to answer questions that we were once unable to. The full nature of our experience with these techniques will be presented.

Functional and Taxonomic Microarrays for Profiling Natural Microbial Populations Involved in Bioremediation

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Two types of microarrays were developed to profile indigenous microorganisms in a variety of environments. The functional gene microarray uses gene probe amplicons derived from various bacterial catabolic pathways for organic pollutants and biogeochemical cycles. The taxonomic microarray has oligonucleotide probes derived from the 16S rDNA gene and the *cpn*60, chaperonin gene. These two microarrays have been used to monitor changes in the indigenous microbial population during a bioremediation project at Eureka, in the high Arctic. Treatment of the hydrocarbon-contaminated soils was started in 2000 and consists of applying nutrients (solid and liquid fertilizers) and tilling the soil during the summer. The effect of this treatment on the composition and activity of the indigenous microbial population has been monitored on a yearly basis in the active and supra-permafrost layers of treated and untreated soils. Total petroleum hydrocarbon (TPH) concentrations in the treated soil have been reduced by 63% in the active zone, and by 75% in the supra-permafrost zone. Although total heterotrophic or diesel-degrading bacterial population sizes have not changed significantly during the treatment, the *ndoB* (naphthalene degradation) and *alkB* (alkane degradation) genotypes increased in 2001 and 2002, respectively. Mineralization assays, using radiolabeled naphthalene and hexadecane, demonstrated a corresponding increase, and functional gene microarray analysis indicated that hydrocarbon degrader genotypes increased, which was supported by a quantitative analysis of target gene signal intensity. Analysis with the taxonomic microarray indicated that the composition of the indigenous population had changed during the monitoring period, and specific microorganisms such as *Pseudomonas*, *Rhodococcus* and *Vibrio* increased significantly, paralleling the increase in corresponding catabolic genes associated with these same microorganisms. The use of functional gene and taxonomic microarrays provides a new method to rapidly

evaluate the composition and functional capacity of indigenous microbial communities, and to monitor their responses to, and recovery from, stress.

Kinetics and Microbial Ecology of Perchlorate-Reducing Bacteria: Implications for Remediation

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Perchlorate bioremediation at trace levels may be more difficult than at high levels, due to slower microbial reduction rates and smaller selective pressure for perchlorate-reducing bacteria (PCRB). We used kinetic and microbial ecology tests to investigate this. For kinetic studies, we used *Dechloromonas* sp. PC1, a PCRB isolated from a perchlorate-reducing bioreactor. With hydrogen as an electron donor, PC1's doubling time was around 24 hours and its apparent K_m was 150 µg/L. K_m was significantly lower than values reported in the literature, but high enough to significantly slow reduction rates at µg/L perchlorate levels. At high perchlorate concentrations, chlorate accumulated as a transitory intermediate, a novel finding for PCRB. Kinetics suggests perchlorate alone cannot sustain PCRB below 12 µg/L, and that nitrate or oxygen, used concurrently with perchlorate, is needed as a primary electron acceptor. We studied the effect of perchlorate on the microbial ecology of a mixed denitrifying community using four identical reactors, inoculated with a denitrifying culture and continuously supplied with 5 mgN/L nitrate and 8 mg/L oxygen. At steady state, the effluent contained no measurable oxygen and 0.05 mgN/L. Subsequently, 0, 100, 1000, and 10,000 µg/L perchlorate were added to the influents of the reactors. Perchlorate reduction initially was small, but greatly improved over several weeks, suggesting enrichment for PCRB. This was confirmed by denaturing gradient gel electrophoresis **(**DGGE), fluorescent *in-situ* hybridization (FISH), and perchlorate-reduction activity tests. A *Dechloromonas* strain was present at 14%, 22%, 31%, and 49% of total bacteria in reactors with 0, 100, 1,000, and 10,000 µg/L perchlorate, respectively. Results suggest that perchlorate gave PCRB an advantage in competing for oxygen and nitrate, producing PCRB biomass far in excess of the expected yield on perchlorate. Our kinetics and microbial ecology results suggest oxygen and nitrate play a key role in trace perchlorate remediation.

Preliminary Knowledge Base of the Association between Molecular Techniques and Other Site Parameters for Better Evaluating Reductive Dechlorination Potential

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Substantial research has been conducted to understand the microbiology of reductive dechlorination. This research has lead to the isolation of genera known to dechlorinate (e.g. *Dehalococcoides, Dehalobacter*, etc.) as well as the isolation of specific functional genes (tceA, BAV1) associated with certain steps in the dechlorination process. Recently, modern molecular techniques (such as Bio-Dechlor CENSUS^{sm}) have been applied to quantify the abundance of specific bacterial groups involved in reductive dechlorination and also to quantify functional genes of interest. Microbial Insights has pioneered this field, and has realized that creating a database that includes these microbial indicators along with associated contaminant concentrations and other geochemical parameters could provide essential information for effective site management and decision making. Preliminary results on the distribution of known dechlorinating bacteria in association with other site specific parameters have been combined into this Knowledge Database. This presentation will discuss the trends that have been observed thus far, based on data from over 1,000 samples from a wide range of sites.

Environmental Forensics

NAPL Source Chasing – A Forensics Evaluation
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Kelley Race, Weston & Sampson Engineers, Inc., Peabody, MA

Using Isoprenoid Hydrocarbon Ratios to Calculate Percentage Mixing Different Distillate Fuels in the Subsurface Environment
Michael J. Wade, Wade Research, Inc., Marshfield, MA

Combining Passive Soil Gas Sampling, GC/MS Analysis, and Non-Conventional Interpretation to Identify Fuel Sources
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Fingerprinting Dioxin-Furan Contamination in the Lower Roanoke River Basin
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Applications of Forensic Chemistry for Contaminant Identification In Sediments Near an MGP Site, Wisconsin
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The Application of the Federal On Road Diesel Fuel Sulfur Reduction Act of 1993 to the Age Dating of Diesel Fuels: A Case Study
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NAPL Source Chasing – A Forensics Evaluation

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During a routine site investigation, greater than ½ inch of light non-aqueous phase liquid (LNAPL) was detected in a site monitoring well. Investigation activities were implemented to evaluate the source of free-phase petroleum product in the subsurface beneath a maintenance bay of a bus maintenance garage. Product samples were submitted for petroleum fingerprint analysis (modified EPA method 8015B) to compare product detected in the monitoring well to waste oil from a historic overfill of an underground storage tank located nearby. The analytical results of the LNAPL samples contained different petroleum constituents and LNAPL sources may have commingled.

The subsurface investigation and forensic activities utilized to evaluate the source and extent of petroleum in the subsurface included:

- Abandoning the monitoring well and excavating the soil around the well to observe if well drilling activities breached the floor drain system
- Dye testing and water flushing the floor drain system and assessing the excavation area and nearby monitoring wells for the presence of dye/water
- Evaluating the floor drainage system within the maintenance bays including piping materials, drainage plans, and integrity
- Advancement of monitoring wells surrounding the well containing product
- Evaluation of groundwater flow direction to observe downgradient wells for LNAPL
- Evaluating oil/water separator connections associated with the garage and
- Confirmatory soil sampling from the sidewall and bottom of the excavation area associated with the well containing LNAPL
- Delineation of LNAPL extent

The results of the site investigation activities and floor drain system assessments revealed that the LNAPL areas had not commingled, the floor drain was not breached and excavation activities had removed the extent of LNAPL associated with the release.

Using Isoprenoid Hydrocarbon Ratios to Calculate Percentage Mixing Different Distillate Fuels in the Subsurface Environment

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Subsurface mixing of a Jet A fuel/kerosene component with a No. 2 fuel oil/diesel fuel component presents a particular problem for the environmental forensics community. Determining the percent contribution of a lighter distillate fuel component such as Jet A/kerosene mixed with a heavier distillate fuel component such as No. 2 fuel oil/diesel fuel can be important in apportioning recovery costs and cleanup among different potentially responsible parties. The fact that different types of distillate fuels are deliberately formulated to have different physical parameters can prove useful in the determining percent contributions to subsurface plumes using chemical data from gas chromatographic analyses. Gas chromatographic analysis of subsurface aqueous phase liquid (NAPL) samples collected from a series of groundwater monitoring wells at a large fuels storage facility revealed a chronic leak of a jet fuel tank into a surrounding plume of No. 2 fuel oil/diesel fuel. Initial chemical analysis revealed complicated chromatograms. However, numerical analysis of the chromatographic data resulted in a clear picture of mixing of different distillate fuels in the immediate vicinity of a jet fuel storage tank. Percent contributions of jet fuel were calculated for each monitoring well, showing a clear trend toward a jet fuel composition the closer the monitoring well was to the jet fuel storage tank. Percent calculations were facilitated by taking advantage of the inherent differences in the early to later isoprenoid hydrocarbon in different fuel types. A two end-member mixing model was developed that allowed the percent calculation of both distillate fuel end members regardless of the extent of environmental weathering of each separate distillate fuel. The mixing model can be applied to any mixed component plume to calculate amounts of different distillate fuels present in a combined subsurface plume.

Combining Passive Soil Gas Sampling, GC/MS Analysis, and Non-Conventional Interpretation to Identify Fuel Sources

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Passive soil gas technology is proven to be a useful tool for identifying source areas and the extent of soil and/or ground water impact following fuel releases. Property owners facing the prospect of expensive cleanup operations do not want to be responsible for contamination from offsite sources. Due to inherent biases in soil gas toward the more volatile components, linking observed contamination with the actual fuel source(s) is difficult to begin with, and becomes more complex when multiple fuel types are present. A non-conventional interpretation of soil gas data, collected with the GORETM Module, was able to yield significant information regarding the actual source determination for fuel releases at a facility in the southeastern US. This presentation will discuss how the soil gas data, fuel samples, and GC/MS analysis were used to link the signal observed in the passive soil gas survey to the fuel sources, when conventional soil gas data interpretation did not accomplish this goal adequately.

Fingerprinting Dioxin-Furan Contamination in the Lower Roanoke River Basin

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Previous investigations of sediments and wetland soils in the lower Roanoke River Basin reported measurable dioxin-furan concentrations in the range of 5,000 to 12,000 ng/kg. Using the FALCON fingerprinting process (Fingerprint Analysis of Leachate CONtaminants), it was possible to identify two distinctive dioxin-furan fingerprint patterns based on graphical pattern recognition and regression analysis. One pattern, associated with a pulp and paper mill facility, was characterized by a major peak for 2378-TCDF and progressively smaller peaks for 1234678-HpCDF, OCDF, 2378-TCDD, and 1234678-HpCDF. This pattern had an estimated reproducibility of 90 percent. A second pattern associated with sources up river from the pulp and paper mill was characterized by a dominant peak for 1234678-HpCDD, and smaller peaks for OCDF and 1234789-HpCDF. This fingerprint had an estimated reproducibility of 99 percent.

The two identified fingerprints were used to characterize the dioxin-furan contamination of the lower Roanoke basin in a two step process. The first step consisted of calculating dioxin-furan fingerprints for various binary mixtures of the two source patterns. The second step consisted of statistically comparing the actual dioxin-furan distribution in down river sediments with the calculated fingerprint patterns. This assessment indicated that 35 to 40 percent of the down river dioxin contamination could be attributed to the pulp and paper mill and the remainder was due to up river source(s). However, because the pulp and paper mill dioxin had a relative toxicity that is more than five times greater than the up river source(s), it represents 75 to 79 percent of the dioxin TEQ risk in the lower river basin.

Applications of Forensic Chemistry for Contaminant Identification In Sediments Near an MGP Site, Wisconsin

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A survey of Duluth-Superior harbor materials identified the presence of concentrations of PAHs in the sediments. The Wisconsin Department of Natural Resources (WDNR) assumed that the source of the PAHs was a nearby former manufactured gas plant (MGP) site. Forensic chemistry, both “chemical fingerprinting” (GC/MS) and “isotopic fingerprinting” (GC/IRMS) was conducted on sediment and former MGP soil samples, in order to determine the origin of the contamination. Environmental forensic chemistry involves specific analytical testing in order to decipher the exact mixture of organics and, in some instances, determine their age, fate in the environment and source(s). These analytical techniques have been increasingly applied to the analysis of former MGP site wastes, particularly tars, for comparison to low-level concentrations of PAHs present in “urban background” samples from the surrounding vicinity, including sediments. Analysis of samples using forensic chemistry techniques generates unique “fingerprints” of the sample, depending upon the method used. The fingerprints may then be compared; in order to identify the source of the waste. Locations impacted with tar materials from a variety of sources are problematic in legal disputes for ownership or liability for cleanup. This is particularly relevant in cases involving contamination resulting from typical urban activities (“urban background” wastes). Low-level urban background contamination can be often misinterpreted as MGP waste. Using a new technique of compound-specific, isotope ratio (CSIR) analysis, urban background concentrations may be discerned from specific source material. This is highly useful in the identification of wastes in sediments. In this study, soil samples from the former MGP site, sediment samples from the boat slip and storm sewer samples were subjected to forensic analysis. The fingerprinting results were used to determine if PAH in the boat slip was derived from the known MPG or from other sources.

The Application of the Federal On Road Diesel Fuel Sulfur Reduction Act of 1993 to the Age Dating of Diesel Fuels: A Case Study

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Accurately determining the age of environmental contamination is an inherently difficult process due to the number of critical variables that are often undefined at a site (e.g., degradation rates). For example some age dating methods rely on the relative degradation of two hydrocarbons (e.g., *n*-C_{17}/pristane) compared to a linear degradation pathway/rate to estimate time of release. These methods are often oversimplified or depend upon assumptions about preexisting site-specific conditions and as a result they are frequently challenged.

The defensibility of NAPL age-dating approaches increases dramatically when concentrations of product additives (e.g., tetraethyl lead or MTBE) or naturally occurring compounds within the products (e.g., sulfur) are regulated by federal or state environmental protection agencies. In some cases, the regulations provided a broad transition period for the petroleum industry to retool its operations in order to achieve the desired results (e.g., removal of tetraethyl lead from gasoline). However, in other cases, order of magnitude reductions in fuel components were legislated with well defined dates. These large changes in product composition, combined with strict monitoring and enforcement by federal and state agencies, provide the forensic chemist a scientifically defensible approach for product age-dating investigations.

This work discuses the application of the Federal On-Road Diesel Fuel Sulfur Reduction Act of October 1, 1993 to the age dating of diesel fuel at retail sites. A case study will be presented that combines traditional GC/MS and GC/FID fingerprinting tools with total sulfur data to conclusively differentiate a recent release of diesel fuel at a large highway fuel dispensing site from a prior release of diesel fuel at the same facility. This data was then used to conclusively identify the principal responsible party for the recent release. A novel approach to estimating product total sulfur content in soils and sheens using dibenzothiophene/phenanthrene ratios will also be discussed.

Environmental Terrorism

Environmental Detection of Microbial Weapons
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Use of GIS to Coordinate Medical Response
Richard B. Wait, Baystate Medical Center, Springfield, MA

Coordination of Emergency Response Actions Using an Integrated Decision Framework
Abhi Deshmukh, University of Massachusetts, Amherst, MA

National Guard Response to Environmental Terrorism – A Review of Homeland Defense Initiatives
Lieutenant Colonel Thomas Hook, National Guard Bureau, Arlington, VA

Wireless TeleCare for Mass Casualty Situations
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Environmental Detection of Microbial Weapons

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The presence of pathogens constitutes a potential or actual threat to our health making it crucial to detect and identify pathogenic bacteria reliably and rapidly in investigations of food, water, pharmaceuticals and personal care products, and for the intentional unleashing in bioterrorism. With bioterrorism increasingly appearing as an additional threat a specific interest has notably emerged for techniques for the environmental detection of microbial weapons. This detection should, at a reasonable cost, be able to rapidly assess the presence of microbial weapons. Multiple detection systems exist for the detection of pathogenic bacteria.

A detection system has to be specific for a certain pathogen, sensitive enough to detect small amounts of targeted cells in the background of a matrix such as food, not too expensive, and preferably fast enough to allow a rapid response to the result of the investigation. The key challenge associated with bacterial detection in environmental samples is to obtain cell numbers, in the presence of interfering components, large enough to satisfy the sensitivity requirements of a reliable detection. For bio-threats, real-time selective recognition of cells is an important capability in medicine, molecular biology, and environmental science. In addition to an overview of current detection techniques one specific method will be reported. A cell-selective polymer film, obtained via polymerization of a thin film of functionalized monomers, is created in contact with a target cell. Under controlled conditions, the replica maintains exceptional structural memory of both shape and surface functionality of the initial bacterial cell. High selectivity is observed between bacteria featuring different cell surfaces (Gram-positive vs negative), shapes (rods vs spheres), and cell arrangements (single cells vs short chains vs clusters). Interfacing to a quartz crystal microbalance provides real-time, selective detection of bacteria at environmentally relevant concentrations.

Keywords selective cell recognition, surface templation, direct-contact biosensors, real-time detection, pathogen, bioterrorism

Use of GIS to Coordinate Medical Response

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Geographic information systems (GIS) are useful in integrating data critical for decision making in many aspects of homeland security. Most data with geographic attributes are able to be integrated in this fashion. Although GIS are routinely used in epidemiologic studies and healthcare planning, only recently have these systems been introduced to aid in medical asset management and deployment in emergency and disaster scenarios, both natural and terrorist initiated. This paper outlines the unique healthcare problems associated with mass casualty events and demonstrates specific proposed uses for GIS in the integration of the many data sets required for meaningful and effective medical planning, preparedness and response to disasters in the post 9/11 era. The importance of pre-disaster data and metadata preparation as well as use of GIS in disaster training scenarios will be discussed, as will the economic necessity for making these systems dual use by both public and private healthcare sectors.

Coordination of Emergency Response Actions Using an Integrated Decision Framework

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Recent terrorist attacks on the US soil, massive electric grid outages in the northeast, and significant losses due to wildfires in the western states have made it clear that assessing vulnerabilities in the key elements of social infrastructures and responding to these events in an effective and timely manner is a challenge that has yet to be overcome. In many cases first responders and emergency care providers did not have accurate information, localized gridlock in the ground transportation network caused massive delays in evacuation, food and water supplies were disrupted for several days after the disasters, air transportation system came to a standstill, area hospitals and health care providers saw demand surge in some areas whereas others were sitting idle waiting for patients. The defining characteristics of emergency situations that make coordination and effective management difficult are uncertainty/noise/granularity of available information, continually evolving situations, interdependence between different processes and infrastructures, and the rarity of the event. This paper presents a comprehensive emergency response framework that will 1) allow first responders to make decisions based on real-time information made possible by the integration of hardware, application and policy/decision-making layers, 2) allow participants to evaluate the impact of their local decisions and processes on the overall situation and 3) allow emergency personnel to train for rare events using realistic models. This paper will specifically focus on information architectures and decision tools to allow effective emergency response management.

National Guard Response to Environmental Terrorism – A Review of Homeland Defense Initiatives

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Prior to the attacks of September 11, 2001, the National Guard had begun to establish units designed to designed to provide consequence management support to local and state agencies following a terrorist incident involving Weapons of Mass Destruction. These units, known as Weapons of Mass Destruction Civil Support Teams, conduct sampling and analysis of radiological, chemical, and biological materials following an incident, and can also conduct monitoring prior to an incident. The teams also provide a plume modeling capability, and can assist local agencies with communication interoperability and technical reachback. The National Guard now has 32 of these teams located in 31 states, and is in the process of adding 23 more teams. In addition to these teams, the National Guard is providing training and equipment to selected units in order to establish a regional casualty decontamination capability that can assist other local and state agencies at an incident site. With the possibility that terrorists may use environmental terrorism, such as an attack on an industrial facility in an effort to cause casualties and damage the US economy, these National Guard initiatives provide a critical response capability that addresses the response gap between the arrival of the emergency responders immediately following the incident and the deployment of Federal assets to the incident site.

Wireless TeleCare for Mass Casualty Situations

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A quick setup of an effective communication system that supports the limited resources of the trauma team treating mass casualty events can reduce mortality and morbidity. Since mass casualty events can happen due to natural disasters, terrorism, transportation accidents, and epidemic diseases at unexpected locations, deficiencies of medical resources and traditional communication systems are certain. It is expected that traditional communication infrastructures such as landline wires and communication towers will default and be damaged. We present the challenges and proposed solution developed at the Multimedia Networks Laboratory at UMASS to deploying an ad-hoc wireless network. Such solution will support the communication needs of tens and hundreds of patients and personnel, increasing the effectiveness of the medical and rescue operations. Each client (e.g., patient, trauma team, logistic personnel) will be equipped with a Personal Digital Assistant (PDA) that supports medical needs, can be connected to a plurality of medical devices provisioning vital life signals, and support the ad-hoc wireless network internal needs. The proposed architecture employs off-the-shelf Wi-Fi IEEE 802.11 standard hardware which will be equipped with our developed software.

Heavy Metals

Removal of Lead (II) from Drinking Water Using Plant Based Product
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Chitosan Immobilized on Sand – An Innovative Cu Adsorbent
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Gold Mining and Mercury Pollution in the Ghanaian Pra River Basin, West Africa
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Formation and Stability of Mixed Metal Hydroxide Phases in Contaminated Soils
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Electrokinetic Treatment of Copper, Chromium and Arsenic Contaminated Soil from Wood Preservative Industries
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On-Line Monitoring of Mercury and Arsenic Below Regulatory Levels
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Removal of lead (II) from Water Using Plant Based Product

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Sources of lead in the environment include lead based paint, lead contaminated soil, air and dust, lead contaminated food and lead contaminated drinking water. Lead enters water primarily as a result of the corrosion, or wearing away, of materials containing lead in the water distribution system and household plumbing. This can prove to be harmful to the human health. Currently used water treatment technologies involving chemical precipitation and the use of ion exchange resins are expensive and sometimes ineffective especially, when metals are present in solution at very low concentrations. Conversely, the use of natural plants is an emerging field of interests for decontamination of heavy metals from contaminated sites. In the present paper, the efficacy of a plant based product has been investigated for the removal of lead (II) from water.

Chitosan Immobilized on Sand – An Innovative Cu Adsorbent

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Metal contamination of soils and waters reported all over the world has a severe impact on environmental and human health. The development of innovative metal-clean up technologies remains a challenge as the currently used procedures are generally expensive, disruptive, and only efficient at certain concentrations. Chitosan, a biopolymer with repetitive amino groups, is a well-known metal chelator, but its use in practice is limited due to the relative high costs of constructing clean-up devices (filters) from chitosan alone. In the current study, we investigated an innovative adsorbent material based on chitosan immobilization on sand (5% chitosan content). This new material was studied for its copper adsorption capacity for different contact times (two and four hours) and the results were compared with copper adsorption capacities of chitosan and sand alone. Also, copper recovery from adsorbent with possible reuse of the adsorbent material was evaluated in leaching tests. Chitosan-coated sand had a better copper adsorption capacity (260 mg Cu adsorbed/g chitosan) than both chitosan (184 mg Cu adsorbed/g chitosan) and sand (2.04 mg Cu adsorbed/g sand) when used alone, regardless of the initial copper concentration. The possibility of recovering the copper from chitosan-coated sand with the reuse of adsorbent was proved, with more than 90% of copper removed by acid leaching. Increasing the contact time between Cu solution and adsorbent from two to four hours had almost no effect on Cu adsorption capacity, but determined the creation of slightly stronger bonds of Cu-adsorbent. These preliminary results indicate the possibility of using chitosan-coated sand to build inexpensive filters for metal removal from contaminated surface and groundwaters.

Gold Mining and Mercury Pollution in the Ghanaian Pra River Basin, West Africa

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Mercury (Hg) toxicity awareness increased after Minamata disaster in Japan in the 1950s. In consequence several studies coupled later with the outlawing of this toxic metal in historic gold mining sites, in developed nations such as USA and Canada, were initiated. Moreover, whereas studies of the environmental consequences of gold mining by Hg amalgamation in the tropical ecosystems of South America (particularly the Brazilian Amazon) were commenced about two decades ago, after the "*new gold rush*" in the 1980s, the case of Ghana, in West Africa remains barely investigated. And artisanal mining of gold with Hg has been ascending after its legalization in 1989 by the government. In this work, the levels, speciation and the spatial/temporal distribution of Hg in the Pra River basin in Southwestern Ghana were investigated to assess the environmental impact of Hg introduced into the waterways by artisanal gold mining operations. Surface water, sediment, soil and human hair samples collected along longitudinal transects from locations upstream of known point sources down to the river delta were analyzed. Our results show that total-Hg concentrations are very high in river waters, as well as in soil samples collected near sites of amalgam roasting. Total-Hg concentration riverine sediments are relatively low as compared with most published values from Hg-contaminated sites. However, the determination of total-Hg in the sediment fraction < 2mm and the use of the geo-accumulation index (I_{geo}) tend to suggest moderate pollution. Observed total-Hg levels in human hair samples were quite low compared with some proposed safe limits. Methyl-Hg was also detected in all samples, and in contrast to well-studied Hg contaminated systems in America and Europe, methyl-Hg levels in analyzed Ghanaian sediment samples were 2 to 3 times higher than most published values. More interesting is the fact that, the Brazilian Amazon, which is very similar to these Ghanaian systems (i.e. tropical climate, hydrology, ongoing artisanal gold mining, etc), and where safety levels for fish (0.5mg/Kg) are considerably exceeded, comparatively, has both total- and methyl-Hg levels up to 3 orders of magnitude lower than that of Ghana. Finally, laboratory experiments using riverine sediments were conducted to assess the potential rates of Hg methylation and methyl-Hg demethylation in these tropical settings, and obtained data were compared with those from gold mining impacted aquatic systems worldwide.

Formation and Stability of Mixed Metal Hydroxide Phases in Contaminated Soils

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Understanding the fate of toxic metals in the environment is crucial to the remediation of contaminated soils. Metal sorption and precipitations reactions are particularly important in determining metal speciation and toxicity in ways poorly described by current models. Previous research has shown that a number of metals of environmental interest, including Co, Cr, Cu, Ni and Zn, form polynuclear metal hydroxide complexes and precipitates with aluminum on the surfaces of clay minerals and metal oxides under laboratory conditions. Formation of these metal hydroxide phases substantially reduces metal mobility and leaching from the substrate, and may be an important mechanism for metal retention and sequestration into relatively bio-unavailable phases. In this work, macroscopic and molecular scale studies have been conducted on field and laboratory contaminated soils in order to determine the factors controlling the formation of these layered double hydroxide (LDH) phases in natural soils. Kinetic studies of Ni and Zn sorption and desorption were carried out over pH ranges from 6- 8, in the expected region for LDH formation, for three soils with varying mineral phases and organic matter content. X-ray absorption spectroscopy was used to determine the identity of precipitate phases formed during these reactions. In soils with a high clay fraction, there is rapid formation of precipitate phases resistant to proton promoted dissolution. The exact nature of these phases, however, depends on the dissolution of aluminum and silicon ions from the dominant mineral phases present. In sandy loam soils, formation and stability of LDH precipitates is most heavily influenced by the concentration of natural organic matter in the soil. In all cases, precipitate stability appears to increase with aging. Combined with thermodynamic studies of LDH stability, these studies will aid the development of better models for predicting the fate of contaminant metals in the environment.

Electrokinetic Treatment of Copper, Chromium and Arsenic Contaminated Soil from Wood Preservative Industries

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Electrokinetic remediation is an emerging technology that could be very effective in the removal of charged contaminants from soil. The feasibility of electrokinetic technique was tested on soil (20% soil + 80% sand) spiked with copper, chromium and arsenic (CCA solution) from the wood preservative industry. In order to better understand the ionic mobility within the soil and to detect the generation and advancement of acidic front, sampling ports were provided across the cell. Three tests were performed at different current densities of 5.92, 2.85, and 1.42 mA/cm^2 for a period of 15 days, to determine the optimal current density. The initial concentrations of Cu, Cr and As in the soil were 4800, 3100,and 5200 mg/kg respectively. Dilute nitric acid was used as an amendment to neutralize the hydroxyl ions produced at the cathode end of the cell. Based on the percentage removal calculations, the amount of power supplied, and the cell operation period, the optimal current density was 2.85mA/ cm^2. The results also indicated that the advancement of acid front favored desorption of metals from the soil and the metals were mobilized either as free cations or metal complexes. Tests are being conducted on fabricated soil (60% soil + 40% sand) spiked with CCA solution, and soil from a CCA contaminated site under a constant current operation of 2.85 mA/ cm^2. The results of these tests will be presented.

On-Line Monitoring of Mercury and Arsenic Below Regulatory Levels

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Most natural water systems and process and waste streams are monitored using periodic grab sampling and analysis. Spot monitoring like this results in a low-resolution understanding of a stream’s chemistry. With a limited number of data points, brief high or low concentration spikes may not be detected, at the same time in cases were they are detected, brief spikes may bias an analyte’s average concentration. To better understand and monitor temporal variability of mercury in complex matrices Frontier Geosciences has developed an innovative continuous mercury monitoring system. The system utilizes online sample preparation involving chemical, thermal, and UV digestion. Detection is achieved by cold vapor atomic florescence spectrophotometry (CVAFS). The analyzer is run using ether EPA method 1631 or 245.7 to achieve a detection range of sub-ppt to 100 ppb levels. The system is capable of measuring mercury concentration at 5-minute intervals. This interval can be increased as needed by the operator. Modifications to the physical instrument, to the analyzer chemistry, and to the analytical method have been made, optimizing the system to run matrices ranging from drinking water to petroleum hydrocarbon, and organic rich process water from a natural gas plant. Due to the increased interest in arsenic, we have also built an on-line monitoring instrument for arsenic. This instrument uses a similar sample pre-treatment system suitable for As and uses Anodic Stripping Voltammetry. Continuous monitoring achieved using these systems increases data resolution enabling researchers and plant operators to better understand chemically complex and temporally variable systems. Geochemical trends that are not apparent under spot monitoring may come to light. Dischargers can better tailor treatment systems and insure proper operation in rapidly changing situations. The instrument can be built to collect samples from various parts of process for continuous mass balance determinations. The details of the method and results of a number of field studies will be presented.

Heavy Metals at Training Ranges

Application of Geochemical Evaluation to Identify Metals Contamination in Soil at Firing Ranges

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Tungsten Effects on Soil Environments

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Washington Braida, Stevens Institute of Technology, Hoboken, NJ
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Corrosion Behavior of Tungsten Alloys in the Environment

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Evaluation of Phosphate Treatment Methods to Reduce Lead Mobility at Military Small Arms Training Ranges

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Recovery and Recycling of Tungsten and Lead from Small Arms Firing Range Soils

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Vertical Distribution and Speciation of Lead at a Recreational Firing Range in Eastern Massachusetts

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Application of Geochemical Evaluation to Identify Metals Contamination in Soil at Firing Ranges

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Lead, antimony, copper, and zinc are expected contaminants in soil at firing ranges due to their presence in bullets and shell casings. These metals are also naturally occurring in soil, so it is important to distinguish between naturally high background concentrations and actual contamination during site investigations. Standard statistical tests are prone to high false positive error rates, however, and cannot provide mechanistic explanations for the elevated metal concentrations. A geochemical evaluation technique has been successfully applied during firing-range investigations to properly identify the contaminated soil samples. These evaluations are based on the well-established associations of trace elements with specific minerals in the soil matrix. Correlation plots of trace element concentrations versus major element concentrations are constructed to explore these specific associations. For example, lead has a natural affinity to adsorb on the surfaces of manganese oxide minerals, and a positive correlation between lead and manganese concentrations is observed for uncontaminated samples. Anomalous samples that may contain a component of contamination are readily distinguished from uncontaminated samples by their elevated lead/manganese ratios. Plots of antimony, copper, or zinc versus lead provide supporting evidence for the contaminant source; in oxic soils, covariance of these metal concentrations is not expected unless contamination is present. These evaluations utilize existing analytical data obtained during typical site investigations, and require only minimal level of effort to perform. Examples are provided from several firing-range investigations at military installations across the United States, and illustrate the technique's utility in a variety of geological regimes, soil types, and project sites. These evaluations have been successfully used to delineate the extent of contamination, identify hot spots for removal actions, confirm the success of remediation efforts, and facilitate site closure decisions.

Tungsten Effects on Soil Environments

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Tungsten alloys have been used to manufacture different caliber ammunition and kinetic energy penetrators. However, information on the impacts of tungsten on environmental systems is very limited. The objective of this study was to investigate the effects of tungsten on soil community and soil-plant systems. Target compounds were chemical pure tungsten, ammunition grade tungsten, and common alloying elements such as nickel and cobalt. Several different techniques were utilized: soil respiration, TOC (total carbon) analysis, direct microscopic observation on the degradation of starch and micro-cellulose, and plant toxicity using ryegrass. Dissolution of munitions grade tungsten powder significantly acidified soil solution. Other alloying elements behave different, cobalt increased soil pH while nickel reduced soil pH but not significantly. Changes in the soil microbial community were analyzed by the spread plate dilution method. Tungsten powder and soluble tungsten were added to soil at ratio ranging from 0.01% to 10%. Tungsten has strong toxic effect on soil microbial community, soil microfauna (nematodes and mites) and plant growth. Tungsten mixed with soils at rates higher than 1% (w/w) inhibited glucose, micro-cellulose and starch degradation. The CO_2 evolution was raised several times in tungsten-polluted soils suggesting the death of a substantial fraction of soil organisms. After three months of incubation, TOC analysis shows that soil amended with 1% and 5% of tungsten (w/w) lost 5.9% and 10.5% of total carbon through CO_2 production, respectively. The changes on soil microbial community after tungsten amendment continue after several weeks. The death of 95% of soil bacteria was observed after 4 months in soils amended with 3% (w/w) of tungsten. The toxicity of the tungsten alloy components to environmental systems appears to follow the order munitions grade W ≅Co.>> Ni.

Corrosion Behavior of Tungsten Alloys in the Environment

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Tungsten-based alloys are being used or are under evaluation for potential use, in the manufacturing of kinetic energy penetrators for various munitions applications. Tungsten heavy alloys are mainly composed of tungsten (88-95%) with nickel and cobalt making up usually the remaining fraction of the formulation. Iron and copper may also be present depending on the particular alloy composition. Tungsten has a wide variety of stereochemistries and oxidation states, making its chemistry the most complex of the transition elements. The limited studies available in the literature on soil adsorption do not address the basic mechanisms of release and transport of tungsten and the effects of complexation on solubility and subsequent bioavailability. The rate of release of ions from the alloy surface and the formation of solid coatings is generally controlled by the redox phenomena prevailing in the surrounding medium. Factors affecting the rate of corrosion in soils include the soil pH, redox potential, moisture content and its mineralogical and chemical composition. Corrosion of the metal alloys by exposing the solid surface to aqueous solutions or more realistically in soil matrices is currently under study. The corrosion behaviors of 5 munitions grade alloys of interest are being examined. The corrosion products deposited on the alloy surface and the thickness of the surface coating is determined by X-ray diffraction, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Aqua and oxo complexes of tungsten are of special interest for assessing its subsurface mobility. The dissolution of tungsten and the subsequent formation of condensed polytungstates involve complicated chemical processes. Characterization of the complexes formed as intermediate products of this process is attempted using FTIR techniques. Preliminary experimental results have suggested the presence of non-stoichiometric tungsten oxides as possible intermediates in the process. XRD analysis shows the presence of tungsten bronzes with general formula $H_xWO_3.yH_2O$ and intermetallic compounds.

Evaluation of Phosphate Treatment Methods to Reduce Lead Mobility at Military Small Arms Training Ranges

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The primary goal of the United States Military is to train and equip troops to maintain military readiness to defend the United States and its interests. Small arms range (SAR) training represents a major element in keeping the military ready to accomplish this mission.

Projectiles utilized as part of SAR training have accumulated in the soil at the SARs as a result of many years of use. These projectiles are composed of toxic metals. The projectiles, with weathering, change form allowing the metals to migrate to surface and ground water sources. Due to the toxicity associated with the metals, the SAR may pose a threat to humans and the environment. Current lead remediation techniques are costly and inefficient thus new cost effective remediation techniques must be developed and implemented.

Studies show that the treatment of the soil with phosphate-based binders may react with the metals, which results in lowering the solubility of the lead and other metals. The phosphate based-binders react with the metal ions, such as lead, to form insoluble metal phosphate complexes called pyromorphites as shown in equation 1.
$10M^{2+} + 6H_2PO_4^{-} + 2OH^{-} \rightarrow M_{10}(PO_4)_6(OH_2) + 12H+$ Eq (1).
Several types of phosphate binders can be used to form the desired pyromorphites, however, the kinetics of the reaction depend on the phosphate complex. This may be due to the ability of the specific binder to mix efficiently in the contaminated soil or due to the reactive nature of the specific form of phosphate applied to the site.

This paper presents the results of a study to investigate the effect of phosphates on the lead contained in soils collected at military SAR training areas. Laboratory evaluations consisted of adding various phosphates at different dosages to SAR samples. After treatment the soils were subjected to a series of leaching tests. The result of laboratory effort as well as the planned field activities will be presented.

Recovery and Recycling of Tungsten and Lead from Small Arms Firing Range Soils

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A significant mass of tungsten has been used to produce 5.56 mm ammunition for use at military training facilities as a substitute for lead bullets. The mass of tungsten used in fixed target/fixed firing position ranges has produced soils that are expected to contain tungsten in the percent by mass concentrations, in addition to legacy lead from past training. The tungsten industry has been recycling tungsten materials from metal scrap for decades. The reactivity of tungsten in water, especially in alkaline waters, is exploited in the recycling process. Tungsten is treated with alkaline water to form soluble tungstates. This water, laden with high concentrations of tungstates is then neutralized and solid ammonium para-tungstate is separated from the solution and used to produce tungsten metals. Using the previously developed chemical recovery system coupled with state of the art soil washing techniques, a potential recovery system has been designed for removal of tungsten, as well as legacy lead, from small arms training range berms.

Vertical Distribution and Speciation of Lead at a Recreational Firing Range in Eastern Massachusetts

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A soil sampling and analysis study was performed to characterize the distribution and speciation of lead shot and lead species at a recreational skeet and trap range in Eastern Massachusetts. Results indicate the majority of lead is present at 0-2” as both lead shot and lead shot fragments retained on #8 and #16 sieves. While lead speciation in soils varied with soil cation exchange capacity (CEC), soil acidity and organic carbon content, carbonate species of lead were predominate in soils below a depth of 0-2”. Concentrations of lead in respirable soil particles were also measured.

Soil samples were collected in locations at four distances from shooting platforms including prior to, within and beyond the fall zone of the range. A 0-6” core was collected from each sample location. The core was separated into three sections (0-2”, 2-4” and 4-6”). For each section, a particle size distribution was determined. Samples from each sieved fraction were then analyzed for lead content. Lead shot and fragments from sieved fractions were also separated and quantified.

Lead analysis was performed by flame atomic absorption spectroscopy. A sequential extraction procedure was performed to measure the speciation of lead in each sieved fraction. The sequential extraction procedure was used to distinguish exchangeable, soluble, organic, carbonate, and residual forms of lead in each sample.

Indoor Air

Indoor Air Background Subpopulations and Seasonality at the CDOT MTL Site, Denver, Colorado

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Context-Based Benchmarks for Indoor Air Evaluation

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Indoor Air Background Subpopulations and Seasonality at the CDOT MTL Site, Denver, Colorado

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The CDOT MTL Site in Denver, Colorado has been the subject of extensive indoor air sampling for over eight years. Beginning in October 1998 24-hour SUMMA canister samples were analyzed using TO-15 SIM, with results reported down to the method detection limit (MDL). While several publications have documented background indoor air concentrations of chlorinated chemicals in residences at this site (Indoor Air 2002, MSRAS 2002, 16th Int. Conf. Soils, Sediments and Water 2000, etc.), additional results on background data seasonal variability and sub-populations are now available from the several thousand indoor air samples collected on a quarterly basis. A detailed examination of the variability of background and its relationship to residence specific factors are presented.

Benzene, chloroform, methylene chloride (DCM), tetrachloroethylene (PCE), bromodichloromethane (BrDCM) and 1,2-dichloroethane were routinely measured in all indoor air samples in addition to the groundwater-derived chemicals of interest.
Several distinctive results have been found in the background indoor air data from this site. There is a very strong correlation of BrDCM, with chloroform. This suggests that, similar to chloroform, BrDCM is derived from chlorinated tap water.

There is a highly significant difference in the background indoor air concentration of benzene between single family homes with and without attached garages. Homes with attached garages have concentrations averaging two times greater (5.5 ug/m^3) than those without (2.8 ug/m^3). The other gasoline related hydrocarbons show similar behavior.
There is a notable seasonality to background indoor concentrations of chloroform and methylene chloride. Chloroform concentrations tend to peak in summer and reach minimums in winter. DCM concentrations generally peak in summer and fall.

Context-Based Benchmarks for Indoor Air Evaluation

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Evaluation of potential health risks to indoor air contaminants typically entails two risk management issues. First, assuming that the focus of evaluation rests on a specific source (such as vapor intrusion from subsurface soil or groundwater), it is often desirable to compare source-based contributions against background indoor air quality (*i.e.*, concentrations of the same chemical(s) that would be present in the absence of the contaminant source). Second, toxicity-based benchmarks must be selected to evaluate potential hazards to health.

Selecting appropriate benchmarks for comparison relative to both of these objectives involves multi-faceted considerations. Regarding the selection of a background concentration benchmark:

Should building uses and types be differentiated (*e.g.*, residential *v.* industrial/commercial)?
Should indoor air sources such as environmental tobacco smoke be considered in establishing background air quality?
Should source-related impacts even be evaluated relative to background (*e.g.*, should modeled values smaller than background be viewed as acceptable)?
In the absence of measurable background levels, should analytical detection limits be used as surrogate measures of background?

Regarding toxicity-based benchmarks:

Should values be selected from traditional risk assessment databases such as the Integrated Risk Information System (IRIS), or should applicable occupational or workplace standards be applied in some settings?
How should significant uncertainties in toxicological values be handled?
Should risk-based limits be established in conjunction with risks associated with background air quality?

Lacking definitive federal guidance or professional consensus, the answers to these questions are debatable. In some cases, state regulatory programs provide relevant constraints and policies that effectively guide the evaluation process. Insufficient and uncertain data also make it difficult to answer some of the relevant questions. However, decisions must be made as indoor air risks become increasingly important in the evaluation of sites with soil and groundwater contaminated with volatile chemicals. This paper will provide suggestions for developing a framework for addressing indoor air risks that selects benchmarks appropriate to the context of the exposure setting. Examples that reflect current issues of interest will be drawn from project experience.

In Situ Chemical Oxidation

Modified Ferrous Ion Activated Persulfate Oxidation for In Situ Remediation of Trichloroethylene
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Chemical Oxidation Using Ozone, Hydrogen Peroxide, and Air Injection Systems for BTEX, MTBE, and TBA
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The Application of In Situ Chemical Oxidation for Treatment of Chlorinated Solvents in a Naturally Reducing Environment
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ISCO Technology Overview – Do You Really Understand the Chemistry
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Rapid Controlled Oxidation and Biologic Enhancement of Petroleum Contaminants in Clayey, Silty, and Sandy Soils
Thomas D. Douglas, P.E., AET, LLC, Pensacola, FL
Ian T. Osgerby, Ph. D., P.E., US Army Corp of Engineers, Concord, MA
Thomas A. Reed, DeepEarth Technologies, Inc., Avarda, CO

COVC Source Identification through In Situ Chemical Oxidation in Fractured Bedrock
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Modified Ferrous Ion Activated Persulfate Oxidation for In Situ Remediation of Trichloroethylene

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It has been postulated that the persulfate anion ($S_2O_8^{2-}$) can be thermally or chemically activated to produce a powerful oxidant known as the sulfate free radical ($SO_4^{-}\bullet$) with a standard redox potential of 2.6V, which is capable of destroying groundwater contaminants such as trichloroethylene (TCE). The objective of the laboratory study is to examine the capability of ferrous ion (Fe^{2+}) activated persulfate oxidation of TCE in both aqueous and soil slurry phases. Experiments using various molar ratios of persulfate/Fe^{2+}/TCE in an aqueous system indicate that TCE degradation occurred almost instantaneously and then the reaction stalled far from completion. Sequential addition of Fe^{2+} resulted in an increased TCE removal efficiency. Therefore, it appeared that Fe^{2+} played an important role in generating $SO_4^{-}\bullet$. Either cannibalization of $SO_4^{-}\bullet$ in the presence of Fe^{2+} or the rapid conversion of all ferrous ions to ferric ions limited the ultimate oxidizing capability of the system. An observation of oxidation-reduction potential variations revealed that the use of Fe^{2+} activated persulfate-thiosulfate redox couple could significantly decrease the strong oxidizing conditions and result in an improvement of TCE removal. In addition, a chelating agent was used in attempt to manipulate the quantity of Fe^{2+} in solution. A comparison of chelating agents was initially conducted. The use of chelated Fe^{2+} resulted in the maintenance of the Fe^{2+} in solution and promoted more efficient destruction of TCE.

Chemical Oxidation Using Ozone, Hydrogen Peroxide, and Air Injection Systems for BTEX, MTBE, and TBA

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There can be many challenges with providing cost-effective and aggressive remediation solutions to sites impacted with BTEX, MTBE, and TBA compounds. Groundwater & Environmental Services, Inc. has developed and utilized various innovative ozone, hydrogen peroxide, and air injection systems, which can remediate BTEX, MTBE, and TBA impact at costs significantly below conventional methods and within a relative short time frame. Case studies will be presented where BTEX, MTBE, and TBA impact in soil and groundwater was remediated through the combination of ozone and hydrogen peroxide injection or through the combination of hydrogen peroxide and air. The two technologies which will be presented will detail various case studies where contaminated soil and groundwater was aggressively remediated through monthly and short-term (daily/weekly) remediation solutions. Case studies will be presented where short-term mobile hydrogen peroxide and air injection systems were utilized to remediate soil and groundwater impacted with BTEX and MTBE at relatively low life-cycle remediation costs ($15,000 to $200,000).

The case studies to be presented are from sites exhibiting varying lithologies and within different regulatory environments. The presentation will include a discussion on evaluating life-cycle costs for chemical oxidation and other remediation technologies. The discussion will also evaluate various methods available to perform on-site feasibility tests and off-site bench tests which can be utilized to evaluate the potential effectiveness of in-situ chemical oxidation using ozone and hydrogen peroxide injection or hydrogen peroxide and air injection systems.

The Application of In-situ Chemical Oxidation for Treatment of Chlorinated Solvents in a Naturally Reducing Environment

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In naturally reducing subsurface environments, many common chlorinated solvents (CSs) can undergo biodegradation by indigenous microorganisms capable of halorespiration. This process often limits the ultimate extent of dissolved CS plumes in ground water and may be relied upon in part or whole as a site remediation strategy. A common regulatory criterion for approval of such "natural attenuation" or "intrinsic biodegradation" strategies is source control for unsaturated and saturated soils in areas where CSs were released to the subsurface. In such areas, CSs, often in the form of dense non-aqueous phase liquids (DNAPL), would otherwise undergo slow leaching and/or dissolution into ground water, thereby acting as long-term sources of CS plumes.

A technology that is increasingly being used for CS source control is in-situ chemical oxidation (ISCO) by permanganate or other oxidants. An effective ISCO program for CS source areas has the potential, however, to disrupt the halorespiration of dissolved CSs, which requires reducing conditions. This presentation describes the results of a potassium permanganate ($KMnO_4$) ISCO source control program at a site characterized by the presence of tetrachloroethylene (PCE) DNAPL beneath an operating facility. A ground water plume of tetrachloroethylene (PCE) and its degradation by products trichloroethylene (TCE), cis-1,2-dichloroethylene (1,2-DCE) and vinyl chloride exists downgradient of the source area, but is undergoing highly effective halorespiration facilitated by naturally reducing conditions. This presentation focuses on the design considerations necessary for an effective ISCO application in a reducing environment and discusses the results of a monitoring program that was specifically designed to both: (1) evaluate the effectiveness of $KMnO_4$ ISCO source control for saturated soils containing DNAPL, and (2) evaluate the effects of ISCO on subsurface geochemical conditions previously conducive to on-going effective biodegradation by halorespirating microorganisms.

ISCO Technology Overview - Do You Really Understand the Chemistry?

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The reaction chemistry of ISCO is presented for the common oxidant systems employed in ISCO: catalyzed peroxide propagations (Modified Fenton's), permanganate, ozone/ozone-peroxide (peroxone), and persulfate. All of these oxidant systems, with the exception of permanganate are described by reaction schemes employing free radical generation, and all are dependant to some degree on local conditions such as water chemistry and pH. A less familiar reactant condition may be the influence of inorganic and organic compounds in the soil matrix, which can have a strong influence over the intended outcome of the ISCO application. Thus, naturally occurring organic compounds may overwhelm the contaminant demand for oxidant or prevent the transition of the adsorbed contaminant to the aqueous phase where ISCO reactions occur. Naturally occurring inorganic compounds may actually cause destruction of the oxidant or modify the catalytic component. Some experience with soils having markedly different matrix properties will be discussed to provide an illustration of some of the difficulties which may be faced in the practice of ISCO.

Rapid Controlled Oxidation and Biologic Enhancement of Petroleum Contaminants in Clayey, Silty, and Sandy Soils

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Clean up of petroleum in clay or low yielding soils is often difficult, problematic, expensive, or impractical; however, a controlled in-situ chemical oxidation process "CISCOP™" has been successfully used at several sites in northern Florida where soil with high clay content, carbonates, high organic content, and/or silty soil are present. Recent treatments have demonstrated that petroleum mass is rapidly reduced in both soil and groundwater, with significant and substantial biologic enhancement demonstrated. This process has been used adjacent to active tank pits and pump islands and where free phased product is present, with low risk. The process uses metallic peroxides and hydrogen peroxide to oxidize contaminants to molecules that are used as a food by native bacteria following injections or over-spraying of CISCOP™ reagents. Petroleum reducing bacteria counts indicate that bacteria are flourishing in soil and groundwater. The pH of soil and water is buffered; therefore, bacterial reduction of contaminants can be sustained. The combination of chemical oxidation and sustained biologic activity have resulted in the reduction of petroleum contaminants in soil and water of >80% in the vadose, smear, and saturated zones. This process is being applied to the remediation of soils and water both *in-situ* and following excavations and at petroleum stations, even where free phased product is present, with good results. This paper presents data which substantiates that significant petroleum mass reduction and enhanced biologic activity are occurring at sites where CISCOP™ treatments have been performed, even in clayey and silty soils where high carbonate concentrations are present.

CVOC Source Identification Through In-Situ Chemical Oxidation in Fractured Bedrock

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An *in-situ* chemical oxidation (ISCO) pilot program, using Fenton's Reagent (hydrogen peroxide and a ferrous sulfate catalyst), was performed to assess its effectiveness in destroying chlorinated volatile organic compounds (CVOCs) in a fractured-bedrock aquifer. This case study is unique because it was one of the first applications of ISCO in fractured bedrock. In addition, the targeted CVOC reduction from 1,500 to 100 micrograms per liter (μg/L) was relatively aggressive compared to most ISCO applications. This pilot program also provided the opportunity for an independent, third party evaluation of ISCO in a fractured-bedrock environment. The site geology consists of approximately 6 meters (m) of unconsolidated glacial deposits overlying fractured bedrock, with a groundwater depth of approximately 2 m. Initial characterization activities, including injection testing and multi-level packer sampling, identified a pre-ISCO CVOC plume extending approximately 90 m long by 45 m wide and spanning a vertical depth between 3 and 35 m. Packer sampling results indicated the pre-ISCO plume had an asymmetric configuration that was consistent with the injection-test results. The ISCO pilot program involved the injection of 14,237 liters of 50% hydrogen peroxide, combined with a ferrous sulfate and pH-buffering catalyst. Two injection events were performed, with overlapping performance sampling. Samples collected 30 to 45 days after each injection event, showed CVOC concentrations below the treatment objective in many areas of the plume. However, samples collected 60 to 100 days after each event, revealed significant rebound in most areas, at concentrations that approached initial pre-ISCO aquifer conditions. An assessment of the results suggests that the injected oxidants primarily influenced the more transmissive fractures in the treatment zone, whereas the less transmissive fractures were less influenced. Geochemical data and calculations indicate that the peroxide and catalyst may persist in the subsurface for prolonged periods (>200 days), thus complicating the assessment of rebound and the actual effectiveness of the technology. Although the success of treatment was limited, it proved to be successful in enhancing the conceptual site model of the subsurface, better defining the applications and limitations of ISCO treatment in fractured bedrock, and most importantly, clearly identifying the source of residual CVOCs at the site.

Legal Issues

Expert Opinions In Environmental Litigation – Practical Considerations

David G. Ries, Thorp Reed & Armstrong, LLP, Pittsburgh, PA

Natural Resource Damages (NRD) Update

Gail H. Allyn, Pitney Hardin, LLP, Morristown, NJ

Expert Opinions In Environmental Litigation – Practical Considerations

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Environmental litigation almost always involves scientific issues and expert opinions, often with multiple experts in different disciplines. In 1993, the United States Supreme Court issued its landmark decision in *Daubert v. Merrell Dow Pharmaceuticals, Inc.*, 509 U.S. 579 (1993), in which the Supreme Court established (1) a gatekeeping requirement under which federal courts must screen expert opinions for reliability and exclude "junk science," and (2) a new, more flexible test to be used in this process. These standards have now become better defined through their application by courts for over ten years and by amendments to the Federal Rules of Evidence. While admissibility of expert opinions is primarily the responsibility of attorneys, it is important for environmental professionals to understand the issues, both to assist attorneys and to take them into consideration in projects which may later result in litigation. This presentation will explore some of the practical considerations for environmental professionals in performing work for litigation or services which might later be the subject of litigation. It will include such areas as (1) when experts may rely on the work of others, like field investigation, lab analysis and modeling, (2) opinions based on experience rather than on published standards, and (3) the more rigorous analysis, beyond usual environmental protection standards, which is often required for litigation.

Natural Resource Damages (NRD) Update

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For many years, the federal and state governments have had the legal authority to seek payment for damage to natural resources from parties who are responsible for environmental contamination. This was occasionally an element of enforcement actions and settlements associated with large oil spills and other headline events, but less frequently required in more routine remediation cases. More often, the governmental agencies would defer any claims for natural resource damages when approving site cleanups, while perhaps reserving their rights to bring such claims in the future.

Now there is renewed focus on natural resource damages, both on the federal and state level. For example, the state of New Jersey has initiated an ambitious program to make the assessment and collection of natural resource damages a part of every site cleanup. “No further action letters” giving final approval to cleanups will not be issued until a party’s responsibility for natural resource damages is resolved. In addition to individual sites, New Jersey is focusing on entire watershed areas. In 2003, New Jersey issued a directive to 66 companies connected to 18 sites along the lower Passaic River in northern New Jersey, requiring them to arrange for an assessment and interim restoration of the river ecosystem. Recently New Jersey has brought suit against a number of companies to collect natural resource damages using an outside contingent fee attorney. Other states are watching with interest the development of New Jersey’s program, to decide what actions to take in their own jurisdictions.

The evaluation of natural resource damages, especially in complex watershed systems, presents many challenging technical and legal issues. These include the overlapping authorities of federal and state trustees, the problem of quantifying the value of the resource that has been lost, and the issue of what is fair compensation or resource substitution. This presentation will discuss some of the issues that any party faced with a natural resource damage claim must be prepared to address, using examples from recent cases in New Jersey and elsewhere.

Modeling

Contaminant Fate and Transport in the Courtroom
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Charles M. Denton, Varnum, Riddering, Schmidt & Howlett LLP, Grand Rapids, MI

Development and Application of a Multimedia Models to Assess Exposure to Persistent Organic Pollutants in South Texas
V. Uddameri, Texas A&M University Kingsville, Kingsville, TX
Srilakshmi K. Ramaraju, Texas A&M University Kingsville, Kingsville, TX

A New Method of Delineating Three-Dimensional Capture Zones with Models
John Glass, CH2M Hill, Herndon, VA
Scott DeHainaut, CH2M HILL, Otis ANGB, MA
Rose Forbes, Air Force Center for Environmental Excellence, Otis ANGB, MA

Leaching of BTEX from Aged Crude Oil Contaminated Model Soils: Experimental and Modeling Results
Michael H. Huesemann, Pacific Northwest National Laboratory, Sequim, WA
Tom S. Hausmann, and Tim J. Fortman, Pacific Northwest National Laboratory, Sequim, WA

Use of Brute Force Optimization Modeling for Design of Extraction Well Fields
Christopher Abate, AMEC Earth Environmental, Westford, MA
Alan D. Laase, AMEC Earth and Environmental, Westford, MA
Mark Applebee, AMEC Earth and Environmental, Westford, MA
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Contaminant Fate and Transport in the Courtroom

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Modeling of contaminant fate and transport in soils, groundwater, air and other environmental media can be a critical component of permitting, remedial action planning and design, site characterization, and source identification. Modeling of emissions and contamination can result in significant cost-savings as compared with additional sampling and analysis, and is frequently utilized by potentially responsible parties as well as governmental agencies for air permitting, remedial investigations, corrective measures studies, and engineering design. The science of modeling has been challenged in federal and state courtrooms across the country. Questions have been raised as to the reliability, predictability and specificity of contaminant fate and transport modeling by various adversaries, including former operators, neighboring owners, and liability insurers. This paper will discuss the scientific rigors of environmental modeling, its many uses and acceptability within the scientific community, as well as its limitations. The paper will also review and discuss recent court rulings and evidentiary issues regarding contaminant fate and transport modeling in litigation and related expert witness testimony.

Development and Application of a Multimedia Models to Assess Exposure to Persistent Organic Pollutants in South Texas

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The region of South Texas along US-Mexico border is undergoing rapid growth in recent times. Human health and ecological risks due to persistent organic pollutants (POPs) has been a critical issue in this region as several pesticides like DDT and others have been used extensively both on the US side (till their ban in 70s) and till very recently in Mexico. The long-range transport potential of these pollutants, their recalcitrant nature and their ability to exist in multiple compartments simultaneously, requires a set of holistic assessment tools to quantify their exposure via multiple pathways and to various receptors. The objective of this study was to develop a suite of mathematical modeling tools to estimate exposure concentrations in various compartments. These models were developed in an iterative fashion starting with simple Level I type calculations and extended to more complex Level III/Level IV formulations. A Geographic Information System (GIS) was used to assimilate data necessary to parameterize the model and visualize model results and disseminate risk-based information. Fuzzy set theory was used to evaluate imprecision arising from model assumptions and lack of suitable data. The presentation will discuss salient results obtained from this exposure assessment study and illustrate the utility of information technologies like GIS and fuzzy set theory in carrying out multimedia exposure assessments.

A New Method of Delineating Three-Dimensional Capture Zones with Models

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The Air Force Center for Environmental Excellence operates several groundwater remediation systems at the Massachusetts Military Reservation (MMR). These systems involve multiple extraction and injection wells designed to provide complete or partial hydraulic containment of contaminant plumes. It is important in the design and optimization of these systems to be able to accurately delineate their hydraulic capture zones, which are three-dimensional and irregularly shaped. Traditional delineation techniques are based on visual identification of the envelope of pathlines leading to the extraction wells, the pathlines being generated by either backward or forward particle tracking in the simulated flow field. A new technique being used at the MMR involves forward tracking of particles from a dense three-dimensional array of starting locations without actually plotting the pathlines. Instead, the particle-tracking outcome is used to define a grid-based three-dimensional continuum of capture parameter, which can then be contoured in two-dimensional projections or otherwise rendered visible by three-dimensional visualization software. The resulting capture parameter is a three-dimensional scalar field that can be considered a quantitative spatial property of the flow regime. It can be combined with other scalar fields defined in the same grid, such as the concentration field, for visualization or for volumetric calculations. Arithmetic comparisons of capture parameter arrays generated at different pumping rates are also useful in sensitivity analysis.

Leaching of BTEX from Aged Crude Oil Contaminated Model Soils: Experimental and Modeling Results

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It is commonly assumed that soil properties such as organic matter content, porosity, and mineral surface area have a significant effect on the bioavailability and leachability of aged petroleum hydrocarbons. In order to test this hypothesis, nine model soils or sorbents (i.e., fine and coarse quartz sand, montmorrilonite and kaolinite clay, peat, 60Å and 150Å silica gel, a loam soil, and non-porous glass beads) were spiked with a crude oil at 50,000 mg/kg and 100,000 mg/kg, aged for 27 months in the laboratory, and transferred to glass columns for the performance of continuous flow leaching experiments. The column effluents were sampled and analyzed for BTEX until they were no longer detectable in the leachate. A one-dimensional flow model for predicting the dissolution and dispersion of individual hydrocarbons from a multi-component NAPL such as crude oil was developed and used to fit the leaching data (i.e., the BTEX concentration versus time curves) by adjusting the equilibrium oil-leachate partitioning coefficient (K_{ol}) for each respective hydrocarbon. The Peclet number, which is a measure of dispersion and a required modeling parameter, was measured in separate bromide tracer experiments for each soil column.

Results indicate that the BTEX leaching curves could be successfully fitted with the one-dimensional NAPL dissolution flow model for all sorbents with the exception of montmorrilonite clay and that the fitting parameter K_{ol} for each hydrocarbon is similar to the K_{ol} values that were independently measured for the same crude oil by Rixey et al. (*Journal of Hazardous Materials B*, 65: 137-156, 1999). In addition, the fitted K_{ol} values were very similar for BTEX leaching from aged compared to freshly spiked loam soil. These findings indicate that leaching of BTEX in the aged soils is not affected by soil properties or aging but rather is governed by the equilibrium dissolution of these hydrocarbons from the crude oil NAPL that is coating the soil particles.

Use of Brute Force Optimization Modeling for Design of Extraction Well Fields

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Brute Force, an optimization technique based on sequential MODFLOW and MODPATH runs, was used to simultaneously design both containment and time-specific extraction well fields for different contaminants having a range of concentration standards. Brute Force, also known as particle tracking optimization (PTO), uses particles as surrogates for groundwater contamination. The particles are assigned unique identifiers corresponding to dissolved contaminant mass and required capture time, which can be different for each particle so an extraction system can be optimized for both containment and time-specific contaminant removal. Because Brute Force uses particle track modeling it is inherently faster than transport modeling and an optimized time-specific design, for both well locations and pumping rates, can often be found in the time it would take to perform only a few transport runs. Accuracy is not sacrificed for speed as verification modeling using MT3D shows that the Brute Force extraction well field designs perform as specified.

For this application extraction well fields that included injection wells for the return of treated water were designed for containment and 10, 15 and 30 year contaminant removal times. Based on MT3D simulations, the designs were effective at removing multiple dissolved contaminants within the specified time-constraints with the majority of the contaminant mass being captured in the earlier period of system operation.

Oxygenates

Methyl *tert*-Butyl Ether (MTBE) in Public and Private Wells in Southeast New Hampshire
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Denise M. Argue, U.S. Geological Survey, Pembroke, NH
Frederick J. McGarry, New Hampshire Dept. of Environmental Services, Waste Mgmt. Division, Concord, NH

Maine's Experiment With Gasoline Policy to Manage MtBE in Groundwater
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Assessment, Control and Remediation of a Diving and Rapidly Moving MTBE/Benzene Plume to Prevent Impacts to Down-Gradient Public Water Supply Wells in the Town of Palmer Massachusetts
Michael Scherer, Massachusetts Department of Environmental, Springfield, MA

Electrical Resistance Heating Technology Coupled with Air Sparging and Soil Vapor Extraction for Remediation of MTBE and BTEX in Soils and Groundwater in Ronan, Montana
Jeffrey Kuhn, Montana DEQ, Butte, MT
Kenneth Manchester, MSE Technology Applications, Butte, MT

Ozone Sparging for In-Situ Oxidation of MTBE
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Enhanced In Situ Groundwater Bioremediation of Petroleum Hydrocarbons and Oxygenates – Field Applications and Data Evaluation
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Methyl *tert*-Butyl Ether (MTBE) in Public and Private Wells in Southeast New Hampshire

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The occurrence the gasoline oxygenate MTBE (above 0.5 micrograms per liter) in public water supply wells in New Hampshire has increased steadily over the past several years. Occurrence rates increased from 12.7 percent of wells tested in 2000 to 15.1 percent in 2002. In Rockingham County, where reformulated gasoline (RFG) usage is mandated, the percentage of public wells with MTBE above 0.5 micrograms per liter (µg/L) increased from 20.3 percent in 2000 to 23.1 percent in 2002 based on data from the State of New Hampshire. New data collected from randomly selected wells in Rockingham County indicate that in 2003, 26.2 percent of the public wells had MTBE concentrations that exceeded 0.5 µg/L. Overall, 40 percent of water samples from public wells and 21 percent from private wells in the County had measurable concentrations of MTBE, based on a low laboratory reporting level of 0.2 µg/L. Further, MTBE occurrence varied for public wells by type of establishment served; 67 percent of public wells serving residential properties have MTBE concentrations above 0.2 µg/L, whereas lower rates were found for wells serving commercial entities (41%), schools (23%), and large communities (27%). MTBE concentrations correlated significantly with urban factors, including population density and distance to gasoline underground storage tanks; however, the most significant correlation was with well depth for public supply wells. Water from deep bedrock public supply wells, had higher MTBE concentrations than shallower bedrock wells. This relation is contrary to the conventional thought that deep bedrock wells are less vulnerable to contamination than shallow wells. In Rockingham County, where water availability is a major concern, wells are being drilled deeper in search of increased supply.

Maine's Experiment With Gasoline Policy to Manage MtBE in Groundwater

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The gasoline additive MtBE has become one of the most commonly detected contaminants in groundwater nationwide and has caused much concern in the state of Maine. In 1998 the Maine Department of Human Services conducted a statewide survey of groundwater wells and MtBE was detected in 16% of private and public wells tested. These findings resulted in the state regulatory agencies deciding to opt out of the reformulated gasoline (RFG) program in 1999. Subsequently, the average concentration of MtBE in gasoline dropped from ~15% to 2% by volume to protect water resources. This major policy change provided a microcosm to study the economic and environmental effects of this gasoline additive. In order to test the effect of this policy on water quality, groundwater samples were analyzed over a period of six years (1998-2003) from 19 wells distributed across a sand and gravel aquifer in Windham, Maine. MtBE continues to occur in detectable concentrations in 30 to 40% of the study wells despite Maine's decision to opt out of the RFG program in 1999. Although recent detected concentrations are lower than in previous years, this study confirms MtBE's temporal and spatial persistence in the environment. Reducing MtBE concentrations in gasoline may not be sufficient to eliminate its occurrence in groundwater. The economic perspective is that MtBE increases the cost of groundwater remediation, as compared to MtBE-free gasoline. Economic data for spills are being analyzed to assess if reducing MtBE concentration in gasoline has affected remediation cost. Preliminary results suggest that MtBE increases costs, even when present in low concentrations in gasoline.

Assessment, Control and Remediation of a Diving and Rapidly Moving MTBE/Benzene Plume to Prevent Impacts to Down-Gradient Public Water Supply Wells in the Town of Palmer Massachusetts

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The catastrophic failure of a gasoline tank results in the sudden injection of approximately 12,000 gallons of premium gasoline to the groundwater within the Zone 2 of a public water supply well. Immediate actions to address the release were not taken by the MADEP due to a substantial delay in notification by the owner.

Initial assessment reports completed for the property owner indicated that the LNAPL area was stable and that the gasoline plume was contained on site. However, MADEP required that additional monitoring wells be installed at depth and that existing down gradient monitoring wells installed as part of another site investigation involving solvents were also to be sampled for MTBE. Samples from several of these down gradient monitoring wells installed as part of the MADEP investigation and other pre-existing monitoring wells identified that an MTBE plume had migrated at depth far beyond the original release site. Monitoring at depth down gradient within the aquifer indicated that MTBE and later Benzene were migrating at a rapid rate deep within the aquifer towards the Town Water District's active drinking water supply wells, located approximately 500 feet from the leading edge of the plume.

Initial shallow recovery wells that were installed to recover gasoline in the release area were ineffective in containing the MTBE plume. Additional recovery wells installed at depth further down gradient proved effective in containing the plume and preventing impacts to the public water supply wells. After containment of the plume was effected, intensive remedial efforts were undertaken to address the remaining source area by several injections of potassium permanganate solution. Initial injections of permanganate solution were completed in December 2003.

Electrical Resistance Heating Technology Coupled with Air Sparging and Soil Vapor Extraction for Remediation of MTBE and BTEX in Soils and Groundwater in Ronan, Montana

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Gasoline from a leaking underground storage tank located in Ronan, Montana contaminated the soil and groundwater with methyl tertiary butyl ether (MTBE), benzene, toluene, ethylbenzene, xylenes (BTEX), and other gasoline compounds. Complete clean-up of the site was made difficult because the contaminant plume extended beneath Highway 93, a primary highway in the area. Common remedial technologies such as soil vapor extraction (SVE) and air sparging have been used historically at the site and have been moderately effective in reducing contaminant levels. To more aggressively remediate the site, specifically a defined volume of soil and groundwater beneath Highway 93, MSE combined traditional air sparging and soil vapor extraction technologies with an innovative electrical resistance heating (ERH) technology. Twelve air sparging electrodes, six SVE wells, and eight auxiliary air sparge points were placed under the highway. Temperatures in the treatment volume exceeded 100ºC and input power to the electrodes varied between 12 kW and 17 kW for 142 days. Soil and groundwater samples collected from the treatment volume before the demonstration had a significant amount of MTBE and BTEX contamination. Post groundwater and soil samples had undetectable concentrations of MTBE and BTEX.

Ozone Sparging for In-Situ Oxidation of MTBE

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Bench-scale and pilot-scale studies were conducted to evaluate the efficacy of ozone sparging for in-situ remediation of methyl tertiary butyl ether (MTBE) and associated petroleum hydrocarbons and fuel oxygenates in shallow groundwater at a petroleum terminal in northern California.

Bench-scale laboratory tests conducted on groundwater and soil from the subject site indicated that MTBE was completely destroyed by oxidation, rather than volatilized, during these tests. Residual breakdown products of MTBE were limited to transient accumulations of tertiary butyl alcohol (TBA) and acetone, which were subsequently oxidized. These tests required between 20- to 100-times theoretical stoichiometric amounts of ozone in groundwater and groundwater-plus-soil slurry samples, respectively, to completely oxidize MTBE. The increased ozone demand was attributed to gas-to-liquid phase mass transfer limitations of ozone and to non-target compound oxidant demand. Application of ozone to slurries of groundwater and soil resulted in oxidation of ferrous iron (Fe^{+2}), and increases in total suspended solids related to precipitation and flocculation of dissolved metals, with a mean particle size of approximately 50 microns.

Based on the successful results of the bench-scale tests, a pilot-scale test was designed and implemented at the subject site. The pilot test included the injection of an air:ozone mixture into a single sparging well, and completion of monitoring of five surrounding wells for organic and inorganic constituents. Monitoring was conducted to assess potential effects of iron precipitation on aquifer hydraulic conductivity, and potential formation of target compound breakdown products (i.e., TBA, acetone), bromate, hexavalent chromium, and other redox sensitive metals. During the one-month pilot test, monitoring wells within 40 feet of the sparge well exhibited MTBE concentration decreases between 76 to 99 percent from pre-test and background conditions, with comparable decreases in other petroleum hydrocarbons and fuel oxygenates. Only transient increases in TBA were observed, and no other breakdown products were detected. In addition, bromate was not detected despite the presence of bromide in groundwater, and hexavalent chromium was not detected despite the presence of chromium in groundwater. While the bench-scale tests indicated that 180 to 900 grams of ozone were required to oxidize one gram of MTBE, pilot test results indicated that only approximately 20 grams of ozone were required to destroy one gram of MTBE. The lower ozone demand observed during the field test, relative to the bench-scale tests, may be due to excessive ozone demand during intensive mixing of the soil-groundwater slurry sample and ozone loss through the sample column, as well as the potential occurrence of biodegradation resulting from increases in dissolved oxygen in groundwater and the longer duration of the field test. Finally, no significant changes in aquifer hydraulic conductivity were noted despite the reduction in dissolved ferrous iron and increase in total iron in groundwater.

Enhanced In Situ Groundwater Bioremediation of Petroleum Hydrocarbons and Oxygenates – Field Applications and Data Evaluation

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Oxygen enrichment in gasoline-impacted groundwater has been shown to enhance intrinsic biodegradation of MTBE and BTEX and accelerate site cleanup. Oxygen enrichment takes place using a variety of technologies that add air or oxygen directly in groundwater and indirectly using in situ chemical oxidation (ISCO). Direct addition of oxygen results in higher dissolved oxygen (DO) concentrations than air or ISCO.

This work presents field experiences from several retail gasoline service stations where direct oxygen addition and ISCO were implemented. Data are evaluated from sites in New Jersey, Connecticut, New York, and Indiana. Subsurface soils ranged from silty clays to fine/medium sands. Oxygen was added directly using diffusive probes or indirectly by injecting a proprietary chemical oxidant blend. Diffusive probes were installed in 2-inch diameter monitoring wells or were buried directly in the boreholes. The chemical oxidant was injected using a Geoprobe™.

Prior to system startup or chemical injection, baseline groundwater samples were collected for MTBE, BTEX, BOD, COD, TOC, nitrogen, phosphorus, and ferrous iron analysis. Baseline DO levels were also measured. After oxygen addition or chemical injection, groundwater samples were collected periodically for analysis of the above parameters. Monitoring wells were located and screened so as to provide data necessary for remedial action performance evaluation.

Shortly after oxygen addition or chemical injection, DO levels increased to 50 to 60 mg/L at sites where diffusive probes were used and 10 to 15 mg/L where chemical oxidation took place. DO influence downgradient and sidegradient from oxygen infusion wells occurred within two months from startup. BTEX reductions over 99 percent and MTBE reductions over 98 percent were documented in several wells within one quarter following oxygen addition. Chemical injection temporarily mobilized residual soil hydrocarbons with subsequent temporary increase in product thickness and dissolved phase BTEX concentrations. Product thickness and dissolved concentrations declined over time.

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

Pay-for-Performance Use of Third Generation Insitu Chemical Remediation as a Replacement for Obsolete, Best Effort / Well Based Fenton's Oxidation
Mark Vigneri, ERFS, Sea Girt, NJ

Pay-for-Performance In-situ Chemical Remediation – A Consultant and Client Perspective
Bruce Nelson, Malcolm Pirnie, Lantham, NY
David J. Glass, Malcolm Pirnie, Inc., Newport News, VA

Pay-for-Performance Site Management utilizing BioAug with On-contact Remediation Model
Robert Steele, BioAug LLC, Clifton, VA
Dave Philbrook, BioAug LLC, Raleigh, NC
Ron Adams, Environmental Remediation and Financial Services LLC, Ponte Vedra, FL

Pay-for-Performance Contracting and Implementation of Embedded Technology Strategies
Matthew Burklew, Shaw Group, Clermont, FL

Advances in Attaining Closure Levels at Pay-for-Performance UST sites utilizing Solid Oxidizers
Richard S. Werner, Environmental Consulting, Inc. (ECI), Norristown, PA
John Tregidgo, Environmental Remediation and Financial Services, LLC (ERFS), Sea Girt, NJ

On Site Configuration via Instrumentation to Deliver Pay-for-Performance Technologies
Ron Adams, P.E., Environmental Remediation and Financial Services, LLC, Ponte Vedra, FL
John Tregidgo, Environmental Remediation and Financial Services, LLC, Sea Girt, NJ

Pay-for-Performance Use of Third Generation Insitu Chemical Remediation as a Replacement for Obsolete, Best Effort / Well Based Fenton's Oxidation

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In the early 1990's, the insitu use of Fenton's Reagent dispensed through a well, became a popular remediation alternative to exsitu systems, such as pump and treat. Early first generation systems were crude, simple, and limited in scope and effectiveness in treating ground water with almost no effect on soil.

Second Generation systems began to appear in 1994. These variations used similar attributes of the basic First Generation concept. Attempted improvements included adding pressure, vacuum assistance, changes in chemistry, specialized injection wells and others to remove organic contamination from ground water and soil. Each field application design change lead to both an improvement as well as a new draw back. For example, pressurization can lead to plume migration; chemistry changes are moot without transport mechanisms; and any use of wells is limited by basic physics.

In 1998, the On-Contact Remediation Process® (OCRP) Model was designed to be the Third Generation of Insitu Chemical Remediation. The innovation is not an actual singular process, but a method to build a set of rules to interconnect physical, chemical and later biological technologies into a unified site specific, coordinated system. Under standard industry practices, these technologies would normally have been deployed as standalone systems and prone to significant deficiencies or failure.

The OCRP methodology has been used commercially for over six years utilizing 13 physical devices with 109 different chemical and biological series on a large number of full scale projects with a 100% success rate. Remediation projects either: 1) Complete as planned; 2) Complete with technology substitutions (usually with no additional remediation cost); 3) By a transition to a closing task, such as Managed Natural Attenuation; or 4) reach closure through risk analysis or by additional treatment of cubic volumes not within the original scope of work.

The presentation will concentrate on the second path to project completion, technology substitutions using many interconnected physical technologies including Propagations SM, ConductivPlanz SM, and Programmable Release Processors (PRPs) SM, Laterals SM and SIPs SM with many types of chemicals and biological field changes.

The efficiency of the Model combined with the Economic Model from last year's presentation (Application Theory & Practice of Pay-for-Performance Remediation) will be compared against Fenton-in-a-Well procedures to illustrate the limited applicability of this common but now limited remediation method.

Pay-for-Performance In-situ Chemical Remediation – A Consultant and Client Perspective

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In-situ chemical oxidation is a remedial technology that can provide distinct technological advantages, including the ability to directly address source areas, minimize site disturbances, minimize off-site disposal liabilities, limit worker exposure to site impacts during remedial action, and expedite site closure.

Increasingly, industrial and government clients are requesting or demanding firm, fixed-price remedial solutions. Accordingly, as the in-situ chemical oxidation remedial market has matured, some vendors have offered firm, fixed price, or pay-for-performance, contracting mechanisms to meet the rising market demand.

Such contract mechanisms can provide several advantages to clients. This presentation will present case studies for two projects for which pay-for-performance in-situ chemical oxidation with Fenton’s Reagent was conducted.

One site is a ground service equipment (GSE) maintenance facility, located at an international airport in upstate New York. Soil and groundwater in a portion of the GSE maintenance facility had been affected by volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) derived from petroleum-based solvents. Concentrations of individual VOCs and SVOCs exceeded applicable state standards and guidance values. Based on the nature, extent, and air-side location of the contamination, in-situ chemical oxidation with Fenton’s Reagent was selected as the remedial approach. Proposals were received from four vendors. One vendor proposed a pay-for-performance contract mechanism that was between approximately 60 and 200 percent of the cost of proposals from vendors that priced a single round of in-situ chemical oxidation with no performance metric. The client selected the pay-for-performance approach and after three rounds of oxidant injection, the site was closed.

The second site is an active painting supply store and warehouse located in Tidewater Virginia at which gasoline compounds, primarily benzene, were present in groundwater in excess of state standards. At this site, more than 10 rounds of oxidant injection have been conducted under a pay-for-performance agreement. Despite this extraordinary effort, gasoline compounds, while significantly decreasing in concentration, persisted at concentrations in excess of state groundwater standards. As such, the conceptual site model has been revised and an additional potential secondary source area under the building identified. The pay-for-performance agreement has been modified to include treatment of this area and concentrations of gasoline compounds continue to decrease. Site closure is expected through the revised pay-for-performance agreement.

Pay-for-Performance Site Management utilizing BioAug with On-contact Remediation Model

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Conventional remediation technologies, such as pump and treat and soil vapor extraction, sparging, etc., rely on mass transfer mechanisms to reduce contaminant concentrations. While contaminant levels can be reduced using these methods, contaminant rebound, due to mass transfer limitations associated with conventional remediation technologies, yields asymptotic constituent concentrations that often precludes achieving site closure. Furthermore, continued use of conventional technologies over a prolonged period will not overcome these limitations Therefore, reducing contaminant concentrations to levels that achieves site closure is the most significant challenge at most sites.

The On-Contact^{SM} Remediation Model is predicated on fact that a single remediation technology will not, in most cases, result in obtaining site closure. Therefore, to reach site closure, an integrated treatment approach is used to overcome such limitations. This involves the application of various chemical and biological treatment conditioners and reagents that are proven to be effective for treatment of a specific constituent. To be effective, the *in-situ* treatment must be directed to those areas where the contamination exists. This can be accomplished using ERFS' ConductivPlanz^{SM} technology to increase the subsurface permeability so that reagents can be delivered to the specific areas where contamination exists. This technology involves the installation of a permeable lens that radiates laterally such that treatment reagents can be directly applied to a targeted treatment area.

In all On-Contact^{SM} Process designs, the subsurface in the targeted treatment area is prepared for high efficiency mass removal or contaminant degradation. Desorbing and liberating contaminant mass within the treatment area soils is the first step in most *in-situ* treatments to address rebound effects. Contaminants are desorbed from subsurface soils using conditioning chemicals, blended on a site-specific basis, and applied prior to the application of chemical or biological remediation reagents within the influence of the ConductivPlanz^{SM}.

Bioaugmentation has emerged as one of the most effective techniques for performing *in-situ* treatment of chlorinated solvent and petroleum contaminated saturated soils and groundwater in a safe and economical manner. In some cases, bioaugmentation is used as the final “polishing” treatment intended to reduce contaminant concentrations to achieve site closure. The technology involves the injection of inoculum, nutrients, and other aquifer conditioning media into the subsurface to establish a bioactive treatment zone. BioAug LLC maintains a mixed consortium inoculum containing *Dehalococcoides Ethenogenes (DHE)* microbes for the dechlorinate PCE, TCE, and their breakdown products to ethene, and BC3 inoculum for treatment of petroleum constituents.

Pay-for-Performance Contracting and Implementation of Embedded Technology Strategies

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Risk based cleanup goals can serve the dual purpose of protecting the environment and reducing environmental liability for site owners. Analysis of contaminant fate and transport and possible receptor exposures can lead to cleanup goals that are two or more orders of magnitude higher than listed cleanup levels. Higher cleanup goals, coupled with in-situ remediation methods that are applied in their proper sequence can result in the most cost-effective approach to removing environmental liability.

This paper will provide an overview of risk-based cleanup goal estimating techniques and their relative applicability under differing conditions. The paper will also review several sequential in-situ remediation methods, including ISCO and bio-stimulation as means to achieve these goals quickly and cost-effectively. Two case studies will be presented where these techniques were employed.

Advances in Attaining Closure Levels at Pay-for-Performance UST Sites Utilizing Solid Oxidizers.

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Several manufacturers are offering new formulations of solid oxidizers for use in in-situ ground water treatment. Products include calcium peroxide, sodium percarbonate, magnesium peroxide and two stage blends of oxidizers with catalytic compounds. The materials are packaged mostly in powered forms requiring hydration during field application. Each manufacturer claims a higher performance in application than either Fenton's Reagent or oxygen generation in the subsurface. The concept is to have a higher degree of control of chemistry in the subsurface, low cost and less material handling. Injection instructions assume well based application.

In an effort to use solid oxidizers to close UST sites faster, Environmental Remediation and Financial Services, LLC (ERFS), implemented use these products at three sites with low levels of BTEX and MTBE preventing closure from previous remediation methods. The treatments used On-Contact® physical methods (Propagations℠ and ConductivPlanz℠) and well based application in separate areas of sites. The manufacturer instructions were used in some instances and ERFS provided alterative mixtures and materials for comparison. The results were surprising and not the expected conclusion.

Data indicated the efficiency of contaminant reduction was mostly associated with the efficiency of the subsurface injection system and was limited in well based application. In all of the test sites, considering cost, time and performance, no oxidizer performed in any significantly higher manner than the others in field application. The controlling factors in the success of the remediation at these sites were the physical in-situ application design and methods for field modifying the compounds as needed during injections.

On Site Configuration via Instrumentation to Deliver Pay-for-Performance Technologies

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Technologies have developed to gain greater accuracy and faster processing for delineating sites. The focus has been on contaminant mass and location. Currently, ERFS has been using the On-Contact Remediation Process® Technical Model for six years with real-time monitoring of process components as they are used. These real-time processes are critical in technology substitutions in the field that support a Pay-for-Performance site contract. A new area is emerging in delineation, real-time testing to identify interferences in technology application and data indicators of sources outside the treatment zone.

Three sites will presented that had non-delineated interferences, how they where detected and field adjustments made, under a Pay-for-Performance contract.

Perchlorate

Perchlorate: Overview of Perchlorate Properties, Sources, & Chemistry.
William Ingersoll, Navy Sea Systems Command (NAVSEA), Goose Creek, SC

Analytical Methodologies for the Detection of Perchlorate
William (Ed) Corl, Naval Facilities Engineering Command (NAVFAC), Atlantic Division, Norfolk, Virginia

The Determination of Perchlorate Anion in High Total Dissolved Solids Water Using LC/MS/MS
Jim Krol, Senior Applications Chemist, Waters Corp, Milford, MA

Overview of In Situ and Ex Situ Bioremediation of Perchlorate in Groundwater
Paul B. Hatzinger, Shaw Environmental, Inc., Lawrenceville, NJ
A. Paul Togna, Ph.D., Shaw Environmental, Inc., Lawrenceville, NJ
Jay Diebold. P.E., Shaw Environmental, Inc., Peuwaukee, WI
William J. Guarini, Shaw Environmental, Inc., Lawrenceville, NJ

Update of Remedial Technologies for Perchlorate-Impacted Sites
Harry Van Den Berg, P.E., ENSR International, Camarillo, CA
Kent Baugh, Ph.D., P.E., ENSR International, Alameda, CA

Perchlorate: Overview of Perchlorate Properties, Sources, & Chemistry

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There has been an increased concern regarding perchlorate in the environment. Perchlorate was added to the EPA's Unregulated Contaminant Monitoring Rule (UCMR) list in 1999. While it is known that perchlorate can inhibit the uptake of iodide by the thyroid gland the potential acute and chronic health effects of perchlorate are still under considerable debate. The EPA has established a draft reference dose (RfD) for perchlorate and several states have already established action levels for perchlorate source waters.

Perchlorate is primarily used as an oxidant in solid rocket fuels and it is widely believed that its presence in the environment is largely due to these sources. However, naturally occurring perchlorate has been detected in Chilean caliches and is suspected to be present in certain regions of the United States. It has been detected in ground water, surface water, soils, and plants. Perchlorate is a stable, water-soluble compound with unique physico-chemical properties that make it a challenge both for detection and in treatment. This presentation will provide an introduction to perchlorate, it's sources, properties, and chemistry.

Analytical Methodologies for the Detection of Perchlorate

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In March of 1997 the California Sanitation and Radiation laboratory developed a new method for detecting perchlorate in water samples using ion chromatography (IC) coupled with conductivity detection. The resulting detection limit of the new method increased the sensitivity of perchlorate detection from 250 ug/L to approximately 4 ug/L. The EPA promulgated method 314 in 1999 following the addition of perchlorate to the Unregulated Contaminant List. Currently, EPA method 314 is the only approved method for the detection of perchlorate in drinking water. The EPA has suggested a RfD equivalent concentration of 1 ppb and some states have already listed provisional action levels for perchlorate ranging from 1 to 18 ppb. Therefore, the currently approved method may not meet data quality objectives for some studies. In addition, because conductivity detection is non-specific, method 314 has the potential to produce false positives/negatives as well. Because of the limitations of EPA Method 314 in both sensitivity and specificity there has been an increased effort within the analytical community to explore other analytical procedures for analyzing media other than drinking water using more powerful methods such as mass spectrometry. This paper provides an overview of EPA perchlorate method 314, including case-study examples of its limitations. The presentation will also provide a general summary of other techniques currently being evaluated as well.

The Determination of Perchlorate Anion in High Total Dissolved Solids Water Using LC/MS/MS

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Using the EPA Information Collection Rule as a data base, drinking water facilities have been reporting higher than anticipated concentrations of perchlorate anion in environmental waters in 22 states. This is a cause for concern because of potential adverse health effects that can occur at low ppb concentrations (µg/L), including interference with iodine thyroid uptake, fetal nervous system development, and a potential carcinogen. Due to its toxicity, perchlorate has an action limit of 4 ppb in Texas and California drinking water. EPA may propose a 1 ppb action limit. DoD and DoE are also interested in prechlorate, an ingredient in many munitions, from a soil contamination perspective.

The current EPA method 314.0 (Determination of Perchlorate Using Ion Chromatography…) uses anion exchange chromatography with suppressed conductivity detection. This method works well but becomes limiting as the total dissolved solids concentration increases, especially sulfate. Sample preparation to remove chloride and sulfate is necessary and the most difficult problem; requires the use of a O^{18} perchlorate internal standard to account for recovery.

This presentation will describe an LC/MS/MS method for perchlorate without the requirement for sample preparation. The key to solution is the chromatography of perchlorate relative to sulfate. As organic modifier concentration increases, perchlorate elutes faster than sulfate allowing the chromatographer to place perchlorate baseline separated between high chloride and high sulfate. With the direct injection of 100 µL of a solution containing 1000 ppm each of bicarbonate, chloride, and sulfate, MS/MS detection can obtain a perchlorate detection limit (3:1 S/N) of 0.2 ppb. Larger injection volumes can be used to increase sensitivity.

Overview of In Situ and Ex Situ Bioremediation of Perchlorate in Groundwater

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Bioremediation represents one of the most effective and economical approaches for treating perchlorate in groundwater. This presentation will describe current data from both *ex situ* and *in situ* biological treatment systems for perchlorate. Laboratory and pilot-scale tests have been performed by several groups to evaluate the efficiency of different biological reactor designs for the ex situ treatment of perchlorate in groundwater. These tests have revealed that fluidized bed reactors (FBRs) and packed bed reactors (PBRs) can provide effective treatment of the oxidant. Three full-scale FBR systems are presently in operation, and additional systems are under construction. These FBRs are currently treating more than 5 million gallons of groundwater per day from influent perchlorate concentrations ranging from 2 to 35 mg/L to effluent concentrations of less than 4 µg/L. The data from both pilot and full-scale bioreactor systems will be presented. In *situ* biological treatment has shown great promise in laboratory studies and field demonstrations. Laboratory studies have revealed that perchlorate-reducing bacteria are naturally occurring in many environments, including groundwater aquifers, and that these bacteria can be stimulated to biodegrade perchlorate to below current regulatory levels with the addition of a variety of organic substrates, including lactate, acetate, and ethanol. Subsequent field demonstrations have verified the potential for *in situ* treatment. Data from a recently completed field project at a US Navy facility in Maryland will be presented along with the design and progress of ongoing field projects at sites in California and Texas. The presentation will provide an overview of the most current biological approaches for remediation of perchlorate in groundwater.

Update of Remedial Technologies for Perchlorate-Impacted Sites

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Perchlorate salts, such as ammonium, sodium and potassium perchlorate are widely used as a strong oxidizer in various industries and consumer products (e.g., road flares). Dissolution of perchlorate salts yields the perchlorate anion, which is highly stable and mobile in surface and groundwater systems. Due to its mobility and stability in an aqueous solution, perchlorate impacts in groundwater can be found at large distances from their source. The inhibitory effect of perchlorate on the uptake of iodide by the thyroid gland combined with improvements in analytical detection methods since 1997 have prompted the regulatory community to propose increasingly stringent action levels as low as 1 microgram per liter (µg/L) in some states.

Although perchlorate is a powerful oxidizer when used in solid form, e.g. ammonium perchlorate in solid rocket fuel, it resists abiotic reduction by strong reducing agents when dissolved in water due to unfavorable reaction kinetics. However, perchlorate can be degraded via biologically mediated reduction and it can be removed from groundwater via membrane processes or sorption onto positively charged media. Several in-situ and ex-situ perchlorate treatment technologies have been developed or are currently under development that are typically based on either biological reduction, which destroys perchlorate, or sorption processes (anion exchange) where perchlorate is removed from the water-phase. Similar to other contaminants, the applicability, effectiveness and cost of these technologies are highly dependent upon site specific conditions, such as hydrogeology, geochemistry, depth to groundwater, perchlorate distribution and the presence of other contaminants.

This paper provides an update of the criteria affecting the selection process and of innovative and established perchlorate treatment technologies and their typical applicability, development status, advantages and limitations, as well as a presentation of relative cost. Innovative technologies that will be highlighted include in-situ bioremediation and the emergence of biological permeable barrier technology for addressing perchlorate. Design and performance criteria of the more proven technologies, such as in-situ and ex-situ bioremediation and selective anion exchange, will be discussed based on actual test and/or operating data. In addition, hands-on operational experience with full-scale ex-situ treatment systems for water impacted by perchlorate and other contaminants will also be discussed.

The selection of currently available ex-situ treatment technologies for perchlorate-impacted water depends mainly on the concentration of perchlorate and, if present, other contaminants. A cost comparison chart based on the authors' experience with perchlorate treatment, encompassing field demonstrations and full-scale systems, will be presented that can be used as a general guide for the selection of ex-situ treatment technologies.

Pesticides

Pesticide and VOC Attenuation at Marzone Superfund Site

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A Novel Method to Attain Groundwater Compliance at a Former Pesticide Formulating Facility

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Pesticide and VOC Attenuation at Marzone Superfund Site

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The selected groundwater remedy for the Marzone Superfund Site was an in-situ, funnel-and-gate system. The system was installed in 1998 and is currently operating to remove the constituents of concern (COCs) from groundwater. Groundwater COCs include α-BHC, β-BHC, γ-BHC, DDD, DDT, methyl parathion, ethylbenzene, and xylenes. Impacted groundwater is collected in the collection channel, conveyed via underground piping to two of the three activated carbon adsorption reactors operated in series. The treated groundwater is then conveyed via underground piping through the soil-bentonite slurry wall and to the distribution channel. Prior to start-up, the projected life of the primary carbon reactor was approximately six months. The system has operated for more than 64 months without a carbon change-out. In July 2003, a dedicated, discrete sampling device was installed within the activated carbon bed of the primary reactor to collect depth-specific groundwater samples and vertically profile the dissolved-phase constituents within the primary reactor. Samples collected from the discrete sampling device indicated nondetectable pesticide concentrations and only nominal and/or nondetectable VOC concentrations. The analytical results suggest that contaminants were being removed from groundwater within the initial two foot of the carbon bed. Preliminary depth-specific microbial studies within the carbon bed have provided results that do not correlate with contaminant distribution. A more detailed investigation is being conducted to evaluate the potential mechanisms for pesticide and VOC attenuation within the primary reactor. The primary reactor provides a unique opportunity to study the natural attenuation processes that are likely contributing to the decreasing dissolved-phase contaminant concentrations observed across the Site.

A Novel Method to Attain Groundwater Compliance at a Former Pesticide Formulating Facility

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Natural attenuation (NA) has become an integral element of site closure in the U.S. While NA of many compounds can be demonstrated unambiguously, it is more complex for purportedly recalcitrant compounds with multiple isomers and low remedial criteria. Such was the situation at a site in Orlando, Florida, where technical grade lindane had been formulated for ~20 years. This product often contains α-BHC (60-70%), β-BHC (5-12%), γ-BHC (10-15%), δ-BHC (6-10%) each of which is regulated at very low (ng/l) concentrations. At the site it was necessary to evaluate natural attenuation for each isomer following a removal action to meet regulatory standards in groundwater. This analysis was complicated by the rapid groundwater velocities (1 foot/day) and water table oscillations (± 1.5m), that were inversely correlated with groundwater BHC concentrations (i.e., higher water table = lower BHC concentrations). However, when BHCs were evaluated on a total mass basis, a clear decline (10% per year) over seven years was apparent ($r^2 = 0.84$) following first-order kinetics. Over this period, the plume center of mass did not migrate in the direction of groundwater flow, remaining within 30 m of its centroid, compared to contemporaneous rapid transit across the site of an MTBE plume originating upgradient. The plume stability in conjunction with the decreasing BHC mass allowed the U.S. EPA and Florida DEP to accept that no further action was necessary to protect potential downgradient receptors. This site represents a novel approach to attaining compliance that would be appropriate for others with similar quasi-recalcitrant compounds.

Phytoremediation

Relation among Subspecies of Cucurbita in Phyto-extraction of Field-weathered *p,p'*-DDE and Exudation of Citric Acid from Roots
Martin P.N. Gent, Connecticut Agricultural Experiment Station (CAES), New Haven CT
Zakia Parrish, Connecticut Agricultural Experiment Station (CAES), New Haven CT
Jason C. White, Connecticut Agricultural Experiment Station (CAES), New Haven CT

Uptake of Polycyclic Aromatic Hydrocarbons in Spartina Alterniflora – Evaluating Risk in Salt Marsh Vegetation
Alison W. Watts, University of New Hampshire, Durham, NH
Thomas P. Ballestero, University of New Hampshire, Durham, NH
Kevin H. Gardner, University of New Hampshire, Durham, NH

Phytoremediation of Lead Contaminated Soils in the Urban Residential Environment using Seed Mustard
Ilana S. Goldowitz, Cornell University, Ithaca NY
Joshua Goldowitz, Rochester Institute of Technology, Rochester NY

Rhizodegradation of RDX Contaminated Soils Using Grass Exudates
Afrachanna D. Butler, Jackson State University, Vicksburg, MS
Victor F. Medina, U.S. Army Corps of Engineers-Engineer Research & Development Center, Vicksburg, MS

Plant Assisted Bioremediation of Pollutants from Aquaculture Water
Kishore K. Krishnani, Stevens Institute of Technology, Hoboken, NJ
Xioaguang Meng, Stevens Institute of Technology, Hoboken, NJ

Phytoremediation Applications for Arsenic in Northern Climates
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Can We Predict the Best Plants for the Phytoremediation of Organic Contaminants?
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Relation among Subspecies of Cucurbita in Phyto-extraction of Field-weathered *p,p'*-DDE and Exudation of Citric Acid from Roots

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Field experiments have shown that two subspecies of *Cucurbita pepo* (summer squash) differ in phyto-extraction of field-weathered *p,p'*-DDE. Three cultivars were selected from each of the subspecies; *Cucurbita pepo* ssp *pepo* (zucchini) with a greater ability to take up DDE, and *Cucurbita pepo* ssp ovifera (summer squash) with a lesser ability to take up DDE. When grown in the field, subspecies *pepo* phyto-extracted about 1.0% of the *p,p'*-DDE, while subspecies *ovifera* removed less than 0.2% of the contaminant. To evaluate whether exudation of organic acids from the roots was involved in uptake of weathered DDE, these cultivars were grown under hydroponic conditions. Phosphorus nutrition played a significant role in exudation of organic acids into the hydroponics solution. For both subspecies, the better the phosphorus nutrition, the more tartaric and less citric acid was exuded. However, subspecies *pepo* showed a greater increase in citric acid exuded under phosphorus depletion than *ovifera*. This was the only response to phosphorus depletion that differed among subspecies. Thus, in a comparison among subspecies of *Cucurbita pepo*, the response to phosphorus depletion of exudation of citric acid was related to the ability to accumulate a higher concentration weathered organic contaminants in soil when grown in the field.

Uptake of Polycyclic Aromatic Hydrocarbons in Spartina Alterniflora – Evaluating Risk in Salt Marsh Vegetation

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Polycyclic Aromatic Hydrocarbons (PAHs) are present in many coastal and salt marsh sediments. Sources include oil spills, urban runoff, and coal gasification byproducts. Plants affect the movement of PAHs in several ways; they may inhibit erosion, enhance microbial degradation, or translocate compounds. Plant translocation can move a compound from the soil or water into the plant. The compound is then either stored in plant tissue, or degraded by microbial or metabolic processes, or excreted into the atmosphere. Contaminants stored in plant tissue may present a risk to the ecological community.

In this study, uptake of PAHs was measured in Spartina alterniflora, a common salt marsh plant. For three months Spartina alterniflora was grown outdoors in PAH-contaminated soil and in clean control soil. The PAH contaminated sediment was collected from an estuary near a former coal gasification plant, and contained an average of 200 ug/g total PAHs. Plant samples were also collected from a PAH-contaminated estuarine marsh and from an uncontaminated reference site. Plants grown in uncontaminated soil produced more flowers, and were taller, but plants grown in contaminated soil had more shoots, yielding a shorter, bushier morphology. The total above-ground biomass at the end of the growing season was similar in the controls and PAH-grown plants.

The harvested samples were separated into leaf and root material and analyzed for individual PAH compounds. Most of the samples were analyzed using a GC/MS/MS system with a chromatoprobe direct-sample-injection device. Small pieces of plant tissue can be analyzed directly by this method, allowing rapid evaluation of individual leaves or roots. However, the detection limit is higher than traditional extraction-injection methods due to the small sample size and co-elution of some plant-derived compounds.

PAHs were detected in both root and leaf tissue. Concentrations in root tissue were approximately an order of magnitude higher than leaf tissue, and plant concentration increased as soil concentration increased. PAH concentrations in plant tissue will be compared to ecological risk levels such as the NOAA ERM/ERLs, and potential ecological risks will be evaluated.

Phytoremediation of Lead Contaminated Soils in the Urban Residential Environment using Seed Mustard

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Lead contamination in the urban environment is a continuing serious public health concern. Historically lead entered the urban residential area though paint pigment and gasoline additives. This legacy persists as the two most important lead sources that affect children in the urban environment: contaminated paint residue and contaminated soil. One technique for remediation of lead in urban soils is phytoremediation.. Previous research has shown *Brassica juncea* (mustard) to be the most promising phytoremediator of lead in soil. Researchers commonly use Southern Giant Curly Leaf Mustard because it is a hyperaccumulator of lead, has extremely high production of mustard green biomass in a short (45 day) growing season, and is adaptable to poor soil conditions. The authors believe that use of this variety in the urban environment may be problematic. The greens are favored as a food, are easily recognized, and may be pilfered and eaten. This research tested the hypothesis that seed mustard, which produces abundant flowers but few greens, would be more suitable. Two $60m^2$ plots were prepared in a Greater Rochester Urban Bounty garden, located at a busy intersection in Rochester New York's impoverished northeast neighborhood. One plot was sown thickly with Southern Giant, and the other with seed mustard. As the plants approached maturity the entire crop of Southern Giant mustard was pilfered, but the seed mustard remained untouched. At maturity the seed mustard produced 550g dry biomass per m^2. Assuming similar maximum lead uptake among mustard varieties, this would yield a lead uptake rate of up to 5 g/m^2. The research also included a germination study. Five standard seed germination tests (400 seeds each) performed in increasingly concentrated lead contaminated soils indicated little variation in germination rate. Thus seed mustard is more suitable for phytoremediation of lead in the urban residential environment.

Rhizodegradation of RDX Contaminated Soils Using Grass Exudates

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Phytoremediation uses living plants for in situ and ex situ remediation of contaminated soil, sludges, sediments and ground water, and is a promising biotechnology for cleanup of contaminated sites. Some advantages of phytoremediation are low-cost, works well at low-risk sites, and may operate with limited maintenance for decades. Disadvantages of this technology are that it may require large expense for relocating operations, buildings, and roads at operating bases and there may be slow plant establishment that may limit the application.

Phytoremediation encompasses a range of processes, which includes rhizodegradation. Rhizodegradation is the breakdown of contaminants in the soil through microbial activity that is enhanced by the presence of the rhizosphere. Our study focuses on RDX, a widely used military explosive. It has been indicated in other phytoremediation studies that RDX degradation inside the plant is slow and possibly incomplete. At the same time, phytoremediation, if effective, could be a useful approach at active firing ranges. This research investigates whether rhizodegradation can be used to degrade RDX contaminated soils. In rhizodegradation, natural substances called plant exudates are released by the plants' roots. These exudates contain organic carbon that act as nutrient sources for soil microorganisms. In our study, wild grasses will be grown hydroponically so that the grass exudates are released from the roots into the water. Those grass exudates will be applied to RDX contaminated soils and RDX degradation will be monitored. Changes in microbial activity will also be studied. As a result, we hope to find that the release of the soluble organic matter from the roots of the grasses stimulate RDX degradation.

Plant Assisted Bioremediation of Pollutants from Aquaculture Water

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Brackishwater aquaculture is the fastest growing food sector, especially shrimp farming which has emerged as a main source of employment and income for hundreds of thousands of people. However, agricultural, industrial and sewage wastes can contaminate aquatic ecosystem through the discharge containing nitrogenous toxicants, pesticides and heavy metals and can affect the aquaculture profitability in certain areas. Most of the previous works highlight the use of commercially activated carbons and ion exchange resins, which are relatively expensive and less feasible to use in developing countries. Furthermore, activated carbon loaded with toxicants is generally incinerated or disposed off on land, thereby causing environmental pollution through different routes. An emerging field of interests is employing certain plants which possess the natural ability to uptake heavy metals for the remediation of environment. In addition, plants release exudates and enzymes that stimulate microbial activity and biochemical transformation, which subsequently increase the biodegradation and biosorption potential. This process is often referred to as plant assisted bioremediation. Development of new economically feasible eco-friendly products from natural plants / agricultural wastes is the objective of my continued research in Central Institute of Brackishwater Aquaculture, Chennai, India. In this direction, attempts have been made to develop products for the decontamination of toxicants in the laboratory condition. Further work is in progress to explore the possibility of the use of these plant products for the remediation of shrimp farm culture water in the ponds / wastewater in the water reuse system. Natural plant products are biodegradable and cause no harm to the environment. Hence the natural plant products may offer a selective, harmonious and eco-friendly approach to remove nitrogenous toxicants and successful studies on this material could be beneficial for shrimp farm wastewater treatment.

Phytoremediation Applications for Arsenic in Northern Climates

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More than 70% of the United States arsenic consumption, representing approximately 37 million pounds of arsenic per year, is used to produce chromated copper arsenate (CCA), a wood preservative. Weathered lumber in decks, docks, playground equipment and garden construction can leach significant amounts of arsenic into soil and water, where it poses health risks to humans and animals. In addition to CCA sources, arsenic was used extensively as a component of many pesticides used in agriculture. Phytoremediation techniques using an arsenic-hyperaccumulating fern (*Pteris vittata*) has been developed as a cost-effective remediation alternative for soils containing elevated arsenic concentrations. One of the key factors in phytoremediation of arsenic is achieving sufficient biomass production by the fern crop to result in significant arsenic removal rates. *Pteris vittata*, a subtropical species that is perennial in Zones 9 and higher, has been effectively used as a summer annual in northern climates for phytoremediation. However, increased costs from annual replanting combined with reductions in biomass yields with shorter growing seasons reduces the cost-effectiveness at some sites.

Recently, several cold-hardy species in the Pteris genus have been identified that also hyperaccumulate arsenic. Expanding the perennial climate range will provide significant improvements in phytoremediation performance. Growth chamber and field studies were conducted to evaluate the potential performance of these plants with existing arsenic hyperaccumulators for both biomass yield and arsenic uptake. Additonal cultural practices designed to extend the growing season were also investigated. The anticipated result of this research is an improved phytoremediation approach that is applicable to many of the arsenic-contaminated soils in northern climates. The results of these and other studies will be presented.

Can We Predict the Best Plants for the Phytoremediation of Organic Contaminants?

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There is a continuing interest in the clean-up of contaminated sites by biological means, because of the improvements in sustainability that they offer. One potential tool in this strategy is phytoremediation. To date there have been a number of studies which have indicated that certain plant orders have the ability to accumulate heavy metals. In one study three orders; the Malpighales, Brassicales and Asterales were found to contain c.85% of the hyperaccumulating taxa. These taxonomic approaches can provide important information when choosing appropriate plant species for a given contaminant and ecological situation. Furthermore such approaches will become more useful as plant classification becomes more informed by genetic information, as this is more likely to provide information on a species' ability to produce enzymes or chelators which may be important in metal accumulation or organic pollutant degradation. The paper will present our initial findings when using phylogentic screening approaches for those plants which may be beneficial for the phytoremediation of organic pollutants.

Regulatory

Is "Presumptive Certainty" Generating Usable Data for Risk Assessment under the Massachusetts Contingency Plan (MCP)?

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New Jersey's Pursuit of Natural Resource Damages – Is Your State Next?

Douglas R. Beal, BEM Systems, Inc., Chatham, NJ
Anita O'Connor, BEM Systems, Inc., Chatham, NJ

Risk Based Corrective Action in Florida

Kathryn S. Salvador, Florida Power & Light Company, Juno Beach, FL

Comprehensive Human Health Risk Assessment Shortforms, SF 2004, Developed by the Massachusetts Department of Environmental Protection: Efficiency, Consistency, and Transparency

Andrew S. Friedmann, Massachusetts Department of Environmental Protection, Boston, MA

How Interstate Collaboration Can Improve Site Cleanups: Triad and the ITRC

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Is "Presumptive Certainty" Generating Usable Data for Risk Assessment under the Massachusetts Contingency Plan (MCP)?

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On August 1, 2003, MADEP finalized a Compendium of Analytical Methods (CAM) recommended to provide “presumptive certainty” for environmental data used to support MCP decisions in submittals made by the Licensed Site Professional (LSP). As the guidelines are now over one year old, this paper offers specific examples of the usability of presumptively certain data for risk-based decisions. Using a comparative approach and based on case studies, we discuss several key measures of data quality incorporated into the CAM *vs.* the needs of human health and ecological risk assessors. Specifically, we compare/contrast CAM and risk requirements for comparability of methods and analyte lists, sensitivity (reporting limit requirements), accuracy (method and matrix-based), precision, and representativeness. We offer recommendations on planning and interpretation of data under the MCP CAM to enhance the generation of data that will be considered usable based on risk assessment regulatory guidance.

New Jersey's Pursuit of Natural Resource Damages – Is Your State Next?

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The topic of this paper is the national implication and precedent of New Jersey's new program to expand Natural Resource Damages (NRD) actions. As of November 2003, New Jersey has settled over $42 million in NRD settlements from a limited number of cases and has publicly announced its intent to expand this successful program by pursuing another 4,000 cases within the state. This precedent has significant financial consequences for national firms, such as a manufacturing companies with multiple facilities and insurance carriers, as other trustees and states are considering pursuing NRD claims, following New Jersey's model.

States such as New Jersey, have been delegated powers by federal authorities, to create and enforce environmental laws. Other states and trustees with similar delegated powers are following New Jersey's lead by seeking their own NRD claims. Compensation for NRD is authorized under several statutes, the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) and the Oil Pollution Act of 1990 (OPA). CERCLA and OPA, allow the governor of each state to designate state officials who may act on behalf of the public as state trustees for natural resources.

Earlier this year, the Yakama Nation (a federal trustee group) brought the first NRD suit against a Department of Energy nuclear facility, the Hanford Nuclear Reservation in eastern Washington. The NRD liability may be as high as $50 billion dollars. The case is expected to raise new issues for addressing NRD for radionuclides as well as tribal NRD claims.
Two new cases are being pursued by a state trustee. Recently, the Burlington Northern and Santa Fe Railway Company (BNSF) agreed to pay $450,000 to the New Mexico Office of the Natural Resources Trustee and the United States Fish and Wildlife Service to plan, acquire and enhance additional wetlands to compensate for damage to natural resources at Santa Fe Lake. New Mexico is also pursuing NRD claims against General Electric over groundwater contamination at the South Valley Superfund site near Albuquerque, New Mexico.

Risk Based Corrective Action in Florida

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The state of Florida Department of Environmental Protection (FDEP) currently has three clean-up programs for which risk based corrective action is available, including the petroleum, dry cleaner, and brownfields programs. After years of debate among the potential stakeholders, Florida's "Global RBCA" bill passed during the 2003 legislative session. This will result in a new state rule that will give responsible parties the ability to apply risk-based corrective action principles to all contaminated sites for which site rehabilitation is required.

The FDEP has recently published a draft rule entitled "Contaminated Site Cleanup Criteria," which provides the mechanisms for application of risk-based principles, and the specific requirements for achieving "No Further Action," either with or without controls, on a state-wide basis. This presentation provides an overview of the key provisions, as well as the specific risk principles that are outlined in the new Global RBCA rule. Specific emphasis is placed on the highly controversial issues surrounding the proposed rule, including the public notice provisions and the proposed application of additivity principles. The rule's projected strengths and pitfalls will also be discussed, with noted implications for the assessment and remediation of historical industrial sites, including former manufactured gas plants (MGPs).

Comprehensive Human Health Risk Assessment Shortforms, SF 2004, Developed by the Massachusetts Department of Environmental Protection: Efficiency, Consistency, and Transparency

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Exposure-specific human health risk assessments are often required in order to determine the level of remediation effort necessary at a site containing contaminated soil and water. The Office of Research and Standards (ORS) has developed comprehensive shortforms, SF 2004, that characterize risks to humans following exposure to up to 117 COPCs in soil. SF 2004 is a collection of self-contained, interconnected Excel spreadsheets that feature drop-down menus for the selection of Contaminants of Potential Concern (COPCs), full documentation for all exposure assumptions, and clear presentation of all mathematical equations used to calculate risks. These shortforms supersede the Residential Risk Assessment Shortform published in 1992. They supplement the Gasoline Release Shortform and the Updated # 2 Fuel/Diesel Shortform published in July of 2002, which include only petroleum-related chemicals. In addition to including an increased number of COPCs, SF 2004 assesses risks not just to residents, but also to construction workers, utility workers, trespassers, and recreational receptors. The objectives of SSF 2004 are to streamline the risk assessment process, increase consistency, enhance transparency, and improve the efficiency of the regulatory site review process.

How Interstate Collaboration Can Improve Site Cleanups: Triad and the ITRC

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The standard practice used by state and federal regulatory agencies that supervise the remediation of contaminated waste sites involves the development of a workplan that pre-defines a limited number of sampling locations, employs definitive laboratory-based analytical methods and evaluates results against pre-determined acceptance criteria. With this practice, the developers, project managers and the regulatory agencies often found insufficient data to support decision making. Follow-up sampling and analysis are needed to fill the data gap. This multi-stage investigative process for remedial action has been proven to be very expensive and time consuming. To overcome this problem, the USEPA has proposed a Triad approach that integrates systematic project planning, dynamic work strategies and on-site analysis for the project management. With this approach, several recent investigations have shown significant savings in time and costs, while providing more reliable scientific data for decision making. The Interstate Technology Regulatory Council (ITRC), a consortium of state agencies, partners with the federal government, the military, academia, industry and other interested parties seeks innovative solutions to improve the working efficiency. The ITRCs Sampling, Characterization and Monitoring (SCM) Team has completed a Technical and Regulatory Guidance summarizing the principles of the TRIAD approach and the scientific and technical requirements to employing this paradigm shift. In this presentation, the work of the ITRCs SCM team will be discussed. Several applications of this process that illustrate its advantages for hazardous site investigation and remediation will be highlighted.

Remediation I

Natural Attenuation of Acid Mine Drainage: Column Studies of Sulfate Reducing Bacteria
Mercedita Monserrate, University of Massachusetts, Amherst, MA
Sarina Ergas, University of Massachusetts, Amherst, MA

Full-Scale Phase 1 Results of ISTD Treatment at Former Alhambra, California Wood Treatment Site
John M. Bierschenk, TerraTherm, Inc., Fitchburg, MA
Ralph S. Baker, TerraTherm, Inc, Fitchburg, MA
Robert J. Bukowski, TerraTherm, Inc., Fitchburg, MA
Ken Parker, TerraTherm, Inc., Fitchburg, MA
Ron Young, TerraTherm, Inc., Fitchburg, MA
Jenny King, Southern California Edison Company, Rosemead, CA
Tony Landler, Southern California Edison Company, Rosemead, CA

Monitored Natural Attenuation (MNA) – Where it Works and Where it Doesn't Using Case-history Examples
Edward Van Doren, Shaw Environmental, Inc., Andover, MA
Olaf Westphalen, Shaw Environmental, Inc., Andover, MA

In Situ Thermal Destruction (ISTD) of MGP Waste in a Former Gasholder: Design and Operation
Ralph S. Baker, TerraTherm, Inc., Fitchburg, MA
John C. LaChance, TerraTherm, Inc., Fitchburg, MA
Mark W. Kresge, TerraTherm, Inc., Fitchburg, MA
James P. Galligan, TerraTherm, Inc., Fitchburg, MA
Myron Kuhlman, MK Tech Solutions, Houston, TX
Edward H. White Jr., National Grid USA, Westboro, MA

In Situ Thermal Remediation of NAPL Using Electrical Resistance Heating at an Active U.S. Army Installation
Pat Cossins, Thermal Remediation Services, Inc., Austin, TX
Greg Beyke, P.E., Thermal Remediation Services, Inc., Memphis, TN
Michael Dodson, Thermal Remediation Services, Inc., Longview, WA
David Fleming, Thermal Remediation Services, Inc., Snoqualmie, WA
Rich Wilson, Ft. Lewis Public Works, Ft. Lewis, WA,

Assessing the Performance of Thermal Conductive Heating for Remediation of Chlorinated VOCs in Saturated and Unsaturated Settings
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Ralph S. Baker, TerraTherm, Inc., Fitchburg, MA
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Remote Telemetry Board Performance

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Natural Attenuation of Acid Mine Drainage: Column Studies of Sulfate Reducing Bacteria

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Acid mine drainage (AMD) a complex contamination problem that occurs due to mining activities, can be naturally attenuated if the proper environmental conditions are present. Natural attenuation of acid mine drainage results in the decrease in concentration of contaminants through naturally occurring processes. Sulfate reducing bacteria are the key players in the natural attenuation in the field site of Davis Mine located in Rowe, Massachusetts, decreasing the amount of acidity and metal contamination present. Some of the characteristics needed for sulfate reduction include a large enough population of sulfate reducing bacteria and the proper substrate and environmental conditions for the bacteria to grow and multiply. Site characterization was done by collecting groundwater and microbial samples from the Davis mine site regularly for analysis. Chemical analysis of groundwater included anions, metals and organic carbon. Together with field measurements of temperature, pH oxidation reduction potential and conductivity, these measurements were used to describe the evolution of microbiology and the geochemistry in the Davis Mine site. Column studies were used to replicate the conditions in the Davis mine site and to provide a controlled environment for the analysis of the system. The central goal of this research was to understand the chemical, structural and microbial factors that control the speciation of sulfur and iron and provide perspectives on remediation processes by the analysis of the field data and column studies. The use of flow-through columns provided a very important link between the microbiological analyses and the field scale modeling. Tracer studies were performed to measure transport parameters using a non-sorbing tracer (potassium bromide). A one-dimensional conservative model was used to estimate a dispersion coefficient of 5.5E-7 m^2/sec and an apparent longitudinal dynamic dispersivity of 0.011m. Sulfate and sulfide concentrations analyzed together with pH and ORP values suggested sulfate reduction in columns and in the field, and thus the natural attenuation of the mine site.

Full-Scale Phase 1 Results of ISTD Treatment at Former Alhambra, California Wood Treatment Site

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At a wood treatment facility for utility poles that Southern California Edison (SCE) operated from 1921 to 1957, subsurface soils are contaminated primarily with polyaromatic hydrocarbons (PAHs), and dioxins and furans (PCDD/PCDF). Approx. 12,390m^3 (16,200 cubic yards) of predominantly silty soil requires treatment, to an average depth of 6 m (20 ft) and a maximum depth of 30 m (100 ft). The CA Department of Toxic Substances Control (DTSC) established soil treatment standards of 0.065 mg/kg benzo(a)pyrene [B(a)P] Equivalents and 1.0 μg/kg dioxin, expressed as 2,3,7,8-tetrachlorodibenzodioxin (TCDD) Toxic Equivalents (TEQ). A feasibility study led to the selection of TerraTherm's patented In-Situ Thermal Destruction (ISTD) technology, which utilizes simultaneous application of Thermal Conduction Heating (TCH) and vacuum to treat contaminated soil without excavation. The applied heat volatilizes organic contaminants within the soil, enabling them to be carried in the vapor stream toward heater-vacuum wells. Because vapors are drawn through superheated (500-700°C) soil in proximity to the heater-vacuum wells, most of the contaminant mass present in the subsurface is destroyed in situ, as evidenced by 11 completed ISTD/TCH projects. Contaminants not destroyed in situ are removed with the vapor stream and treated in an Air Quality Control (AQC) system.

TerraTherm installed 785 thermal wells, including 654 heater-only and 131 heater-vacuum wells, in a hexagonal pattern at 7.0-foot spacing. TerraTherm is carrying out the heating in two phases, shakedown of the first phase of which concluded in June 2003. Each phase requires achievement of inter-well soil temperatures of 325°C (620°F). Subsurface temperature monitoring tracks the progress of heating. The AQC system includes a regenerative thermal oxidizer with demonstrated capability of achieving 99.9% Destruction and Removal Efficiency (DRE); heat exchanger; and granular activated carbon (GAC). A process blower maintains the entire system under vacuum, while a continuous emission monitoring system measures stack emissions. In accordance with DTSC requirements, an independent air measurements contractor is carrying out several rounds of source testing. Results of the first two rounds indicated that the AQC system is meeting all performance standards. Specifically, measured emissions of PCDD/PCDF expressed as 2,3,7,8-TCDD TEQ averaged 0.0113 ng/dscm, relative to a regulatory standard of 0.2 ng/dscm.

The results of soil sampling of Phase 1a indicated that although pre-treatment concentrations were 30.6 mg/kg B(a)P Equivalents (mean of 47 samples), post-treatment concentrations were 0.022 mg/kg (mean of 10 samples), well below the stipulated goal of 0.065 mg/kg. Similarly, post-treatment concentrations of PCDD/PCDF were 0.48 μg/kg 2,3,7,8-TCDD TEQ (mean of 4 samples), well below the stipulated goal of 1.0 μg/kg. It is expected that ISTD remediation at the site will be completed by March 2005.

Monitored Natural Attenuation (MNA) – Where it Works and Where it Doesn't Using Case-history Examples

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Monitored Natural Attenuation (MNA) is often selected as a comprehensive remedial action thought to be capable of achieving a permanent solution. However, not often enough are the site conditions properly characterized to justify MNA. For example, sufficient data to demonstrate that the plume is shrinking is a must. Other indirect evidence of biodegradation should also be obtained in order to demonstrate that biodegradation is occurring. Also, time-series data should be acquired to calculate the length of time necessary to achieve cleanup goals. These calculations are necessary to compare to other possibly feasible cleanup alternatives. Through the use of several case-history examples, this presentation will provide insight as to what conditions are a prerequisite for an MNA solution. Also, some general rules of thumb and red-flags for MNA will be provided. MNA case-history examples will include releases of naphthalene, petroleum, and solvents.

In Situ Thermal Destruction (ISTD) of MGP Waste in a Former Gasholder: Design and Operation

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In Situ Thermal Desorption (ISTD) also known as In Situ Thermal Destruction is being used to remediate a gas holder containing residual coal tar at a former manufactured gas plant (MGP) in North Adams, Massachusetts. When the 62-ft (18.9-m) diameter by 18-ft (5.5-m) deep gas holder was decommissioned, it was backfilled with soil and debris. Water was found to be present at a depth of approximately 0.9 m (3 ft) below ground surface (bgs) within the brick-lined gas holder. Based on soil investigations within the gas holder, residual coal tar was present throughout the soils, and the bottom 1.2 m (4 ft) of soil was saturated with coal tar present as a dense non-aqueous phase liquid (DNAPL). The soil volume requiring treatment totals 2,010 cy (1,537 m^3). National Grid selected ISTD to remediate the gas holder and achieve Massachusetts soil cleanup standards with respect to polyaromatic hydrocarbons (PAHs) and other compounds of concern that are protective of human health and groundwater.

At ambient temperatures, it had been the site owner's experience that the coal tar at this site was minimally recoverable as a liquid. Laboratory results on a sample of the coal tar indicated, however, that a modest increase in temperature from 10 to 66°C (50 to 150°F) would result in a substantial decrease in viscosity, from 400 to 25 centipoise. Thus, TerraTherm proposed that gentle heating would increase the fluidity and recoverability of the tar, after which ISTD would proceed. During the remedial design, TerraTherm and MKTS utilized numerical simulations to optimize the placement of thermal wells and the heating sequence. TerraTherm then installed 25 thermal wells, 16 temperature and 3 pressure monitoring points, two liquid extraction points, an insulating surface seal, electrical distribution equipment, and both liquid and vapor treatment equipment. TerraTherm's remedial operations sequence is as follows: (1) dewatering of the gas holder and treatment of the liquid effluent prior to discharge; (2) gentle heating to remove recoverable tar from the gas holder via two liquid extraction wells; and, (3) ramping up the heaters to their full operating temperature of 650-800°C (1200-1500°F) and heating the soil to an interwell target temperature of 325°C (617°F). In the process, soil in close proximity to the heater wells will become superheated, resulting in substantial in-situ destruction by oxidation and pyrolysis of PAHs and other organic compounds that are volatilized and drawn to the heater-vacuum wells. Air will be injected around the heater-vacuum wells to prevent coke from forming and obstructing subsurface vapor flow. The project is scheduled for completion by early Fall 2004, and is being conducted under a guaranteed remediation contract.

In Situ Thermal Remediation of NAPL Using Electrical Resistance Heating at an Active U.S. Army Installation

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A full-scale Electrical Resistance Heating (ERH) and Multi-Phase Extraction (MPE) system is being implemented for the *in situ* thermal remediation of non-aqueous phase liquids (NAPL), primarily trichloroethylene (TCE), as well as other chlorinated solvents of concern, at the East Gate Disposal Yard (EGDY), Ft. Lewis, Tacoma, Washington. The ERH system includes 106 electrode and MPE locations for the first phase of the project designated as NAPL Area 1, which covers approximately 25,400 square feet with an estimated NAPL mass of 210,000 pounds. The estimated treatment volume for the ERH system is 31,040 cubic yards. This remediation work is being conducted for Ft. Lewis under the direction of the U.S. Army Corps of Engineers, Seattle District (USACE).

In addition to the ERH and MPE system, a liquid waste management system (LWMS) for removal and disposal of NAPL liquid is operating and tied into the ERH process. This project also includes operating a hydraulic control system to maintain a depressed groundwater table within the treatment area to eliminate groundwater migration.

The remediation of NAPL Areas 1, 2, and 3 will include presentation of daily, weekly, and monthly reports regarding sample and process monitoring data. Reports are being presented in an electronic format on a dedicated project website, enabling USACE and the ERH team to analyze and monitor the progress of the remediation.

The work is being conducted in phases starting with the treatment of NAPL Area 1. As the ERH project at Ft. Lewis is a performance-based contract; ERH operations will be continuously evaluated. Based on the performance of the ERH system at NAPL Area 1, USACE and Ft. Lewis will determine if the process will be continued for treatment of the subsequent NAPL Areas.

This remediation is presently underway with remediation operations concluding in NAPL Area 1 in the spring of 2004. Remediation in NAPL Area 2 is expected to begin this summer. It is expected that operational data and results from NAPL Area 1 and possibly Area 2 will be available in time for this conference. Specific operational design parameters as well as results and lessons learned will be presented.

Assessing the Performance of Thermal Conductive Heating for Remediation of Chlorinated VOCs in Saturated and Unsaturated Settings

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TerraTherm's Thermal Conduction Heating (TCH) technology, also known as In-Situ Thermal Desorption (ISTD) was recently used to remediate three separate source zones contaminated with chlorinated volatile organic compounds (CVOCs) at an active manufacturing facility in the USA. Soils within two of the source zones were unsaturated while soil within the third source zone was saturated with water. The total volume of soil remediated within the three source zones was 10,950 cubic yards (8,372 m^3). The results indicate that attaining an interwell soil temperature of 210°F (99°C), the boiling point of water at the site, was effective in reducing CVOCs from maximum pre-treatment concentrations for trichloroethene (TCE) of 4,130 mg/kg to 0.07 mg/kg (average of 54 samples). The post-treatment sampling results were significantly below the remedial goal for TCE of 1 mg/kg and were achieved following 150 days of soil heating. Effective treatment of the source zones provided the basis for a No Further Action (NFA) letter for soils at the site.

TerraTherm installed temperature monitoring points equipped with thermocouples near thermal wells and at representative centroid locations to monitor the progress of heating and to ensure that the coolest locations achieved the target temperature. Pressure monitoring points were located throughout the thermal well fields to monitor the effectiveness of the vapor control/collection system.

Based on the results of the clients' confirmatory soil sampling program, all three source zones achieved the remedial goals for TCE of < 1.056 mg/kg; for 1,1,1-trichloroethane of < 28,500 mg/kg; and for tetrachloroethene of < 5.95 mg/kg. Although nearly all of the targeted soil volume achieved the boiling point of water, the cleanup was accomplished while boiling off only a small fraction of the water content within the TTZ. Monitoring of subsurface conditions enabled TerraTherm to optimize the application of TCH/ISTD to address infiltration and heat losses identified during the remediation, while still enabling achievement of the guaranteed project goals.

Remote Telemetry Board Performance

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A remote telemetry board was installed on and existing horizontal and vertical air sparge system to immediately notify personnel when the system falls out of normal operating ranges and allow personnel to reprogram or restart the system remotely. After installation, an analysis of the system performance parameters have indicated that the PLC board has some additional benefits: improving the system efficiency and effectiveness. Since the implementation of the PLC board, the system ware has run more consistently and shows an increase in the VOC degradation in this vicinity. The remote operation and monitoring of this system has resulted in a decrease in labor costs for the system, as unscheduled site visits are no longer required to check on the system operation or to inspect the system after a failure.

Operations and maintenance activities has been performed on the system for 3 years. Initially the system was operating with one 2-inch leg and one 3-inch leg running in tandem. The airflow was manually changed from the sets of legs on a rotating basis and the system ran with each set of legs operational for approximately 24 to 48 hours. After the implementation of the remote board, the run time for the legs was reduced to 4 hours. The pressure required to overcome the groundwater infiltration into the air pathways after 24 to 48 hours of non-operation previously resulted in stress to the system. Since the installation of the unit, a steady decline in the airflow has been observed, consistent with the required vane replacements that have been scheduled on a quarterly basis. The shorter runtime has minimized the stress to the system and enabled it to run more efficiently.

Remediation II

Remediation Optimization Achieved by Bundling Complementary Treatment Technologies
Richard T. Cartwright, MEC^X, LLC, East Amherst, NY
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Novel Subsurface Biobarriers to Contain and Remediate Contaminated Ground Water
Robert Sharp, Manhattan College, Bronx, NY
Al Cunningham, Montana State University, Bozeman, MT
John Komlos, Jr., Princeton University, Princeton, NJ

Degradation of Carbon Tetrachloride in a Reducing Groundwater Environment: Implications for Natural Attenuation
Andy Davis, Geomega, Boulder, CO
C. Peck, Chevron Environmental Management Co., San Ramon

Treatment of Contaminated Groundwater Using NanoFe™ Technology
Harch Gill, PARS Environmental, Inc., Robbinsville, NJ
Kaiti Liao, PARS Environmental, Inc., Robbinsville, NJ

Optimization of an Extraction Well Using Three-Dimensional Capture Zones
Mary O'Reilly, CH2M HILL, Otis ANG Base, MA
John Glass, CH2M HILL, Herndon, VA
Scott DeHainaut, CH2M HILL, Otis ANG Base, MA
Rose Forbes, Air Force Center for Environmental Excellence, Otis ANG Base, MA

Remediation of Petroleum-Containing Soil and Groundwater at a Former Rail Yard Locomotive Fueling Area
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Bruce R. Nelson, Malcolm Pirnie, Inc., Latham, NY
Scott A. Underhill, Malcolm Pirnie, Inc., Latham, NY
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MRC™ Treatment of a VOC and Metals Impacted Unconsolidated Aquifer
Jonathan K. Child, Fuss & O'Neill, Inc., West Springfield, MA
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Remediation Optimization Achieved by Bundling Complementary Treatment Technologies

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An innovative sequence of four bundled complementary in-situ soil and groundwater treatment technologies has been developed to reduce total contaminant mass encountered at difficult to treat remediation sites. The first step is to pre-condition low permeability soils using either chemical and/or 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 "Total Contaminant Mass Desorption Process".

High temperature (greater than 180^{o}F) applications in the saturated zone have resulted in runaway reactions when the lower explosion limits (LEL) were exceeded. Low temperature (less than 100^{o}F) applications have resulted in problems with dissolved phase contaminant concentration rebound. The new optimized approach, whereby the saturated zone temperature is maintained consistently between 140^{o}F and 170^{o}F, effectively desorbs both adsorbed and absorbed contaminants from the soil matrix.

The desorption extraction step facilitates the third and fourth steps, which are biotreatment polishing steps used to reduce total contaminant mass transferred from the soil matrix into the dissolved phase in the saturated zone. The third step is an aerobic treatment process, which optimally produces stable concentrations of dissolved oxygen to biodegrade hydrocarbons in the contaminated groundwater. A patented process of water electrolysis used with a submersible pump and packer system recirculates oxygen enriched groundwater into the aquifer. It moves water only in recirculation. No water is withdrawn from the aquifer and no handling of water or permitting is required.

If chlorinated contaminants are also present, a fourth anaerobic treatment process is employed. Emulsified food-grade soybean oil is then injected into the aquifer, which slowly dissolves over several years providing a carbon and energy source to accelerate biodegradation. This innovative sequence of four complementary treatment technologies optimizes the reduction of total contaminant mass.

Novel Subsurface Biobarriers to Contain and Remediate Contaminated Ground Water

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This paper describes over a decade of work including laboratory studies, pilot studies and a field demonstrations to develop effective multi-purpose subsurface biobarriers that can be used to significantly decrease the hydraulic conductivity of an aquifer, while simultaneously mineralizing toxic groundwater contaminants. These novel biobarriers rely on starved cell technology to properly place and construct subsurface barriers using environmental isolates obtained at the contaminated sites.

The types of starved cell biobarriers that have been developed include single specie static biobarriers for plume containment and saltwater intrusion abatement, reactive biobarriers for containment and degradation of BTEX and nitrate, and dual-species reactive biobarriers for containment and degradation of chlorinated compounds. One example includes a field demonstration of a reactive subsurface biological barrier that has been in operation for 4 years. Results indicate that the biobarrier can reduce permeability by more than three orders of magnitude over an extended period of time without significant maintenance. Simultaneously, this biobarrier can degrade high concentrations of nitrate (> 100 mg/l) to meet drinking water standards (< 10 mg/l). Other single specie reactive barriers that have been developed include one capable of degrading BTEX and TCE. Bench-scale studies were used to develop a dual-species reactive biobarrier aimed at mineralizing TCE. This reactive biobarrier combines a well characterized TCE degrading environmental isolate with the facultative biofilm producer used in the field study to produce a dual species biofilm capable of partially plugging porous media (90% reduction in K) while completely mineralizing TCE. In addition, the results demonstrate that varying nutrient feed can be used to control both TCE degradation rates and hydraulic conductivity reduction. Additional field installations of this novel technology are planned, including barriers to remediate TCE, gasoline and MTBE plumes. Currently, work is being carried out to develop starved-cell biobarriers that can remediate heavy metals and radionuclides.

Degradation of Carbon Tetrachloride in a Reducing Groundwater Environment: Implications for Natural Attenuation

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Several laboratory experiments have demonstrated degradation of carbon tetrachloride (CT) in groundwater, but there appear to have been no corroborating long-term field studies. Investigations conducted in 1989 and 1999 at an industrial site constructed on an infilled estuarine environment in France provide data over a decade for which CT degradation could be evaluated. A Dense Non-Aqueous Phase Liquid (DNAPL) containing oil and >90% CT that was present in 1989 was absent in the extremely reducing site groundwater in both 1999 and 2000 (average Eh = -170 mV at pH 7, sulfide up to 21 mg L^{-1}, and Fe^{+2} up to 3.2 mg L^{-1}). These conditions facilitated dechlorination of CT to chloroform (CF) present at up to 46 mg L^{-1}, and methylene chloride (up to 75 mg L^{-1}). Carbon disulfide (CS_2), a terminal degradation product in reducing environments in laboratory experiments, was present at a mass ratio averaging 2.4:1 CF:CS_2, indicative of abiotic degradation. The lack of detection of the separate phase CT, the ratio of CF:CS_2, the presence of low molecular weight organic acids (i.e., acetate ~900 mg L^{-1}; citrate 360 mg L^{-1}; and propionate, up to 111 mg L^{-1}) and pyrite in conjunction with excess inorganic Cl in groundwater are all indicators of ongoing degradation of the chlorinated compounds. However, while natural attenuation of chloromethanes may be a viable adjunct to strategies designed to remediate CT in reducing groundwater, its efficacy is hard to quantify in complex field environments where upgradient sources are still present.

Treatment of Contaminated Groundwater Using NanoFe^{TM} Technology

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NanoFe^{TM} Technology is an innovative remediation technology for treating a wide range of recalcitrant contaminants. NanoFe consists of supported submicron ($<10^{-6}$ meter), bacteria-sized particles of zero valent iron (Fe^0) and trace amounts of a noble metal catalyst. NanoFe is an extremely versatile remediation tool given its high reactivity and extremely small particle size (typical particle sizes are on the order of 10-100 nanometers). NanoFe can effect the rapid destruction of a wide range of recalcitrant contaminants on either an *in-situ* or *ex-situ* basis. In the *in-situ* application, a slurry mixture of NanoFe and water is injected under pressure or by gravity into the contaminant plume. These particles have good flow characteristics and remain in suspension over extended periods of time to flow with the groundwater, while offering high reactivity that can dechlorinate chlorinated hydrocarbon contaminants.

NanoFe^{TM} Technology has been applied at several sites to treat groundwater contaminated with a variety of chlorinated hydrocarbons. The injected NanoFe significantly reduces the concentrations of chlorinated contaminants within approximately three days. Additionally, the injected NanoFe produced reducing conditions that fostered continuing natural attenuation of contaminants. This paper presents the results from several field applications and evaluates the distribution and effectiveness of the NanoFe.

Optimization of an Extraction Well Using Three-Dimensional Capture Zones

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Aquifer remediation at several groundwater contamination sites on the Massachusetts Military Reservation (MMR) is being expedited by periodic optimization of the extraction, treatment, and reinjection systems. Optimization activities may involve adjustment of pumping and reinjection rates, addition or removal of wells, or packing off sections of well screens to focus remediation efforts on the most critical depth intervals. Because groundwater flow is fully three-dimensional, system modifications are guided by a combination of groundwater monitoring and three-dimensional modeling. An example is a single-well hydraulic containment system that was installed to intercept a long, narrow trichloroethene (TCE) plume that passes beneath a 1000 foot land mass between two ponds before the plume discharges into the downgradient pond. Based on monitoring results from 1999, the TCE plume was delineated with a width of 50 to 75 feet, a thickness of less than 50 feet, and concentrations ranging up to 2200 micrograms per liter (µg/L). Since startup of the extraction well in January 2000, the plume trajectory has shifted, and TCE has not been detected at concentrations exceeding the maximum contaminant level of 5 µg/L in the upgradient monitoring network. However, influent concentrations at the extraction well remain consistent with the original plume delineation, with concentrations ranging up to 90 µg/L at a pumping rate of 150 gallons per minute (gpm). To optimize the performance of the well and locate the shifted plume, a field investigation program was designed, based on the results of three-dimensional hydraulic capture-zone delineation using the groundwater flow model. Investigation results and additional modeling of optimization scenarios were used to focus the extraction stress on the most contaminated portion of the aquifer while maintaining hydraulic containment of the plume.

Remediation of Petroleum-Containing Soil and Groundwater at a Former Rail Yard Locomotive Fueling Area

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Malcolm Pirnie, Inc. implemented a multi-faceted remedial program at a former locomotive fueling area (FLFA) at a rail yard in upstate New York to address diesel-affected soil and groundwater. Mainline tracks running through the FLFA prohibited removal of affected soil and, consequently, an in-situ remedy was developed. The remedy combines air sparging to provide oxygen to intrinsic diesel-degrading microorganisms and to volatilize petroleum compounds, and soil vapor extraction to actively remove volatilized diesel compounds from the subsurface. System components include vapor extraction and air sparging wells within the FLFA and low flow biosparging wells between the FLFA and down gradient properties. The biosparging wells create an oxygen barrier to migrating diesel compounds. Based on vapor extraction flow rates and the concentration of volatile organic compounds (VOCs) in extracted air, an estimated 1,000 pounds of petroleum mass have been removed by the vapor extraction system to date. Mass removal and biological activity is strongly correlated with seasonal fluctuations in subsurface temperature, which varies by more than eight degrees Celsius in the treatment zone over the course of a year. Analyses of microbial biomass in the treatment area indicate that diesel-degrading organisms increased by four orders of magnitude in unsaturated soil and by three orders of magnitude in saturated soil within five months of system start up. Regulated VOC concentrations in soil have decreased between 83 and 98 percent, while regulated semi-volatile organic compound (SVOC) concentrations in soil have decreased by as much as 90 percent in the treatment area in approximately 18 months. Concentrations of petroleum compounds in groundwater have been reduced to less than standards over the majority of the site. This integrated in-situ approach to the treatment of diesel-impacted soil and groundwater has greatly reduced cleanup costs and cleanup time for the site.

MRC™ Treatment of a VOC and Metals Impacted Unconsolidated Aquifer

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In-situ metals and chlorinated solvents remediation with Metals Remediation Compound (MRC™) is being evaluated as a method for remediating a mixed chlorinated volatile organic compound (VOC) and dissolved metals plume at a former plating facility in Massachusetts. MRC™ is a new, injectable remedial additive developed by Regenesis, San Clemente, CA for the in-situ treatment of co-mingled metal and solvent plumes. The MRC™ product is designed to release a polylactate polymer and a benign organosulfur compound to groundwater and facilitate enhanced reductive dechlorination of chlorinated VOCs and the formation of insoluble metal-sulfide solids to immobilize dissolved metals.

The primary constituents of concern at the site are chlorintated VOCs (primarily 1,1,1-trichlorethane and tetrachloroethene) and dissolved nickel. The source of the release is a former plating facility and associated drywell. Removal of the drywell and approximately 320 tons of soil was conducted in July 2000. Post-excavation assessment and monitoring activities indicate that residual impacts remain in the vicinity of the former drywell source area. Additional remedial measures are required to achieve further source reduction and prevent off-site contaminant migration.

The MRC™ Pilot Test was initiated in December 2003 with the injection of 540 pounds of MRC™ by Geoprobe® within an approximate 250 square foot area. MRC™ was injected over an approximate 15-foot vertical interval between a depth of approximately 5 and 20 feet at nine locations. A baseline groundwater monitoring event was conducted one day prior to MRC™ injections. Geochemical effects of the MRC™ injection are being monitored through three post-injection groundwater monitoring events conducted over a six month period. Each monitoring event includes the measurement of field parameters and a comprehensive suite of laboratory analyses including contaminants of concern, dissolved gases, metabolic acids, and a variety of inorganic parameters.

Risk Assessment and Bioavailability

Detection of Potential Estrogenic Endocrine Disruptor Chemicals Using The LUMI-Cell™ ER Recombinant Bioassay

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The Presence of NDMA in a Drinking Water Supply in Massachusetts and its Potential Health Risks

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Updated Petroleum Hydrocarbon Fraction Toxicity Values for Use With VPH/EPH/APH Data

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Impact of Aging in Soil on the Dermal Bioavailability of Phenol

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Reducing the Bioavailability of Pb in Soil

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Decreasing Arsenic Bioavailability in Soil with Iron Amendments

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Detection of Potential Estrogenic Endocrine Disruptor Chemicals Using The LUMI-Cell™ ER Recombinant Bioassay

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A class of compounds knows as Endocrine Disruptor Chemicals (EDCs), have been shown to have tremendous adverse effects on human and wild life populations. The association between the exposure, and bioaccumulation in the food chain, of EDCs has raised concern worldwide. Identification of EDCs requires a relevant bioassay, which can both detect these chemicals, and provide a relevant estimate of their endocrine disrupting potency. Xenobiotic Detection System (XDS) Inc. developed the LUMI-CELL™ ER bioassay in order to detect EDCs using a high-throughput bioassay system. To detect EDCs, BG-1 cells were stably transfected with an estrogen-responsive luciferase reporter gene plasmid (pGudLuc7ere). The resulting cell line responds to estrogenic chemicals in a time-, dose dependent- and chemical-specific manner with the induction of luciferase gene expression. XDS's LUMI-CELL™ ER bioassay system has tested over 110 chemicals, 53 of these chemicals were recommended by ICCVAM for validation of ER binding and transcriptional activation. Twenty-Eight of the 53 chemicals recommended by ICCVAM have historical data for a positive response, and all of these 28 compounds demonstrated estrogenic activity using the LUMI-CELL™ ER bioassay. Out of the 110 chemicals tested, 69 demonstrated estrogenic activity, while 41 showed no activity. Of the 57 chemicals tested, which were tested as unknowns, 30 were found to possess' estrogenic activity, while 27 showed no activity. The LUMI-CELL™ ER bioassay has an EC50 detection of 1.48×10^{-11} for β-estradiol. This level of detection is far lower than any limit likely to be imposed by any regulatory agency. This data clearly demonstrates that XDS's LUMI-CELL™ ER high-throughput bioassay system is a fast, reliable, and relatively inexpensive method for detection of EDCs, meeting many of the requirements mandated by the EPA and ICCVAMs Tier I (screening) requirements for EDC detection assays. Supported by NIEHS SBIR grant ES10533-03, and Superfund Basic Research Grant ES04699.

The Presence of NDMA in a Drinking Water Supply in Massachusetts and its Potential Health Risks

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N-Nitrosodimethylamine (NDMA) is a chemical used in the production of rubber products and rocket fuel. NDMA is also formed in water treatment processes as a byproduct of chloramination. It has been identified in a number of consumer products and foods. In one community in Massachusetts, NDMA has been detected in four off-line water supply production wells. When the wells were on-line, they supplied up to 50% of the drinking water to the town. Since the detection of NDMA, use of the wells in the affected aquifer has been suspended indefinitely. The presence of NDMA in the aquifer may be linked to the disposal activities associated with several chemical companies that operated at a location near the water supply for many years, beginning as early as 1953 and ending approximately in the mid 1970's. The end result of these disposal practices is approximately 9.2 million gallons of Dense Aqueous Phase Liquid (DAPL) contaminating the aquifer. The DAPL is being investigated as a possible source of the NDMA. The US EPA has classified NDMA as a probable human carcinogen at extremely low concentrations. In the November of 2002, DEP's Office of Research and Standards completed a critical review of the toxicity of NDMA, and developed a drinking water guideline of 0.01 micrograms per liter. This presentation will discuss the fate and transport of NDMA in groundwater, and the risk from exposure to NDMA in drinking water.

Updated Petroleum Hydrocarbon Fraction Toxicity Values for Use With VPH/EPH/APH Data

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The MA DEP (1994) and the TPH Criteria Working Group (TPHCWG) (1999) developed toxicity values for hydrocarbon fractions for use in assessing human health risks from exposures to complex mixtures of petroleum hydrocarbons. An updated set of oral and inhalation non-cancer toxicity values for these fractions has been developed after review of the original supporting laboratory studies for the TPHCWG toxicity values and newer studies. Toxicity values for the MA DEP-defined aliphatic and aromatic fractions will be presented along with rationales for the choices of each of these values.

Impact of Aging in Soil on the Dermal Bioavailability of Phenol

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Phenol is released to soil through accidental spills, manufacturing processes, and waste disposal. Skin is the body's primary route of entry for phenol. In order to assess the potential health risk from dermal exposure to phenol in soil, bioavailability studies were conducted. In vitro studies were performed on dermatomed male pig skin with flow-through diffusion cell methodology and radiolabeled phenol. The rate of penetration and the amount of chemical that penetrated skin into receptor fluid were measured for phenol aged in Atsion and Keyport soils. Total penetration was calculated as the sum of radioactivity in receptor fluid and skin. Bioavailability (total penetration) decreased from 84% for pure phenol to 15% and 8%, respectively, after 3 and 6 months of aging in the Atsion soil while the bioavailability of phenol aged in the Keyport soil was reduced to 22% and 17%,respectively, compared to pure compound. Since less phenol penetrated skin after soil sorption, more phenol was removed from the skin surface by soap and water wash compared to the pure chemical. Decreased bioavailability reduces the potential for toxicity. Therefore, the data indicate that the potential health risk from dermal exposure to soil-sorbed phenol decreases with aging. Furthermore, reduced bioavailability increases the environmentally acceptable endpoints for phenol which can result in less soil cleanup at contaminated sites. (Supported through funding from the Hazardous Substance Management Research Center and the New Jersey Commission on Science and Technology).

Reducing the Bioavailability of Pb in Soil

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Human health concerns have motivated site remediation efforts throughout the United States and elsewhere. The hazard to children by direct soil ingestion is usually acknowledged as the greatest concern at numerous sites containing high concentrations of toxic metals such as lead (Pb).
The objective of this research is to investigate the use of simple, inexpensive amendments to be incorporated into contaminated soils to reduce the bioavailability of Pb to children who ingest the soil. The results of three phosphate-containing amendments are very promising. There is a significant (up to 37%) decrease in the Pb bioaccessibility (a surrogate for oral bioavailability) in all soils amended with 5% by mass phosphate fertilizers and aged up to 200 days. Sulfur-rich materials and organic matter have been found to immobilize Pb in soils. Other possible amendments including pyrite and compost material are also being investigated.
Antimony (Sb) is a known hardening agent used in lead ammunition and is thus a potential contaminant. Measurements of Sb and Pb concentrations in firing range soils reveal a strong linear correlation between the two. Sb is much more mobile than Pb in soil, and the movement of Sb in groundwater could be another important human-health exposure pathway from Pb contaminated soils.

Decreasing Arsenic Bioavailability in Soil with Iron Amendments

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Human health risks associated with toxic metals have lead to the need for site remediation across the United States and the rest of the globe. Direct soil ingestion poses a health hazard for small children at contaminated sites containing high concentrations of toxic metals, such as arsenic (As). The influence of soil physical and chemical properties (Fe and Mn oxides, pH, cation exchange capacity, total inorganic and organic carbon, and particle size) on As(V) adsorption, sequestration, and relative bioaccessibility (as a surrogate for oral bioavailability) were previously studied. These results indicate the primary soil characteristics responsible for minimizing As(V) bioaccessibility are DCB extractable Fe oxides and pH. Arsenic bioaccessibility in soils generally decreases with Fe oxide content and increases with pH. Soils are usually reasonably well buffered at their natural pH, but it is possible to add relatively simple Fe amendments to reduce As bioavailability. By increasing the Fe oxide concentrations in soil, it was shown to decrease the relative bioaccessibility of As. Variables such as Fe source, method of addition, and aging period were examined. This research investigates amendment technologies that increase iron oxides in soil providing a means for As adsorption, sequestration, and an overall decrease in relative bioaccessibility.

Risk Assessment and Remedial Approaches Towards Restoration and Management of Contaminated Rivers

Characterization of Contaminated Sediments for Remediation Projects in Hamilton Harbour
Alex J. Zeman, Environment Canada, National Water Research Institute, Burlington, Canada
Timothy S. Patterson, Environment Canada, National Water Research Institute, Burlington, Canada

Development of Concentration Thresholds for the Hudson River PCBs Residuals Performance Standard
Claire Hunt, TAMS Consultants, an Earth Tech Co., Bloomfield, NJ
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Don Hayes, The University of Utah, Salt Lake City, UT
Len Warner, Malcolm Pirnie, Inc., White Plains, NY
Bruce Fidler, Malcolm Pirnie, Inc., Fair Lawn, NJ

A Spatially-Explicit Probabilistic Approach to Evaluating and Assessing Human and Ecological Risks Associated with PCB-Contaminated Sediments
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An Assessment and Remediation of the Fox River: A Case Study
Edward K. Lynch, PE, Wisconsin Department of Natural Resources, Madison, WI
Mark Velleux, PE, Colorado State University, Fort Collins, CO,

Overview of Sediment Remediation of Tannery Waste Contamination in Tannery Bay, White Lake, Michigan
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In-Pile Thermal Desorption of SVOCs in Riverine Sediments: in the Barge or on the Bank
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Optimizing River Cleanup Planning: Balancing PCB Exposure Risks and Remediation.
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Characterization of Contaminated Sediments for Remediation Projects in Hamilton Harbour

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Hamilton Harbour is located on the western end of Lake Ontario and has an area of approximately 31 square kilometers. The harbour has been designated by the International Joint Commission (IJC) as one of the 42 Areas of Concern (AOCs) within the Great Lakes. Most fine-grained sediments in the harbour exceed sediment quality guidelines at the severe effect level due to contamination both by metals and organic compounds such as PAHs and PCBs. Current investigations are concentrated on two areas of the harbour called Randle Reef and Windermere Arm. The Randle Reef "hot spot" contains the most highly contaminated sediment for PAH concentrations in the harbour. Extensive information on sediment physical and chemical properties was collected by coring and offshore boreholes. Bioassays were carried out to determine sediment toxicity. A range of remediation alternatives has been considered, including removal and ex-situ treatment. The current preferred alternative is an engineered containment facility (ECF), which will contain in-situ contaminated sediments within the footprint of the structure. In addition, dredged sediment from other contaminated sites in the harbour will be placed in the ECF. Windermere Arm is a 50-ha narrow channel situated in the southeast portion of the harbour. Contamination in Windermere Arm is not as severe as that found in Randle Reef. Recent sediment surveys in the area, however, yielded higher PCB values in surficial sediments than previously reported. Sediments in Windermere Arm are also subject to considerable physical disturbance due to extensive ship traffic. For this reason, historical sediment contamination occurring in deeper sediments has also to be considered as a potential risk to the aquatic environment.

Development of Concentration Thresholds for the Hudson River PCBs Residuals Performance Standard

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In 2002, USEPA issued the landmark decision to remediate the Hudson River PCB site that extends 40 miles north of Albany, NY by dredging the contaminated sediments. As part of this precedent setting project, USEPA required three engineering performance standards for productivity, resuspension and residuals. USEPA has since developed draft performance standards that are currently undergoing peer review. This paper describes the development of concentration limits established for the residual performance standard.

The record of decision for this site established a goal of 1 mg/kg Tri+ PCBs residual concentration following inventory removal. Experience from other dredging projects indicates that this level of residual contamination is achievable, but a degree of variability in the residual concentration is to be expected with some areas of higher concentrations likely. Areas of elevated concentration are often associated with difficult subbottom conditions. The standard was developed to allow for some areas of higher concentrations as long as the overall average concentration remained at or below 1 mg/kg Tri+ PCB, by setting upper bound limits on average and individual point concentrations.

The dredging residual concentrations from several sites were analyzed to estimate the upper bound limits. The limits were calculated from the upper confidence limit on the mean and upper prediction limit. As there is no single correct means of estimating these values for the performance standard from non-site specific data, a weight of evidence approach was adopted. The site residual results had different concentration levels depending on the goals set for the remediation and the site conditions. For these results to be related the remedial goal of another project three approaches were taken: a ratio of the mean to the upper limit of the data sets; substitution into the equations describing the threshold concentrations assuming the data are lognormal; and using substitution assuming that the data are neither normal or lognormal (nonparametric). Results of the analysis showed that the threshold levels for these methods were largely consistent.

A Spatially-Explicit Probabilistic Approach to Evaluating and Assessing Human and Ecological Risks Associated with PCB-Contaminated Sediments

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We present the development of a spatially-explicit probabilistic aquatic food-web model, FishRand-Migration. This model was originally developed for the Hudson River RI/FS. Since then, with support from the Army Corps of Engineers, the model has been modified to incorporate the ability to specify spatial patterns of chemical concentrations relative to fish migration and foraging characteristics. The model is fully probabilistic and allows users to specify uncertain or variable distributions instead of point estimates for model parameters. The model predicts population distributions of time-varying concentrations of hydrophobic contaminants with associated uncertainty for each population fractile. We present ways in which these results can be used to support human health and ecological risk assessments. Often, bioaccumulation modeling relies on point estimate site use factors. FishRand-Migration provides more detailed and refined predictions of chemical concentrations in aquatic biota from which seasonal patterns in uptake can be discerned, as well as relationships between potential risks and hazards and the spatial distribution of contamination. We will also discuss required model inputs for application to other river systems.

An Assessment and Remediation of the Fox River: A Case Study

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In October 2001, the EPA and the Wisconsin Department of Natural Resources (WDNR) issued a Proposed Plan for addressing PCB contamination of the Lower Fox River and Green Bay. Development of the Proposed Plan and the selection of a remedy were the end result of an extensive evaluation process consistent with EPA guidelines for CERCLA projects in accordance with the federal National Contingency Plan (NCP). Subsequent to the Proposed Plan, two Records of Decision (RODs) were issued. The remedy selection process used was also consistent with NRC recommendations and other EPA guidance regarding the management of PCB-contaminated sediment sites. In addition to a site-specific Remedial Investigation and Feasibility Study (RI/FS), selection of the proposed remedy was based on consideration of information provided by numerous supporting studies, tools, and public comments. Each of these supporting efforts contributed to the remedy evaluation process by providing a wide spectrum of analyses that consider the full range of possible outcomes for each remediation alternative. The types of supporting efforts contributing to the development of the Proposed Plan include: field studies delineating the extent and distribution of PCB in water, sediment, and fish; human health and ecological risk assessments; analyses of the spatial and temporal PCB concentration trends in sediment and fish; contaminated sediment depth and sediment bed stability; site-specific chemical transport and biota modeling; sediment remediation evaluation and demonstration projects; and public input into the remedy selection process.

When collectively considered with the RI/FS for the site, these tools: 1) clearly demonstrate the need to remediate Lower Fox River contaminated sediments; 2) show that technology exists to implement the selected remedy; and 3) provide an understanding of what may be reasonably expected after the remedy is implemented. Overviews of the supporting studies contributing to the remedy evaluation process as well as discussion of the remedy selection process are presented in two white papers attached to the RODs. These white papers conclude with brief, operable unit (OU)-specific summaries of the selected remedy to restore the environmental quality of the river and bay. The selected remedy is further described in the RODs for the site.

Overview of Sediment Remediation of Tannery Waste Contamination in Tannery Bay, White Lake, Michigan

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White Lake is listed as an U.S. Environmental Protection Agency Great Lakes Area of Concern, because of beneficial use impairments. Tannery Bay is located in the northeast portion of White Lake, and is adjacent to the former Whitehall Leather Company. Historic contamination from former industrial activities at the site, including dumping of leather scraps and discharge of process wastewater containing heavy metals into Tannery Bay, contributed to the degradation of water and sediment quality in White Lake.

State resolutions and public involvement prompted the timely cleanup of Tannery Bay. Through Clean Michigan Initiative funding and consent judgment with the responsible party, sediment containing tannery wastes was dredged from Tannery Bay in 2002 and 2003. The environmental dredge design was based on sediment sampling and analyses information collected by the U.S. Army Corps of Engineers and Michigan Department of Environmental Quality. The criteria used to determine if sediment was adversely impacted included the presence of aesthetic indicators (hide, hair, or burgundy discoloration) and/or elevated chromium or arsenic concentrations, which were determined to be indicative of tannery wastes.

Sediment removal was performed with hydraulic and mechanical dredging equipment. Hydraulically dredged sediment was dewatered through belt filter presses, and liquid in mechanically dredged sediment was bound using an absorbent polymer. All dewatered sediment and debris was disposed of at a municipal waste landfill. Monitoring and engineering controls, including turbidity monitoring and installation of a double silt curtain system, were implemented to ensure that dredging activities were conducted in compliance with permit requirements and did not affect other areas of White Lake. Sediment verification sampling was performed to assure that remediation objects were met. After completion of dredging activities, sand and riprap were placed along Tannery Bay shoreline areas, to create a gently sloping littoral zone and provide shoreline stabilization.

In-Pile Thermal Desorption of SVOCs in Riverine Sediments: in the Barge or on the Bank

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Current overall treatment costs for contaminated dredged river sediments can be as high as $500-700 per ton. This presentation focuses on an innovative thermal treatment method, which is likely to be highly effective at full-scale costs of less than one third of this cost ($130-300 per ton depending on total volume).

TerraTherm's IPTD technology is an ex-situ version of In-Situ Thermal Destruction (ISTD), by which TerraTherm utilizes simultaneous application of thermal conduction heating and vacuum to treat contaminated soil and sediment without excavation. The contaminated solids are placed in piles, interlayered with heater pipes and vapor extraction screens. If necessary, the contaminated material will be dewatered prior to treatment. Each pile would contain a bermed area with a vapor-and liquid-tight bottom and sides, a leachate collection system, heater elements and vapor extraction wells distributed throughout the spoils. A vapor cap is placed over the piles to contain fugitive emissions and allow for application of a vacuum to the pile. For monitoring purposes, thermocouples and pressure transducers are inserted at select locations to document heating progress and vacuum conditions, respectively.

The piles are then heated and treated using electrical heaters, which bring the temperature up to the target, typically around 300 to 350 ^{o}C, depending on the nature of the contaminants. The applied heat volatilizes both water and organic contaminants within the soil, enabling them to be carried in the air stream toward vacuum extraction wells for destruction within the soil and transfer of the remaining vapor to an air quality control (AQC) unit. It is anticipated that >95% of the contaminant mass will be destroyed in the heated soil. Remedial results (post-treatment soil concentrations) depend both on the target temperature and the duration of treatment, with non-detect being a practical goal if necessary.

This presentation will focus on the IPTD technology application for Semi-Volatile Organics such as PCB and chloro-benzenes. Treatability study results and full-scale treatment concepts will be presented, including:

- Laboratory treatability studies showing removal efficiencies for different contaminants and treatment temperatures.
- Drum-scale testing of remedial efficiency.
- Results of a field-scale pilot demonstration of IPTD for SVOC treatment.
- Conceptual design of full-scale IPTD treatment of dredged river sediments/spoils.
- Discussion of treatment of dredged spoils in the barges used to transport the material.
- Estimated treatment costs as a function of the treated volume.

Finally, our recommendations for further analysis of the opportunities and most appropriate applications of the IPTD technology will be presented.

Optimizing River Cleanup Planning: Balancing PCB Exposure Risks and Remediation.

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Managing PCB-contaminated sediments in rivers has long posed a decision dilemma—how can multiple sources of environmental impact (from chemical exposure, destructive remediation, and baseline impairments) be compared objectively and effectively? This dilemma resulted in the preparation and publication of a “A Risk Management Strategy for PCB-Contaminated Sediments” by the National Research Council in 2001. This Strategy Report provides a useful framework for identifying issues and background information regarding the nature of exposure and remediation impacts. However, it does not offer guidelines or comparative assessment techniques for decision making in specific cases. In this presentation, we present an integrated management decision process specifically intended for application in small to medium sized, urbanized and industrialized waterways. The process emphasizes comparative risk analysis, and incorporates chemical exposures, remedial disruption, baseline impairments, and post-remediation restoration as explicit elements. Each element is presented in the context of a holistic, watershed and riparian ecosystem based analysis, whose overall objective is to maximize environmental quality. The analysis presumes that a balance of human use and ecological service flows is desirable, and that some management flexibility is available in both the riparian corridor and the waterway proper. The approach emphasizes phased decision making and staged implementation, with monitoring and adaptive management throughout the program. By incorporating adaptive feedback in a robust analytical structure, a technically sound and scientifically credible foundation can be established for the effective management of waterways in human landscapes.

Sediments

Direct Measurement of the Sudden Uplift of a Low-Permeability Sediment Cap Due to Gas Entrapment
Robert D. Mutch, Jr., HydroQual, Inc., Mahwah, NJ
Egon Weber, Ph.D, HydroQual, Inc., Mahwah, NJ
David Kearney, P.E., Brown and Caldwell, Allendale, NJ

Water Quality Implications of Contaminated Sediments Remediation
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Danny D. Reible, Hazardous Substances Research Center, Louisiana State University, Baton Rouge, LA
Donald F. Hayes, University of Utah, Salt Lake City, UT

Determining Background For Ecological Risk Parameters in Toxic Harbor Sediments
Christopher Leadon, Naval Facilities Engineering Command (NAVFAC), San Diego, CA
Tom McDonnell, Brown and Caldwell, Irvine, CA
Janet Lear, Brown and Caldwell, San Diego, CA
Dave Barclift, Naval Facilities Engineering Command (NAVFAC), Philadelphia, PA

Assessment of Bioavailability of PAH Contaminated Sediments Using XAD-Assisted Desorption
Henry H. Tabak, USEPA, Cincinnati, OH
Li Lei, University of Cincinnati, Cincinnati, OH
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Kinetics and Mechanisms of PAHs Sequestration in Freshwater and Marine Sediments
Denis Brion, University of Québec at Rimouski, Rimouski (Qc), Canada
Émilien Pelletier, University of Québec at Rimouski, Rimouski (Qc), Canada

Sediment Quality Assessment in Four Suburban Massachusetts Rivers
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Janet Robinson, Woodard & Curran, Portland, ME
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Mycoremediation of PCB Contaminated Sediments
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Scott Bodensteiner, MEC Analytical Systems, Inc., Tiburon, CA
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Direct Measurement of the Sudden Uplift of a Low-Permeability Sediment Cap Due to Gas Entrapment

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The potential uplift and deformation of low-permeability sediment cap constructed with AquaBlok^{TM} is being studied using highly sensitive, in-place horizontal inclinometers. The research project involves construction of several pilot scale sediment caps. One such pilot scale sediment cap consists of six inches of AquaBlok^{TM} overlain with six inches of sand. A horizontal inclinometer casing was constructed within the nominally 100 by 80 foot pilot-scale cap overlying the AquaBlok$^{TM.}$ 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. The cap then settled back into position before undergoing another sudden uplift 11 days later. 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. Smaller, intermittent releases of gas have been observed at other points in the AquaBlok^{TM} cap, as well, suggesting more widespread jointing or imperfections in the cap.

Water Quality Implications of Contaminated Sediments Remediation

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The environmental impetus for remediation of contaminated sediments arises from adverse impacts on the overlying water column quality, adverse impacts on the aquatic ecosystem, or both. Water quality impacts occur due to the flux of sediment-associated pollutants from the sediment zone solids and interstitial waters, into the water column. Where sediment remediation is warranted, the array of remedial options (beyond natural attenuation) is limited. The most common remedial technology is dredging. An alternative, sediment capping, is under increasing consideration. Either technology will induce transient and potentially long-term adverse water quality impacts, for an array of water quality pollutants extending far beyond the targeted sediment remedial action pollutant(s). This extended array of pollutants reflects the chemical composition of the sediments and interstitial waters, and includes oxygen demanding organic and inorganic species, toxicants such as ammonia, PAHs and pesticides, and constituents reflective of the typical anoxic sediment zone such as methyl- or mercurous mercury, ferrous iron or sulfide. All sediment remedial actions perturb the quasi-equilibrium between the sediment zone and water column, to the detriment of water column quality. Impacts include sediment compaction and accelerated interstitial water release, and contaminated sediment resuspension and transport. For dredging, large quantities of dredging water are incorporated into the dredged material. This dredge water is heavily contaminated, and is typically segregated from the dredged solids, treated, and discharged back into the water body. Remedial action economic constraints, or limitations of the capabilities of treatment technology, can yield mass pollutants loadings and consequent prolonged water quality deterioration far exceeding in severity initial, pre-dredging water quality conditions. Due to economic or technological inability to achieve mandated water quality-based discharge limits, and anticipated violations of water quality standards as a consequent of the remedial action, environmental agencies rely upon regulatory variances to circumvent water quality standards violations, and the Clean Water Act anti-degradation policy designed to protect existing uses and prevent deterioration of current water quality, as incorporated into federal and states' environmental regulations.

This paper discusses the water quality implications of contaminated sediments remediation, options for and limitations on methods of amelioration of adverse water quality impacts, and regulatory tools available to allow remedial actions to proceed in the face of water quality protection legal barriers.

Determining Background For Ecological Risk Parameters in Toxic Harbor Sediments

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Background characterizations for biological parameters are necessary in ecological risk investigations of harbor sediments contaminated with toxic chemicals. Areas with toxically contaminated sediments are defined as those with concentrations or levels above background for chemical and biological parameters. For determination of ecological risks at contaminated sediment sites, biological parameters can include bioassay tests, bioaccumulation tests, and benthic community analyses. Chemical parameters can include toxic chemical concentrations in sediments and the tissue of biological receptors. Indirectly, contaminated harbor sediments can impact shellfish, fish, and marine mammal populations.

Generally, background reference stations are positioned in relatively clean areas exhibiting the same physical characteristics as nearby areas with contaminated harbor sediments. The number of background reference stations and the number of sample replicates per reference station depends on the statistical design of a sediment eco-risk investigation, developed through the data quality objective (DQO) process. Biological data from the background reference stations can be compared to contaminated site data by using maximum background levels or comparative statistics. The methods used to define background for biological parameters in eco-risk investigations of marine harbor sediments at California Navy bases are summarized in this paper. Background for regional biological indices used to quantify eco-risks for benthic communities in sediments is also described.

Assessment of Bioavailability of PAH Contaminated Sediments Using XAD-Assisted Desorption

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In the bioremediation of soils/sediments contaminated with polycyclic aromatic hydrocarbons (PAHs) it is imperative to determine the fraction of the PAHs that is amenable to remediation. For example, what fraction of the PAHs is available to the indigenous microorganisms, i.e. bioavailable? The bioavailability of PAHs varies with the contamination history and the characteristics of soils/sediments. Research was undertaken to examine the feasibility of using adsorbent-assisted desorption of PAHs for assessing their bioavailability in contaminated sediments containing aged PAHs. The sediment was collected from East River, NY, near Rikers=s Island and contaminated with 2-ring to 6-ring PAHs. The kinetics of desorption of PAHs from sediment were studied using abiotic sediment-seawater slurry systems, where the nonionic polymeric adsorbent XAD-2 was added in various concentrations to the sediment /water slurry to ensure that sufficient adsorption capacoty of the XAD is provided to effect the maximum rate and extent of desorption of PAHs from the sediment. By acting as an infinite PAH sink and by maintaining a constantly low PAH concentration in the aqueous phase, XAD is used to maximize the driving force for the PAHs to desorb from sediment particles without changing the sediment-aqueous phase partitioning coefficient. Batch studies on the microbial activity in the sediment slurry systems were also undertaken under aerobic conditions to investigate the potential for PAH biodegradation by the indigenous microbial consortia. The experiments were considered complete when PAH concentration levels in the sediment ceased to decrease.

A considerable residual level of PAHs was detected at the end of the experiments in both the biodegradation and XAD assisted desorption studies. This is attributed to the fact that a substantial fraction of PAHs is irreversibly sorbed onto the sedimemnt and thus unavailable for either biodegradation or desorption activity. All 2-ring, 3-ring and 4-ring PAHs exhibited significant biodegradation under aerobic conditions, with their residual levels in two studies closely related to each other (the correlation coefficient was 0.94). 5-ring and 6-ring PAHs showed either marginal or no biodegradation activity at all. This trend suggests that these higher ring PAHs might become available but their recalcitrance to biodegradation by the indigenous microbiota limited the biodegradation activity under the experimental conditions used. The adsorption of the desorbed PAHs onto XAD resin was a much faster process than microbial degradation, since the desorption equlibrium was attainable in just 2 weeks, while it took 24 weeks for all PAHs to attain maximum biodegradation. Overall, the results indicate that XAD-assisted desorption could be used to assess the bioavailability and the biodegradation potential of most PAHs in a timely manner, as long as the recalcitrance of PAHs is not the limiting factor in bioremediation of the contaminated sediments. Because XAD-assisted desorption does not change the sediment-aqueous phase distribution coefficients of the contaminants, this process could evaluate the bioavailability of aged PAHs representatively in the contaminated sediments and it can also be applied to other contaminant-matrix circumstances. To our knowledge, this is the first reported representative chemical measurement of bioavailability which does not require exhaustive search or extraction parameters for every specific contaminant-matrix pair

Kinetics and Mechanisms of PAHs Sequestration in Freshwater and Marine Sediments

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Chemical sequestration is a natural process taking place in sediments and soils which reduces the availability of hydrophobic compounds such as polycyclic aromatic hydrocarbons (PAHs). The rate of sequestration following the release of PAHs into the aquatic environment is still unexplored. To measure kinetic parameters and investigate governing factors of sequestration of individual PAHs, natural sediment slurries were spiked with [^{2}H]-PAHs and periodically extracted with a high molecular weight surfactant solution to determine changes in the available fraction over periods of 7 to 28 days. Dissolved [^{2}H]-PAHs were first adsorbed on particles within 4-7 days. Adsorbed molecules became slowly sequestered into sediment particles and were gradually more difficult to extract. An empirical model based on a three-compartment dynamic system was developed to quantify the sequestration rate constants of a group of seven selected PAHs. The sequestration process was assumed to be a first-order consecutive and irreversible two-stage reaction. The model was tested with a low contaminated marine sediment and a highly contaminated freshwater sediment. Adsorption rate constants ranged between 0.056 h^{-1} and 0.017 h^{-1} and were approximately ten times higher than sequestration rate constants. Light PAHs were the faster to enter into the sequestration process. The presence of a large quantity of already sequestered PAHs in sediment played a determining role in the first step of the sorption process.

Sediment Quality Assessment in Four Suburban Massachusetts Rivers

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The investigators evaluated sediment quality to determine the levels of sediment pollutants associated with non-point sources in suburban stretches of four Southeastern Massachusetts riverways: The Charles River (Medway), the Neponset River (Norwood), Cushings Brook (Hanover) and Furnace Brook (Quincy). Six sediment samples were collected from a contiguous reach on each river and analyzed for total organic carbon (TOC), grain size, extractable petroleum hydrocarbons (EPH), polycyclic aromatic hydrocarbons (PAHs), arsenic, lead and chromium. Additionally, water quality parameters (dissolved oxygen, pH, temperature, turbidity, and conductivity) were recorded at each sample station. All river sediments generally consisted of sand and silt, with minor amounts of clay. EPH fractions, PAHs and metals were detected in every sample collected within each river stretch. The concentrations of total PAHs detected ranged from 1mg/kg up to 93mg/kg.   Among all samples from each river stretch, the ranges of concentrations of contaminants were typically within one to two orders of magnitude. The patterns of these constituents were generally reflective of those associated with roadway runoff, with heavier-weight PAHs and EPH fractions predominant. We evaluated sediment quality results with respect to consensus-based ecological sediment screening levels as a means of assessing potential toxicity to benthic invertebrates. In most samples, detected concentrations of constituents exceeded these screening levels. The conclusions of this study document the ubiquitous presence of these contaminants in sediments of suburban rivers and underscore the importance of considering non-point sources of contamination in suburban/urban waterways when planning assessment activities and evaluating impacts to sediment quality.

Mycoremediation of PCB Contaminated Sediments

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Conventional bioremediation techniques applied to soils contaminated with synthetic organic compounds generally consist of nutrient aided amplifications of single bacterial strains. This approach, although partially effective, does not take advantage of the complex interactions that occur among biological communities during the process of natural organic decay. Previous investigations have shown that using complex biological systems with “keystone” species cultured to develop optimal capacity for degrading specific organic soil contaminants (e.g. polyaromatic hydrocarbons) is significantly more effective than monoculture bioremediation. The objective of this study was to evaluate the effectiveness of fungal mycelia as a “keystone” species in a bioremedial process (mycoremediatin) for reducing levels of polychlorinated biphenyls (PCBs) in sediment. Sediment samples laden with significantly elevated PCB concentrations (1,000 ppm as Aroclors) were collected from a creekbed, composited and then subsampled for PCB congener analysis. The remaining composite was used to evaluate the remedial effectiveness of mycelia cultured from excised mushroom (*Pleurotus ostreatus*) tissue. Mycelia cultures successfully proliferated on agar media were transferred to loosely packed wood chips used as a substrate for application to the contaminated sediment. Two layers of sediment (1L each) were interspersed among three layers of mycelliated wood chips. Composite sediment only was placed in a separate container to account for natural attenuation. The mycelium proliferated and inervated the layered sediment at a modest rate over an eight-week period. Afterward, three sample borings were collected from the remediation container, and sediment was separated from the woodchip substrate. Remediated and control container sediment was then analyzed for PCB congeners. Results show that the mean PCB congener concentration was reduced by 35% in mycoremediated sediment, with individual congener reductions up to 62%. These findings indicate that mycoremediation is a potentially effective means for attenuating PCB contamination and warrants additional investigation to identify optimal mushroom strains and exposure strategies.

Site Assessment

Targeted Brownfields Assessment of a Former Power Plant Using the Triad Approach
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Plume Delineation and Monitoring of Natural Attenuation Processes Via *In Situ* Flux Measurement
Andre Tartre, EcoRemediation Inc., Burlington, VT

Unlimited Industrial Closure of Detroit Artillery Armory Using the State of Michigan's "Sampling Strategies and Statistics" Procedures
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Tina Williams, P.E., United States Army Corps of Engineers - Detroit District, Detroit, MI

Use of a GIS-Based Site Conceptual Model for Site Characterization, Regulatory Interaction and Feasibility Analysis, Harbor Point MGP Site, Utica, NY
Ernest Ashley, Camp Dresser & McKee Inc, Cambridge, MA
Amol Daxikar, Camp Dresser & McKee Inc, Cambridge, MA
Terry Young, Niagara Mohawk/A National Grid Company, Syracuse, NY

New Approaches in Data Visualization of LNAPL
Lester B. Engel, The RETEC Group Inc., Atlanta, GA
Jeffrey A. Johnson, The RETEC Group Inc., Houston, TX

Case Study of TCE Attenuation from Groundwater to Indoor Air and Effects of Building Ventilation
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A Targeted Brownfields Assessment of a former power plant was conducted using the Triad approach, through the efforts of EPA Region I and Metcalf & Eddy, the Brownfields Technology Support Center, and the town of Greenwich, Connecticut. The town plans to redevelop the site as a waterfront park. Because coal ash was historically disposed at the site, it was considered probable that site surface soil would show concentrations of contaminants that exceed Connecticut residential direct exposure criteria (RES DEC). Historical information also suggested the possibility of petroleum and polychlorinated biphenyl (PCB) releases. The goal of the investigation was to obtain sufficient data, in one mobilization, to determine the nature and extent of surface soil contamination.

Field analytical techniques included Site Lab® test kits for total petroleum hydrocarbons (TPH) and total polyaromatic hydrocarbons (PAHs), EPA's X-ray fluorescence instrument for metals, and the EPA mobile laboratory for PCBs.   Soil samples were also analyzed by an off-site laboratory for arsenic with 48 hour turnaround.   Sampling locations were added based on feedback from the field analyses. The team located an area of PCB contamination that might have gone undiscovered using traditional sampling approaches. A correlation was developed between the TPH/PAH test kit results and off-site laboratory results, which enabled use of the test kit results to define the extent of soil contamination with TPH and PAHs.

The results showed that site surface soil contains concentrations of arsenic, TPH, and PAHs at levels exceeding RES DEC. The observed concentrations are partially from the coal ash that is co-mingled with site soil. PCBs were identified near an area where transformers had been located. The Triad approach yielded an estimated cost savings of approximately 40 percent, when compared with a traditional approach involving two mobilizations and fixed laboratory analytical methods.

Plume Delineation and Monitoring of Natural Attenuation Processes Via *In Situ* Flux Measurement

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A research has been conducted in Canada over a two-year period to develop an innovative sampling technique for petroleum contaminated sites. This new method quantifies the rate at which vapors or gases are “produced” during a particular period of time under specific conditions of ventilation.

Traditional soil-gas surveys evaluate concentrations of specific vapors that are in chemical equilibrium with dissolved, sorbed or free products in the media. The new proposed sampling technique involves to purge the soil with a non-contaminated gas in the vicinity of a sample probe for few minutes. The soil-gas purge affects the gas-liquid-soil equilibrium causing sorbed and dissolved vapors to transfer to the gas phase. During a period when the static equilibrium is unbalanced, the rate at which vapor contaminants are transferred to the soil gas phase is estimated. After this stabilization period, the purge is reduced or stopped altogether. Rebounds after the purging period indicate if petroleum products are present beside the sampling point. This method constitutes a major improvement for plume delineation at low cost. It delivers results on site within 10 minutes and investigated waste are almost eliminated.

More recently, this new sampling approach has been further developed for the saturated zone. Rebounds are used to locate efficiently Chlorinated solvents pockets or to estimate *In Situ* flux rates of oxygen and biogenic gases. The primary advantages to evaluate biodegradation processes with this method include: [i] better estimates of reactant availability and daughter compounds production rate across a plume, [ii] less interference from temporal and spatial differences in hydrologic and geochemical conditions, [iii] data that are produced on a real-time basis, and [iiii] reducing overall monitoring cost of the natural attenuation option. Field data will be presented.

Unlimited Industrial Closure of Detroit Artillery Armory Using the State of Michigan's "Sampling Strategies and Statistics" Procedures

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The Michigan Department of Military and Veterans Affair and U.S. Army Corps of Engineers contracted DLZ Michigan, Inc. to perform the site closure activities, including soil sampling, statistical analysis, soil removal, and Closure Report preparation and submittal to close the 76-acre Detroit Artillery Armory. This site is located in a prime redevelopment area of Oak Pak, Michigan. A prospective buyer had made an offer on the property contingent upon generic industrial site closure; thus, a fast-track closure with cooperation between several State and Federal agencies was required.

Detroit Artillery Armory was built in 1942 and was used for manufacturing of weapons components. Debris and ash from the onsite waste incinerator was buried in a 6-acre area adjacent to the incinerator. Although several site investigations had been performed over the last 10 years, the Michigan Department of Environmental Quality (MDEQ) required a much more thorough investigation, to meet the requirements of the State's Sampling Strategies and Statistics Training Manual for Part 201 Cleanup Criteria for proper remediation verification. This was the first large-scale implementation of this guidance document for site closure in Michigan.

Using statistical analysis, approximately 69 acres of the 76 total acres were determined to meet appropriate cleanup criteria and did not require any additional investigation. Remediation was focused on the former location of the incinerator and remaining 6-acre area. After review, training and consultation with the MDEQ, DLZ prepared a work plan that included collection of 2,981 soil samples on a 15-foot sampling grid. Samples were analyzed for lead and arsenic, using laboratory methods and X-Ray Fluorescence Spectrometer. Based on analytical data and statistical analysis, excavation was conducted in areas containing soils that exceeded applicable industrial criteria.

Unlimited industrial site closure was granted by the MDEQ in November 2003, 6 months after approval of the work plan.

Use of a GIS-Based Site Conceptual Model for Site Characterization, Regulatory Interaction and Feasibility Analysis, Harbor Point MGP Site, Utica, NY

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Compiling data into a manageable and useful format that can be understood by consultants, clients and regulatory personnel is the goal of the site conceptual model (CSM). Geographic information systems (GIS) can be used to assimilate, evaluate and present large amounts of data from multiple investigations and can facilitate site characterization, interactions with regulators and remedial feasibility study analysis. For a large Manufactured Gas Plant (MGP) site in New York State, a GIS-based conceptual site model was used describe the distribution of constituents of concern (COCs) in various media, the interrelationships of three the Operable Units (OUs), and to identify, evaluate and recommend remedial alternatives. This presentation will describe the challenges of this specific site, the goals of the conceptual site model, the process of creating the GIS, its capabilities and how it was used to advance the remedial process.

New Approaches in Data Visualization of LNAPL

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Historically characterization and subsurface investigations of Light Non-Aqueous Phase Liquids (LNAPL) required significant data management effort and cost. Since many remediation projects involve multiple consultants and engineers often data and graphics have to be recreated due to non-standard approaches. The American Petroleum Institute (API) and the U.S. Environmental Protection Agency (USEPA) have published models and spreadsheets to determine the physical characteristics, movement, and recoverability of LNAPL.

This presentation will demonstrate how new approaches and tools were used to gather, store and share data, including generation of 3-D GIS, for a site investigation. The site involved the contamination of a variety of Constituents of Interest (COI) and LNAPL. To evaluate the distribution and migration of LNAPL, model results were applied with ArcGIS and other visualization software to generate 3-D graphics. The tools allowed for a more cost effective characterization of the contamination and groundwater evaluation. Given the reduced effort required to manage the data, a more detailed and thorough evaluation of the site was possible thereby eliminating misinterpretations and better communication to stakeholders.

Various graphical examples will be given to demonstrate the advantages and explain this approach to subsurface investigation.

Case Study of TCE Attenuation from Groundwater to Indoor Air and Effects of Building Ventilation

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An investigation of groundwater-to-indoor air vapor intrusion (VI) was conducted at a Superfund site in Mountain View, California. Groundwater at the Site is impacted by trichloroethylene (TCE) and has been under cleanup by an extraction and treatment system since 1980s. In 2002, the Environmental Protection Agency (EPA) requested that the responsible parties evaluate the health risks associated with VI at their former facilities. An indoor air sampling program was conducted between May and December 2003 to 1) identify vapor pathways, 2) measure TCE attenuation based on air samples; and, 3) evaluate the effects of ventilation at reducing vapor intrusion.

The investigation involved gathering site-specific information, baseline sampling, HVAC system modifications, and confirmation sampling. Sample location included indoors at pathways and breathing zones and outdoors at the HVAC intake. Twelve-hour time-integrated samples were collected in Summa canisters and analyzed by EPA Method TO-15 Selected Ion Monitoring (SIM) for the Site's groundwater constituents of concern.

Groundwater TCE concentrations ranged between 77 to 270 parts per billion (ppb). Baseline pathway air sample results indicated that subsurface TCE vapors could enter the building at concentrations two order of magnitude greater than those measured in the breathing zone. Differential pressure measurements taken prior to HVAC modifications indicated that the building was not under positive pressure. Following HVAC modifications, confirmation sample results indicated that ventilation had reduced TCE concentrations in pathway samples to the same level as indoor air breathing zone TCE concentrations. Differential pressure measurements taken during confirmation sampling indicated that the building was adequately pressurized.

The investigation concluded that indoor air TCE concentrations did not pose an unacceptable risk to tenants. Without proper ventilation and building pressurization, floor cracks could result in increased indoor air TCE concentrations. However, a properly operated ventilation system was an effective mitigation measure to prevent subsurface vapor intrusion.

Tuesday, October 19, 2004

Poster Session- Acid Mine Drainage

Acid Drainage from Rich-in-Pyrite Mining Wastes in a Uranium Deposit

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Acid Drainage from Rich-in-Pyrite Mining Wastes in a Uranium Deposit

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The uranium deposit Curilo, Western Bulgaria, for a long period of time was a site of intensive mining activities including both the open-pit and underground mining techniques as well as in situ leaching of uranium. The ore was rich in pyrite and, apart from uranium, contained several non-ferrous metals. The mining operations in the deposit were ended in 1990 but since that time the dumps consisting of mining wastes are, after rainfall, a large source of acid drainage waters. These waters have pH in the range of about 2 – 4 and contain radioactive and heavy metals (uranium, radium, iron, manganese, copper, zinc, cadmium, nickel, cobalt), arsenic and sulphates in concentrations usually 2 – 10 times higher than the relevant permissible levels for waters intended for use in the agriculture and/or industry.

The investigations carried out in the deposit revealed that the generation of the polluted waters was connected with the activity of the indigenous acidophilic chemolithotrophic bacteria, which oxidized the pyrite, other sulphides and uranium bearing minerals present in the dumps. Acidithiobacillus ferrooxidans and Leptospirilum ferrooxidans were the prevalent microorganisms of this group and their number usually exceeded 10^8 cells/g mining wastes. The growth and activity of these bacteria markedly depended on some essential environmental factors such as pH, temperature, and water, oxygen and nutrient contents in the dumps. These data will be used for development of technology to inhibit the microbial growth and activity and in this way to prevent the generation of polluted waters from the dumps.

Poster Session- Bioindicators of Environmental Health

Wildlife Indicators of Environmental Mercury Contamination: Results of a SETAC Workshop

E.J. Zillioux, M.F. Wolfe, D. Evers, T. Atkeson, W. Bowerman, J. Burger and M. Murray

Wildlife Indicators of Environmental Mercury Contamination: Results of a SETAC Workshop

E.J. Zillioux, M.F. Wolfe, D. Evers, T. Atkeson, W. Bowerman, J. Burger and M. Murray

A workshop was sponsored by the U.S. Environmental Protection Agency and the Electric Power Research Institute on 15-18 September 2003 to identify indicators and propose a monitoring plan to detect environmental changes in mercury inputs, particularly those from direct and indirect atmospheric deposition. The primary impetus for the project is to provide a basis for measuring anticipated reductions in Hg deposition expected to accrue in response to emerging regulatory source controls in the U.S. Four working groups included Indicators for Airsheds and Watersheds, Water Quality and Sediment Indicators, Aquatic Biota Indicators, and Wildlife Indicators. This poster will present issues and conclusions of the Wildlife Group.

Wildlife species are good indicators of the status of contaminants in the environment because they reflect not just the presence but the bioavailability and trophic proliferation of the contaminant of interest, integrate over time and space and between local and atmospheric sources, and respond to toxic insult in ways that are relevant to human health at both the whole organism and sub-organismal level. Selection of the best currently available indicators to detect mercury trends on a continental scale must consider geographical and habitat differences, methodological issues, host factors, strength and predictability of response, and the existence of a well-developed literature. The most useful indicators are those that have had the connections between exposure, effects and tissue residue concentrations clearly worked out through laboratory dose/response and field levels/effects studies. Selection criteria were developed that incorporate both these indicator-specific factors and the practical goal of detecting changes in mercury ecosystem proliferation on a broad scale that may result from regulatory control of mercury emissions. Wildlife indicators were then selected and ranked among taxonomic categories of birds, mammals and herptiles according to these criteria. Also considered were design factors for an indicator sampling network that would provide both quantitative trend detection and interpretation capabilities for mercury signals entering the environment both within North America and at global background sites.

Poster Session- Environmental Biotechnology

New Strategies for the Development of Environmental Biosensors

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New Strategies for the Development of Environmental Biosensors

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The environmental industry is now being impacted by a paradigm shift in analytical measurement that has been traditionally called the “bench to in-line shift”, but in reality is a “bench to biosensor shift”. The latter is tied to the recent biotechnology revolution and offers a promise for a host of “better, faster and cheaper” means of obtaining data in the field. Biosensors at their most fundamental level are small-scale binding reactions between a sensor molecule and the target analyte. The term biosensor is invoked here because the sensor molecule in our system is a DNA-protein complex that can react with the target analyte. These reaction chemistries are then coupled to special detection and signaling platforms. Regenesis has completed proof-of-concept work that shows it is possible to detect inorganic species, such as arsenic, at very low levels with minimal interference and with an output measured in a few minutes. This technology can be extended to other inorganic species, as well as organic molecules. Ultimately these devices will be conveniently field portable and hand-held.

A discussion of basic binding, specific detection, and signaling interactions will be discussed in contrast to current options. Eventually, the goal is to multiplex the system to give a suite of results at one time in the field as an alternative to expensive and time-delayed results that require off-site laboratory services. Currently, the value of individual contaminant tests is great as witnessed by the recent need for arsenic monitoring under the lowered U.S. drinking water standard (10 µg/L).

Poster Session- Heavy Metals

Treatment of Tungsten Contaminated Water using Ti-based Sorbent: Column Studies
Kruti Oza, Stevens Institute of Technology, Hoboken, NJ
Washington Braida, Stevens Institute of Technology, Hoboken, NJ
Christos Christodoulatos, Stevens Institute of Technology, Hoboken, NJ
Dimitris Dermatas, Stevens Institute of Technology, Hoboken, NJ
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Use of Silica-Supported, Modified Silica Based Reagents in the Remediation of Cadmium(II), Nickel(II), Silver(I) and Lead(II) Ions: An Environmental Cleanup Technology
Craig A. Bowe, Saint Leo University, Saint Leo, FL
Dean F. Martin, University of South Florida, Tampa, FL

Evaluation of Heavy Metal Availability in the Mining Areas of Bulgaria
Penka S. Zaprjanova, Institute of Tobacco and Tobacco Products, Markovo, Bulgaria
Violina R. Angelova, University of Agriculture, Plovdiv, Bulgaria
Krasimir I. Ivanov, University of Agriculture, Plovdiv, Bulgaria

Apatite from Different Natural Sources and its Suitability for Remediation of Contaminated Media
Anna S. Knox and D. I. Kaplan, Westinghouse Savannah River Company, Aiken, SC

A Metal Detector Study to Locate Inactive, Un-Maintained Small Arms Firing Range Impact Areas
W. Andy Martin, Applied Research Associates, Inc., Vicksburg, MS
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Average Particle Size Ratios and Chemical Speciation of Copper and Zinc in Road Dust Samples
Adnan M. Massadeh, Jordan University of Science and Technology, Irbid, Jordan
Qasem M. Jaradt, Mutah University, Al-Karak, Jordan

Management of Lead in Soil during Highway Construction or Urban Redevelopment Projects: A National Perspective.
Kathleen Sellers, PE, AMEC Earth and Environmental, Westford, MA
Maria Pologruto, AMEC Earth and Environmental, Westford, MA

The Pollution of Soils with Heavy Metals
Vasile Viman Ph.D, Anca Mihaly Cozmuta Ph.D, Gheorghe Vatca PhD., eng. Leonard Mihaly Cozmuta, Dorin Suticau, North University of Baia Msare, Baia Mare, Romania

Metals Remediation Compound (MRC™): A New Slow-Release Product for In Situ Metals Remediation.

Anna Willett, Regenesis, San Clemente, CA
Stephen S. Koenigsberg, San Clemente, CA

Roadside Accumulation of Heavy Metals in Soils in Franklin County, MA and Surrounding Towns

Trevor L. Woodard, University of Massachusetts, Amherst, MA
Dula Amarasiriwardena, Hampshire College, Amherst, MA
Baoshan Xing, University of Massachusetts, Amherst, MA

Effect of Sulfate and Phosphate on Adsorption of Molybdate and Tetrathiomolybdate by Pyrite

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Treatment of Tungsten Contaminated Water using Ti-based Sorbent: Column Studies

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Tungsten heavy alloys (WHA) are currently been considered for use in new munitions systems. Our research indicates that under common environmental conditions, metallic tungsten and WHA will dissolve resulting in tungsten dissolved concentration in the mg/l level. As a result of that, there is a potential need for development of remedial technologies addressing the removal of tungsten from contaminated aqueous streams. This research presents preliminary data on the use of an innovative Ti-based sorbent for the remediation of tungsten contaminated aqueous streams. Column studies were performed to assess the suitability of the sorbent and the influence of phosphate on tungsten uptake by the sorbent was also assessed. The sorbent proves to be successful in removing dissolved tungsten and other alloying elements (iron, copper). Phosphate anions appears to compete with tungsten for the active sites of the sorbent resulting in an early breakthrough of tungsten and diminishing sorbent's tungsten sorption capacity. Distribution coefficients for tungsten alone and in the presence of phosphate were estimated by fitting the 1D advection-diffusion model to the experimental data.

Use of Silica-Supported, Modified Silica Based Reagents in the Remediation of Cadmium(II), Nickel(II), Silver(I) and Lead(II) Ions: An Environmental Cleanup Technology

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The pollution of freshwater sources by dissolved heavy metals is a major environmental problem faced worldwide. Treatment of freshwater sources by treated silica based composites is an inexpensive, alternative environmental cleanup technology that is an emerging field. Previous work describing the use of silica-supported reagents has established the possibility of using known chelating agents supported on silica based support for the removal of such heavy metals as lead, cadmium, copper, silver, and nickel from aqueous media. Silica based materials are currently being used as a solid support for various straight-chain monofunctional and bifunctional compounds such as mercaptans and mercaptoalcohols. The use of mercapto alcohols which have been attached covalently to the silica matrix has also been investigated. The current study reports the results of an investigation involving the use of these composites in the removal of cadmium(II), nickel(II), silver(I) and lead(II) ions from standard aqueous solutions.

Evaluation of Heavy Metal Availability in the Mining Areas of Bulgaria

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An evaluation of content and availability of Pb Zn and Cd in mining regions of the East Rhodopes, Bulgaria was made. The preliminary survey showed that the soils in the evaluated region are heavily polluted by heavy metals (Pb - above 2000 mg/kg, Zn – above 1300 mg/kg and Cd - above 12 mg/kg). The data of the total content however does not provide enough information about the quantity of these heavy metals accessible and potentially available by plants. In order to clarify this question we defined the mobile forms of Pb, Zn and Cd with the help of various extragents (salts solutions, chelating stuff and weak acids), as well as their content in dominant grass species. It was established that despite the low pH values, the light mechanical composition and the weak humus content in the soils of the surveyed region, the part of the mobile forms of heavy metals is considerably below the expected. Only 15% of the total quantity of cadmium and 8 % of the total quantity of the Pb and Zn are potentially assimilable by plants. This was decisively confirmed as well by the analyses made on the plant samples. The obtained results are explained by the established fact that heavy metals in the surveyed region are found principally under the form of weakly soluble and difficult for assimilation by plants sulphides. The main conclusion is that the total heavy metal content cannot be used as an explicit criterion for ecological evaluation of soils with regard to their exploitation for agricultural activities.

Apatite from Different Natural Sources and its Suitability for Remediation of Contaminated Media

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Researchers have reported that apatite, a calcium-phosphate mineral, immobilized Pb and other ions such as Mn, Co, Cu, Cd, Zn, Mg, Ba, U, or Th in contaminated media. Immobilization of these elements occurs due to precipitation, adsorption and isomorphic substitution.

Nine commercially available phosphate minerals, representing >95% of the phosphate production in the country, were evaluated for suitability for remediation of contaminated media. The following were approaches will be addressed in this paper: solubility, concentration of trace metals, and leachability of trace metals. Processed and mined rock phosphate contain high total concentration of As, Co, Cr, Cu, and Sr, however, they did not exceed the RCRA TCLP limits. The use of stronger extractants indicated that these elements were very strongly bound by most apatite material; therefore, if they were applied to contaminated sediment at a rate sufficient for remediation, they would not increase environmental risk. The biogenic apatite (fish bone) contained significantly lower metal impurities than processed and mined rock phosphate and was appreciably more soluble, i.e., it had a $\log K_{sp}$ of -45.2 compared to -57.0 for the mined rock phosphate samples.

There are many phosphate sources that can safely and effectively be used in remediation of contaminated soils. By combining biogenic and mined phosphate it will be possible to obtain a wide range of phosphate solubility, permitting rapid immobilization of contaminants, while at the same time providing a slow release of phosphate for continued sediment treatment.

A Metal Detector Study to Locate Inactive, Un-Maintained Small Arms Firing Range Impact Areas

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Precise locations of older firing ranges at many military bases are often unavailable, because the records for training have either been destroyed or are vague and non-descriptive. We conducted an “environmental forensics study” of a 25-acre site at a large military facility in order to locate impact areas of a Thompson sub-machine gun range that was last used over 50 years ago. Preliminary assessment activities included historical map and aerial photography review, site visits, and interviews with range control personnel, which suggested sub-machine gun training in the general area. However, site visits did not indicate any visual features signifying range use, and the site had been overgrown with vegetation covering all traces of bullets. We used a Garrett Infinium metal detector to successfully locate several small impact areas. The impact rounds were identified, marked, and the location coordinates were identified using GPS. The study was completed in 4 days, and at a fraction of the cost of physical. The characterization will be used in future development of the site.

Average Particle Size Ratios and Chemical Speciation of Copper and Zinc in Road Dust Samples

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Road dust samples were taken from areas of high traffic flows in Irbid city; Jordan. A series of <90, 90-<106, 106-<125, 125-<250, 250-<1000 and 1000-< 2000 μm of road dust particle size fractions were investigated throughout to evaluate the ratio between metal content in each particle size fraction and total metal contents. Atomic absorption spectrometry technique was used throughout. Sequential procedure was used for chemical speciation in road dust samples of <90μm. This procedure permits a reproducible evaluation of the partitioning of Cu and Zn among the various chemical forms in which they are present in street dust.
Two reference standard materials BCR-CRM 142R and NIST-SRM 2709 were tested to validate the proposed method. Results show that there was no significant between the measured values for Cu and Zn and their certified values with RSD of less than 5%.

Keywords: copper, zinc, chemical speciation, road dust, atomic absorption spectrometry.

Management of Lead in Soil during Highway Construction or Urban Redevelopment Projects: A National Perspective.

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Construction crews working in industrialized areas often encounter lead contamination in soil. Although lead is a naturally occurring element found in small amounts everywhere, the soil near heavily-used streets and roads has typically accumulated lead in excess of natural levels due to the historic use of anti-knock lead compounds in gasoline and the use of lead tire weights. Other sources of lead in surface soil include lead-based paint and crude oil/gasoline at ambient levels. Lead may pose a public health threat if leached into groundwater or ingested by children. The need to manage lead-contaminated soil appropriately can add significantly to a construction project's cost and schedule. Different states and highway authorities address this problem differently. The authors will review the criteria, guidelines and case studies established in several states, including California, Michigan, New Jersey, and Massachusetts. Common themes and practical insights will be discussed in the paper.

The Pollution of Soils with Heavy Metals

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In areas where have been developed ores extraction activities, theirs processing in order to obtain the contented metals produces the pollution of air, waters and soils with sedimentable powders which contain heavy metals.

In searched area the ores contain Pb, Cu and Zn as major components and Cd, Au, Ag as minor or traces components.

Extracted ores are up-graded by flotation and the resulted concentrates are processed pyrometallurgical in order to obtain Pb, Cu Zn or hydrometallurgical to Au obtain. All these stages are potentially soil pollutant sources because of waste dumps generated by the mines, waste waters coming from flotation process and suspensions or sedimentable powders from pirometallurgy.

In order to evaluate the soil's pollution level with heavy metals were established the points for collection the samples placed at different distances from pollutant sources. The samples were collected from surface and both 20 and 30 cm depth of the soil.

A weight of 0.1 – 0.2 g of each dried and calcinated sample was dissolved using the acid disintegration in a microwave oven. The obtained solutions were diluted with bi-distillated water and analyzed using ICP-AES method.

The obtained concentrations are in range 420-5121 ppm for Pb, 151-992 ppm for Cu and 371-3122 ppm for Zn.

Based in these results can be noticed a decrease of concentrations of elements with the increase of distance from the pollutant sources. Near the sources the concentrations of heavy metals exceed the maximum admitted limits and the variation with depth are irregular.

The types of chemical combinations of metals and the properties of soil as pH, texture, structure, ionic exchange capacity, permeability and size of particles both influence the mobility of heavy metals in soil.

High pollution level of soils has negative consequences of crops that can be decreased up to 50%. Also, the losses in the forestry are around 40%, because of low quality of wood. Indirectly are affected the human health because the pollution affects the plants and animals used in food industry.

Metals Remediation Compound (MRC™): A New Slow-Release Product for In Situ Metals Remediation.

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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 MRC's ester bonds 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. Results from these laboratory investigations and field applications will be presented.

Roadside Accumulation of Heavy Metals in Soils in Franklin County, MA and Surrounding Towns

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Metals play an important role in the environment. However, some metals can build up to levels in soils toxic to biota. This is thought to be the case with a number of metals increasingly found in roadside soils, most likely due to anthropogenic activities. Soil samples were collected along roads in towns in Franklin County, MA (including some adjacent towns). This was done by sampling local sites in triplicate of soil 0.5 meters from the edge of the road and 10 to 15 centimeters deep (a mix of A and B horizons). Descriptions of the road (paved or dirt) and car counts (to evaluate use) were done. Four sites were in natural areas and represent non-polluted soils. Soils analyzed were sequentially extracted into five phases (exchangeable, carbonate, Fe/Mn oxides, organic matter, and residual) for inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis for V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pd, Cd and Pb. Results should indicate soil fertility, anthropogenic accumulations of heavy metals and their bioavailability, and the potential need for remediation. Preliminary results indicate increased Pb along high-traffic areas.

Effect of Sulfate and Phosphate on Adsorption of Molybdate and Tetrathiomolybdate by Pyrite

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Molybdenum enrichment has been used as an accepted indicator for the presence of sulfidic, anoxic conditions or reduction condition during sediment deposition and genesis. To understand the mechanisms involved in retention by pyrite (FeS_2) of two major molybdenum species, molybdate (MoO_4^{2-}) and tetrathiomolybdate (MoS_4^{2}), within natural anoxic environments, batch experiments were performed using of MoO_4^{2-}- and MoS_4^{2-}- pyrite suspensions in 0.1M NaCl under anoxic conditions. The pH range covered was from 3 to 10 and all experiments were performed at 25°C. The effects of sulfate and phosphate on the adsorption of MoO_4^{2-} and MoS_4^{2-} by pyrite were also studied. The results showed that MoO_4^{2-} and MoS_4^{2-} adsorption obeyed a Langmuir model at low pH. MoS_4^{2-} adsorbed strongly in the pH range from 3 to 5 while MoO_4^{2-} presents a maximum adsorption at pH 4.5, and decrease rapidly with increasing pH with complete desorption after pH 7. On the other hand, 30% of the MoS_4^{2-} remained sorbed at pH values as high as 10. The adsorption of MoO_4^{2-} and MoS_4^{2-} decreased moderately with the addition of phosphate. The degree of reduction of MoS_4^{2-} adsorption is lower than MoO_4^{2-}, which suggests that MoS_4^{2-} likely forms strong inner-sphere complexes. Sulfate and silicate had a negligible effect on the adsorption of MoO_4^{2-} and MoS_4^{2-}.

Poster Session-Indoor Air

Comparison of Measured Indoor Air Concentrations and Site-specific Modeling with EPA Guidance

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Amy Sidell, Philip Services Corporation, Kent, WA

Site-Specific Modeling of Vapor Intrusion at a Former Co-Disposal Landfill Site in Ohio

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Steven M. Harris, Conestoga-Rovers & Associates, Waterloo, ON
John A. Buyers, Conestoga-Rovers & Associates, Waterloo, ON

Johnson & Ettinger Model Validation with Soil Gas Sampling

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Comparison of Measured Indoor Air Concentrations and Site-specific Modeling with EPA Guidance

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PIONEER Technologies Corporation (PTC) teamed with Philip Services Corporation (PSC) to evaluate the Vapor Intrusion (VI) Pathway at PSC's Georgetown Facility in Seattle, Washington. The facility is located in a mixed (residential and commercial) neighborhood and has an off-site groundwater plume containing volatile organic compounds (VOCs) in the water table sample interval, which is approximately seven to fifteen feet below ground surface. PSC has conducted co-located multi-media sampling (indoor air, ambient air, sub-slab soil gas, and groundwater) at twenty-five commercial and residential locations between August 2002 and February 2004.

The sample collection procedures and analytical procedures used for all sampling events have been approved by the regulatory agencies involved, as well as the consulting firm representing local residents. Groundwater samples were collected primarily using direct push technology. Air samples were collected over 24 hours using 6 Liter (L) Summa® canisters. A complete building survey was performed prior to collecting all samples. A professional data validator has validated all data and a rigorous CLP-style Quality Assurance/Quality Control (QA/QC) review was performed on at least 10 percent of all analytical data.

Trichloroethylene (TCE), benzene, ethylbenzene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene are consistently found in both indoor air and ambient air and results show a good correlation between indoor air and ambient air. This indicates that ambient air concentrations have a significant impact on indoor air concentrations. None of the analytes showed a good correlation between soil gas and indoor air, because of lack of detection in soil gas or inconsistent results with soil gas and indoor air.

Data selected for comparison with modeling approaches were detected in both groundwater and indoor air during co-located sampling events. Both measured indoor air concentrations and corrected indoor air concentrations (i.e., measured indoor air values corrected for ambient air) were compared with predicted indoor air using: 1) EPA's default attenuation factors (AFs) provided in Figure 3 of the November 2002 VI Guidance, 2) site-specific parameters in the Johnson and Ettinger Model (EQM, 2003) and 3) Washington State Department of Ecology-approved site-specific groundwater-to-indoor-air-volatilization-factor (GIVF) developed for the Georgetown site using results from multi-media sampling.

Preliminary results show corrected indoor air values (corrected for ambient air) to be in general agreement with values predicted using both the site-specific GIVF and site-specific JEM. Indoor air values predicted using EPA's attenuation factors from Figure 3 are over 2 times the corrected measured values and site-specific modeled values.

Site-Specific Modeling of Vapor Intrusion at a Former Co-Disposal Landfill Site in Ohio

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A site-specific modeling analysis of vapor intrusion was conducted within the larger scope of a CERCLA RI/FS being undertaken at a 100-acre former co-disposal landfill site in Ohio. The site is located in a mixed urban, commercial, industrial, and residential area on a relatively flat parcel of land that has experienced considerable grading and filling associated with historic gravel mining and landfilling operations. Concentrations of volatile organic compounds (VOCs) in soil vapor samples collected at the site perimeter exceeded conservatively calculated preliminary remediation goals. Based on that observation, the site work plan required that the vapor intrusion into indoor air pathway be evaluated. A site-specific modeling analysis of vapor intrusion was conducted using the Johnson and Ettinger (1991) subsurface vapor intrusion model (J&E Model). The modeling analysis used a combination of measured input data and default input data. Default inputs were obtained from USEPA's November 2002 Draft Subsurface Vapor Intrusion Guidance where the measurement of these data was impractical. The site-specific modeling analysis was conducted in conjunction with a combined soil vapor and indoor air sampling program at 13 residential buildings adjacent to site. The site-specific J&E Model analysis involved estimating soil vapor attenuation factor values from the mid-point of soil vapor probes installed adjacent to basement foundations (at an average separation distance of 0.55 metres below the basement floor). The soil vapor and indoor air sampling program did not indicate any correlation between contaminants detected in soil vapor and indoor air confirming that the site was not impacting the indoor air quality of the adjacent residential buildings. The results of the J&E Model analysis are presented below, including a comparison of the average calculated site-specific soil vapor attenuation factor value to the attenuation factor values presented in Figure 3a of the Draft Subsurface Vapor Intrusion Guidance.

Sampling Design/Sample Representativeness, and Sampling and Analysis QA/QC

Indoor air samples were collected on the lowest floor of each residence (11 basement samples and 2 ground floor samples) using SILCO canisters equipped with regulators calibrated to collect the samples over a 24-hour period. Soil vapor samples were collected from permanent soil vapor probes installed immediately adjacent to each residence (on the side closest to the landfill) and screened over a depth of 5 to 10 feet below ground surface. The soil vapor probes were installed using a direct-push method, constructed of ¾-inch diameter PVC materials, with the uppermost 2 feet of the annulus sealed using bentonite. Prior to sample collection, each probe was purged of a least 2 volumes at a rate of 250 mL/min using a personal air sampling pump. Following purging, soil vapor samples were collected in SILCO canisters equipped with critical orifice devices calibrated to collect the samples at a rate of 250 mL/min (i.e., 24 minutes to fill a 6L canister).

Field QC sampling included collection of duplicate samples at a rate of 1 per 10 investigative samples. The quality assurance evaluation criteria used to assess the data were established by the method, and included review of holding time periods, instrument performance check data, initial and daily calibration data, method blank sample data, internal standards data, surrogate compounds data, laboratory control sample/laboratory control sample duplicate data, field duplicate data, and completeness. The data were found to be suitable for their intended use with minimal qualifications.

Tabulation of Site Conditions Used in the J&E Modeling

As identified above, site-specific measurements were used as inputs for many parameters in the J&E Model analysis. Vadose zone soil (consisting of a sand and gravel) properties were average values determined from several dozen vadose soil samples collected during the RI. Building properties were average values determined through interviews with residents as well as physical measurements taken at each residence. Below grade building surface area and building volume were determined by physical measurements of the lowest floor of each residence and measuring the floor depth below outside ground surface. It was anticipated that the foundation thickness would be measurable by examining sumps; however, such measurements were not possible in practice because sump construction (where present) was such that the floor thickness was not visible. Also, no residents were aware of the thickness of their basement floor, other than to comment that it is likely compliant with the minimum of 4 inches required by the local building code. The distance from the building floor to the soil gas impact was calculated to be 0.55 metres (1.79 feet) by subtracting the average depth of basement floors below ground surface (5.38 feet) and the average thickness of basement floors (4 inches) from the midpoint (7.5 feet) of the adjacent gas probe screen (i.e., 7.5 feet – 5.38 feet – 4 inches = 1.79 feet = 0.55 metres). The vadose zone/building pressure differential was measured using an AXD550 digital manometer which measured the pressure differential (at a resolution of 0.5 Pa) between the gas probe adjacent to each residence and the pressure in the basement (or ground floor) of each residence by routing a pressure line into the residence through a slightly opened door. The pressure differential measurements ranged from a low of 0.0 Pa to a high of 3.5 Pa (i.e., soil vapor pressure equal to or higher than indoor air). The input parameter values used in the J&E Model analysis were as follows:

Parameter	Value Used	Source
Vadose Zone Soil Properties		
soil moisture content	6.1%	average of numerous site-specific measurements
porosity	39%	average of numerous site-specific measurements
dry bulk density	1.69 g/cm^3	average of numerous site-specific measurements
hydraulic conductivity	3.1x10^{-2} cm/s	average of numerous site-specific measurements

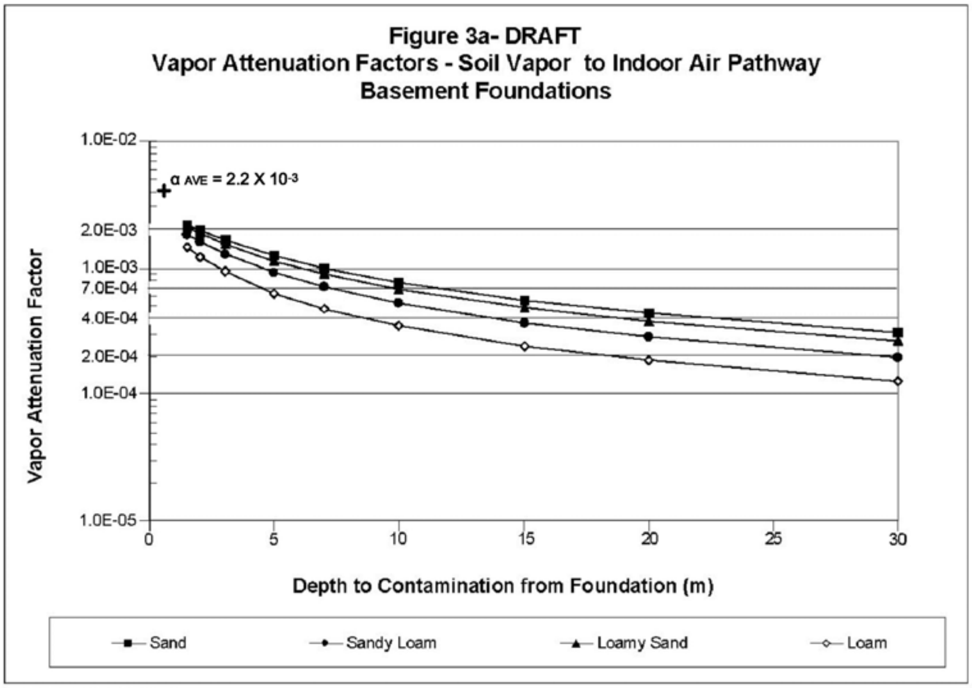
Building Properties	Value Used	Source
below grade building surface area	136 m^2	average of 13 site-specific measurements
building volume	165 m^3	average of 13 site-specific measurements
indoor air exchange rate	0.5 ac/hr	mean exchange rate after USEPA (2002; Appendix G)
foundation thickness	10 cm	site-specific building code
distance to soil gas impact	0.55 m	site-specific average
ratio of crack area	0.02%	default presented in USEPA (2002; Appendix G)
vadose zone/building pressure	1.5 Pa	average of 13 site-specific measurements

Site-Specific J&E Model Results and Data Evaluation

The attenuation factors for each VOC are dependent on chemical-specific properties, but on average, the J&E Model yielded a site-specific soil vapor attenuation factor value of $2.2\text{x}10^{-3}$ using the above inputs. Individual modeled attenuation factors for selected parameters were as follows: benzene (2.4×10^{-3}), tetrachloroethene (2.2×10^{-3}), trichloroethene (2.3×10^{-3}), cis-1,2-dichloroethene (2.3×10^{-3}), 1,2-dichloroethane (2.5×10^{-3}), and vinyl chloride (2.5×10^{-3}).

Figure 3a of USEPA's Draft Subsurface Vapor Intrusion Guidance presents soil vapor attenuation factor values for differing soil types at a minimum depth to contamination of 1.5 metres, which is deeper than the 0.55 metres modeled above. Extrapolating the Figure 3a "Sand" curve to a depth of 0.55 metres shows that the average site-specific attenuation factor presented above compares favorably with Figure 3a (see below). The average site-specific attenuation factor might be slightly higher than that predicted by extrapolating the "Sand" curve of Figure 3a, however, this may be attributed to the fact that the site-specific modeling was based on more permeable sand and gravel rather than the sand applied in the development of Figure 3a.

The soil vapor and indoor air sampling program did not indicate any correlation between contaminants detected in soil vapor and indoor air confirming that the site was not impacting the indoor air quality of the adjacent residential buildings.



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Johnson & Ettinger Model Validation with Soil Gas Sampling

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USEPA and PADEP Guidance for vapor intrusion evaluations includes the options of both modeling and sampling to support risk assessments from the vapor intrusion pathway. This poster provides a summary of the modeling effort to evaluate potential off-site health risks to neighbors at an industrial facility. Groundwater in the shallow bedrock aquifer is contaminated with low levels of trichloroethylene, tetrachloroethylene, and chloroform. Soil is not contaminated. Exposure to residents in homes above the groundwater plume (depth of 20 ft bgs) was modeled using the Johnson & Ettinger Advanced Groundwater Model to predict indoor air concentrations of the constituents as they migrate in the unsaturated zone through a building foundation into a basement. Results indicate that predicted indoor air concentrations do not pose an unacceptable risk to the facility's neighbors from the vapor intrusion pathway. In an effort to validate this modeling, soil gas sampling was undertaken in the location of maximum groundwater concentration at two discrete depths (5 ft and 15 ft) and during two seasons (winter, spring) in accordance with USEPA and PADEP Guidance (and with their approval of the workplan). All soil gas samples were less than PADEP risk-based medium-specific concentrations for soil gas, confirming the risk evaluation. Additionally, a comparison of modeled versus measured attenuation coefficients indicated relatively good agreement with the model. Trichloroethylene and chloroform attenuation was underpredicted by the model (the model predicting higher concentrations by a factors ranging from 7 to 26 times). Tetrachloroethylene attenuation was overpredicted by the model with the model predicting 16 to 27 times lower concentrations than measured.

Poster Session- Phytoremediation

Development of a Genetically Engineered Seaweed That Can Detoxify TNT in Marine Waters
Paula Bernasconi and Donald Cheney, Northeastern University, Boston, MA
Tavi Cruz-Uribe and Gregory Rorrer, Oregon State University, Corvalis, OR
Neil Bruce, University of York, York, United Kingdom

Metabolism and Breakdown of Methyl Tertiary Butyl Ether in Phytoremediation
Robert H. Kim, Savannah River Ecology Laboratory, Aiken, SC
Lee A. Newman, University of South Carolina, Columbia, SC /Savannah River Ecology Laboratory, Aiken, SC

Plant Response and Accumulation of Lead, Cadmium, and Barium from a Superfund Site Soil
Quentin M. Flory, Ball State University, Muncie, IN
John Pichtel, Professor, Ball State University, Muncie, IN

Development of a Genome-wide Screening Method to Identify Gene Candidates Involved in the Degradation of Halogenated Hydrocarbons Using Ion Chromatography
Sarah Strycharz, University of South Carolina, Columbia, SC
Lee Newman, University of South Carolina, Columbia, SC and Savannah River Ecology Lab, Aiken, SC

Comparison of Native Southeastern Conifers to Hybrid Poplar for Suitability to Phytoremediate Trichloroethylene
Sarah Strycharz, University of South Carolina, Columbia, SC
Daniel Heenan, University of South Carolina, Columbia, SC
Lee Newman, University of South Carolina, Columbia, SC and Savannah River Ecology Lab, Aiken, SC

Phytoremediation to Oil Contaminated Wetland Soil Treatment by Aquatic Plant (*Typha orientalis* Presl)
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Hung-Ta Lin, Sun Yat-sen University, Kaohsiung, Taiwan
Lei Yang, Sun Yat-sen University, Kaohsiung, Taiwan

Development of a Genetically Engineered Seaweed That Can Detoxify TNT in Marine Waters

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2,4,6-Triitrotoluene (TNT) is one of the most recalcitrant and toxic of all military explosives. It occurs in coastal sites as a result of leakage from exploded and unexploded ordinance as well as runoff from firing ranges and munition dumps on land. Current methods for eliminating toxic compounds like TNT from contaminated waters and sediments involve dredging and disposal, and are extremely costly and potentially harmful to the environment. This project's goal is to develop a strain of seaweed capable of "phycoremediating" TNT in marine waters. Our model seaweed is a fast-growing, fast-reproducing strain of the red marine macroalga Porphyra yezoensis, which we genetically transform using a strain of Agrobacterium tumefaciens carrying the plasmid pNITRED3. This plasmid carries the bacterial nitroreductase gene, nfsI. Preliminary toxicity experiments determined that a TNT concentration of 5 mg/L could be used for isolating single lines of TNT-tolerant plants. Several lines have been produced which demonstrate a striking ability to take up, tolerate and detoxify TNT in seawater. One line, for example, can completely remove 10mg/L TNT from seawater in less than 3 days and still grow, whereas wild-type plants stop photosynthesizing and die. The presence of the nfsI transgene has been confirmed using PCR probes and has been shown to be both inheritable and stable (i.e. present through at least the T3 generation and inherited in the absence of selection). In addition, the products of TNT reduction by nitroreductase have been detected. This research is supported by a grant from the Office of Naval Research.

Metabolism and Breakdown of Methyl Tertiary Butyl Ether in Phytoremediation

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Since 1979, EPA has mandated the use of octane boosters in gasoline to improve fuel efficiency and reduce atmospheric pollutants. While many organic compounds were originally tried as replacements for lead, methyl tertiary butyl ether (MTBE) was the compound that had the most widespread use due to its ease of mixing with gasoline. However, MTBE releases into the environment have moved EPA in the opposite direction with MTBE tentatively planned to be phased out nation-wide as a gasoline additive by 2015 in accordance with the National Energy Bill. As of January 1, 2004, MTBE is no longer used as an additive in California.

MTBE releases to the environment have proven to be much more problematic than gasoline or BTEX compounds. MTBE in water moves rapidly through the soil column and then tends to continue moving with the aquifer. This characteristic of MTBE has led to wide-scale aquifer contamination and, in many places, an inability to determine the exact source of MTBE contamination due to the size of the plumes and the possibility of multiple sources.

Remediation of MTBE is problematic due to this high degree of solubility; air stripping is much more energy-demanding as MTBE prefers to stay in the aqueous phase. Due to its chemical structure, biodegradation is not common and often requires injection of one of the few isolates that have been shown to degrade MTBE. Phytoremediation has shown some promise as a remediation technique for MTBE. Plants that have been studied (poplar, eucalyptus, pine) all take up MTBE readily from soil or water. The problem with regulator acceptance of phytoremediation as an MTBE solution is that there is no indication as to the fate of MTBE when taken up by plants. Previous studies have shown that MTBE is taken up by plants and is transpired through the leaves. Additionally, cell culture studies have shown limited metabolism to carbon dioxide (CO_2). Studies have demonstrated that volatile organic compounds (VOC's), such as MTBE, are released through the stems of plants exposed to those VOC's. None of these studies, however, addressed the problem of MTBE metabolism and metabolites in plants. It is known that MTBE self-degrades into tertiary butyl alcohol (TBA) in water and can also be broken down into TBA in metabolic pathways by the MTBE 3-monooxygenase enzyme. TBA is also a toxin of concern so breakdown of MTBE into TBA is not necessarily beneficial unless this is further metabolized into less toxic compounds.

Research presently in progress at The University of South Carolina and The Savannah River Ecology Laboratory is focusing on the uptake and metabolism of MTBE in hydroponically grown sterile tobacco plants. A series of laboratory studies are planned which include the hydroponic dosing of sterile tobacco seedlings with MTBE. Preliminary results have shown the presence of MTBE and TBA in the tobacco seedlings after 24 hours of dosing.

Planned studies include both hydroponic and soil-based exposure of plants to MTBE and tissue analysis of a variety of plants to identify metabolites. Sterile plant cell cultures and will be performed in an attempt to separate out the role of the plants versus the plant rhizosphere bacteria. Field sampling of plants will be performed and tissues analyzed for metabolites, transpiration, and volatilization through the trunks and stems of mature plants.

The results of this study could lead to increased regulatory acceptance of phytoremediation as a viable strategy for treating MTBE-contaminated aquifers. Being able to predict and monitor the fate of MTBE in plant systems may lead to greater implementation of this technology.

Plant Response and Accumulation of Lead, Cadmium, and Barium from a Superfund Site Soil

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The ability of green plants to extract lead (Pb), cadmium (Cd), and barium (Ba) from a Superfund soil in Indiana was studied in the greenhouse and in the field. In the greenhouse, maize (*Zea mays)*, soybean (*Glycine max)*, Indian mustard (*Brassica juncea*), and sunflower (*Helianthus annuus*) were grown on soil containing average Pb, Cd, and Ba concentrations of 29,000, 3.9, and 1100 mg/kg, respectively. All species were capable of both accumulating and distributing soil Pb to upper plant parts. Addition of diethylenetriaminepentaacetate (DTPA) and dilute HNO_3 augmented Pb phytoextraction. No species extracted soil Ba and some extracted trace Cd into various plant parts. Metal uptake was partly a function of the forms occurring in the soil. For example, tissue Pb correlated with soluble and exchangable soil Pb concentrations. Significant ($p<0.05$) differences were measured in chlorophyll a, chlorophyll b, and carotenoid concentrations with regard to treatment. Chlorophyll content in *G. max* was particularly affected by soil Pb concentration. In a column study, significant ($p<0.01$) differences in Pb mobility were measured with regard to both treatment and time. Scanning electron microscopy/energy dispersive x-ray analysis indicated Pb accumulation in discrete aggregates on both leaf and root tissue. Field plots were established at the Superfund site, treated with a mixed NPK fertilizer, ethylenedinitrilotetraacetic acid (EDTA), dilute HNO_3, or a mixture of EDTA and acid. Plots were seeded with mixed grasses (*Festuca*, *Poa*, *Phleum*) and redclover (*Trifolium pratense*). Preliminary results indicate that soil Pb and Cd tended to accumulate in roots with variable translocation to upper plant parts. Barium uptake from the soil was negligible for all treatments. Dry matter production was greatest for the NPK treatment and lowest for the EDTA + acid treatment. No significant leaching of Pb, Cd, or Ba occurred in any treatment.

Development of a Genome-wide Screening Method to Identify Gene Candidates Involved in the Degradation of Halogenated Hydrocarbons Using Ion Chromatography

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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). TCE and ethylene dibromide (EDB) are both metabolized by the same primary enzyme in humans, cytochrome P450 2E1. Other potential enzymes that may be involved in TCE degradation in plants include additional cytochrome P450s, peroxidases, dehalogenases, laccases, and reductases. In order to screen for multiple enzyme types, we have developed an assay in which bacterial cultures expressing a commercially purchased tobacco leaf (*Nicotiana tabacum*) cDNA library can be examined for the ability to degrade a halogenated hydrocarbon, EDB. EDB is being used instead of TCE as the bromide ion (Br-) is not prevalent in culture media whereas chloride ion (Cl-) can be found at high levels. Following 72 hours of growth to high density, cultures are concentrated and resuspended in a phosphate buffer containing glucose and 100 ppm EDB. Degradation of EDB is measured by detection of Br- release using an ion chromatograph. We hope to narrow the number of possible candidate genes by comparing the ability of cDNA library cultures to degrade EDB, with the ability of a control culture expressing a gene known to degrade EDB.

Comparison of Native Southeastern Conifers to Hybrid Poplar for Suitability to Phytoremediate Trichloroethylene

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Phytoremediation of trichloroethylene (TCE) from contaminated groundwater has been extensively studied using the hybrid poplar tree (*Populus spp.*). Hybrid poplars are capable of rapid growth in which they take up large quantities of water and also possess the capacity to effectively metabolize TCE. Several metabolites of TCE have been identified in the tissue of poplar including trichloroethanol (TCEOH) and di- and trichloroacetic acids (DCAA, TCAA). This study follows a greenhouse-based comparison of four different native Southeastern conifers to a hybrid poplar species for the ability to take up and degrade TCE. Longleaf pine (*Pinus palustris*), Leyland cypress (x *Cupressocyparis leylandii*), two varieties of Loblolly pine (*Pinus taeda*), and hybrid poplar species OP-367 (*Populus deltoides x P. nigra*) were examined for the concentration of TCE and its metabolites in their tissue using gas chromatography following treatment with either a low dose of TCE (50 ppm) or a high dose of TCE (150 ppm) for two months. The amount of water taken up, height of the tree, TCE transpiration, and total fresh weight were also recorded. Our goal is to expand the effectiveness of phytoremediation in combination with land reclamation by supplying the option of creating a heterogeneous forest system for contaminated groundwater treatment.

Phytoremediation to Oil Contaminated Wetland Soil Treatment by Aquatic Plant (*Typha orientalis* Presl)

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Oil contaminated on land was occurred via oil transportation, oil spills or producing sites in many countries of the world. Physically removing oil can also result in more ecological and physical damages than using natural treatment processes. The objectives of this study were to determine the potential of phytoremediation for diesel contaminated wetland soil, to compare aquatic plant (*Typha orientalis* Presl) presence or absence of soil microbial activity, and to determine the fertilizer in enhancing phytoremediation induced oil degradation. After 75 days incubated inside a greenhouse, the degradation rate TPH-D in wetland system planted with *Typha orientalis* Presl was measured equal to 70% at day 45, while the control system without vegetation was measured equal to about 60%. Thus, it was concluded that the wetland systems with vegetation could enhance the microbial activity on the rhizosphere of wetland plants, which would help to biodegradate the TPH-d in wetland soil contaminated by oil spills.

Poster Session- Radionuclides

Influence of Home Size on the Risks from Soil-Gas and Waterborne Indoor Radon

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Douglas Mose, George Mushrush, Center for Basic and Applied Science, Culpeper, VA

Development of Radon Enrichment in Soil Gas over Quartz-Mica Schist in Virginia

Charles Chrosniak, Paul DiBenedetto, George Mason University, Fairfax, VA
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Influence of Home Size on the Risks from Soil-Gas and Waterborne Indoor Radon

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In a recent study of @ 1000 homes in Virginia and Maryland, three month measurements of airborne radon derived from soil gas combined with indoor radon derived from potable water in the home ranged from @ 1-40 pCi/L. The radon in well water ranged from @ 100-8,000 pCi/L; the radon in reservoir water was less than 100 pCi/L. In a study set composed of small homes using well water, the indoor (airborne) radon concentration was related to waterborne radon concentration. Intermediate size homes showed a weaker correlation, and large homes did not show an airborne verses waterborne correlation. In the study set of all the homes using reservoir water (no waterborne radon), the indoor radon concentrations were not found to be correlated with home size. In terms of the risk of developing lung cancer, the greatest risk is experienced by people using well water while living in small homes.

Development of Radon Enrichment in Soil Gas over Quartz-Mica Schist in Virginia

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A major portion of northern Virginia is underlain by a quartz-muscovite soil, approximately 10 meters thick, that has developed on a bedrock of polymetamorphic schist. The schist formed from an ancient clay-rich sediment, subsequently recrystallized several times as the modern Appalachian rocks were heated deep in the Earth, and subsequently exposed by erosion. The total-gamma radioactivity and the permeability of the schist are higher than average, and combine to generate a radon-rich soil-gas that can be brought into homes by the pressure differential normally present in the local homes that commonly are well-insulated and have basements. More than half of the homes, based on three-month measurements, exceed the U.S. Environmental Protection Agency recommended maximum for indoor radon of 4 pCi/L. Fortunately, while the area is experiencing a rapid increase in new home construction, it is possible to avoid areas of high soil-gas radon and high permeability, and to use home construction methods that can reduce soil-to-home movement of radon emanating from the soil.

Poster Session- Remediation

Use of Organoclay at Military Installations
George Alther, Biomin, Inc., Ferndale, MI

A Proposed Geochemical Barrier to Reduce Phosphorus Loading to a Kettle Hole Pond
Jonathan G. Blount, CH2M Hill, Otis-ANG Base, MA
Jon Davis, Air Force Center for Environmental Excellence, Otis-ANG Base, MA

DNAPL Remediation Combining Thermal Extraction and Reductive Dechlorination
Rob Bogert, P.E., BEM Systems, Inc., Orlando, FL
Harlan Faircloth, BEM Systems, Inc., Orlando, FL
Phil LaMori, BEM Systems, Inc., Orlando, FL
Mark Kershner, Patrick AFB, FL

An Overview of the Hydraulic Testing of the Final Fuel Spill-1 Remedial System Design at Massachusetts Military Reservation
Ronald J. Citterman, CH2M Hill, Otis ANGB, MA
John Glass, CH2M Hill, Herndon, VA
Frank Lewis, CH2M Hill, Englewood, CO
Jason Dalrymple, CH2M Hill, Otis ANGB, MA
Paul Clement, CH2M Hill, Albuquerque,
John Schoolfield, Air Force Center for Environmental Excellence, Otis ANGB, MA

Methodology for Integrating Direct Sensing Tools With In-Situ Remediation Injection Technology to Facilitate Effective Treatment of Groundwater
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Todd Hanna, Vironex, Inc., Santa Ana, CA
Frank Stolfi, Vironex, Inc., Santa Ana, CA

Pilot Engineered Wetland for Treatment of Dilute Waste Streams
M. Talaat Balba, Darlene Coons, Sophia Dore, Alan Weston, CRA, Inc., Niagara Falls, NY

Cyclodextrin Enhanced Remediation at Patrick Air Force Base, Florida
Harlan Faircloth, BEM Systems, Inc, Orlando, FL
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Installation Methods for Subsurface Placement of EHC™ (Solid) and EHC-L™ (Liquid) Amendments

David Hill, Adventus Remediation Technologies Inc., Mississauga, Ontario, Canada
James Mueller, Adventus Americas Inc., Bloomingdale, IL
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Joanna Moreno, Adventus Americas Inc., Denver, CO
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In Situ Flushing Selective Phase Transfer Technology (SPTT$^{\text{TM}}$) Cost Effective Soil & Groundwater NAPL Remediation Including NAPL and Chlorinated Solvents

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Monitoring Improvement in Water Quality Following Reclamation of Acidic Coal Refuse with Biosolids

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Thomas C. Granato, MetropolitanWater Reclamation District of Greater Chicago, Cicero, IL
Richard. I. Pietz, MetropolitanWater Reclamation District of Greater Chicago, Cicero, IL
Carl Carlson, Jr, MetropolitanWater Reclamation District of Greater Chicago, Cuba, IL

Composition, Peculiarities and Methods of Utilization of Oil Wastes

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E.K. Ongarbayev, Al-Farabi Kazakh National University, Almaty, Kazakhstan

Reductive Dechlorination of Solvents in Groundwater using Controlled Release Carbon with ZVI

James Mueller, Adventus Americas Inc., Bloomingdale, IL
Scott MacFabe, Malcolm Pirnie, Inc., Schaumburg, IL
John Vogan, Michael Duchene, EnviroMetal Technologies, Inc., Waterloo, Canada
Alan Seech, David Hill and Kerry Bolanos-Shaw, Adventus Remediation Technologies Inc., Mississauga, Canada

Modeling the Market for Long-Term Monitoring

Carlos Pachon, U.S. EPA Office of Superfund Remediation & Technology Innovation, Washington, DC
Danielle Gratton, Tetra Tech EM Inc., Reston, VA
Sashi Vissa, Tetra Tech EM Inc., Reston, VA
Peter Shields, Tetra Tech EM Inc., Reston, VA

Design/Build of an Emergency Multiphase Extraction System

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

Overcoming Site Challenges to Optimize an Inactive LNAPL Containment & Recovery System

Frank Ricciardi, Weston & Sampson Engineers, Inc., Peabody, MA
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Useful Design and Cost-Estimation Tool for Air Handling Systems on Temporary Structures for MGP Sites

Anthony Mazzoni, TIGG Corporation, Bridgeville, PA
John Sherbondy, TIGG Corporation, Bridgeville, PA

Optimization of a Pump and Treat System at the Massachusetts Military Reservation

Nigel Tindall, CH2M HILL, Otis ANG Base, MA
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Evaluating Monitored Natural Attenuation as a Possible Remedial Technology on a Contaminated Site

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Use of Organoclay at Military Installations

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Organoclays have been used as a pre-polisher for activated carbon, or post-polisher for oil/water separators and DAF units, for the removal of small amounts of oil, grease, PCB, PNA, BTX and other organic hydrocarbons of low solubility for the cleanup of groundwater and wastewater. The end user can save 50% or more of his operations costs by removing large hydrocarbons which plug the pores of activated carbon beforehand, allowing carbon to remove the last 5 ppm or less of volatile compounds. Organoclays can remove 7 times as much oil and other organic hydrocarbons of low solubility, as does carbon.

This Article describes what organoclay is, how it is used, and presents several case histories of large systems at military bases and other places.

A Proposed Geochemical Barrier to Reduce Phosphorus Loading to a Kettle Hole Pond

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Ashumet Pond is a 215-acre kettle hole pond near the Massachusetts Military Reservation (MMR) on Cape Cod. This pond is fed primarily by groundwater and it has no surface water outlet. A phosphorus-rich groundwater plume that originated at the former MMR sewage treatment plant (STP) is discharging to Ashumet Pond. Most of the phosphorus discharge is occurring through a small near-shore section of the pond bottom that is approximately 300 feet long and extends 80 feet out into the pond. Elevated levels of phosphorus (up to 3 mg/L) are expected to discharge through this section of the pond for decades.

Tests indicate that phosphorus is the limiting nutrient for algae growth in Ashumet Pond. Historical data from previous ecological investigations indicate that phosphorus concentrations and algae content in the pond have substantially increased over the last 30 years. These changes in the pond are thought to primarily reflect the cumulative impacts of phosphorus loading by the STP plume. The development of more extensive and frequent nuisance algae blooms are expected if phosphorus loading is not controlled. Consequently, AFCEE proposes to install a geochemical barrier along the plume discharge area in the pond. The barrier will consist of a mixture of quartz sand, native sediment and Zero Valence Iron (ZVI). Upon exposure to groundwater and to shallow surface water, the ZVI will slowly oxidize to form ferric hydroxide, a compound that will sorb phosphorus from the plume, thereby reducing the phosphorus load to the pond. This approach is appropriate in aerobic pond or lake environments containing sediment with low levels of natural iron. The target zone in Ashumet Pond has these characteristics.

DNAPL Remediation Combining Thermal Extraction and Reductive Dechlorination

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The ability to effectively access pore space and overcome obstacles impeding successful remediation of dense non-aqueous phase liquid (DNAPL) sites has been overcome by applying a hybrid of technologies. An innovative remediation approach combining thermal treatment with reductive dechlorination in order to increase mass removal and lower remediation costs has been demonstrated with promising results. This approach involves the use of large-diameter auger in-situ soil mixing equipment to deliver a mixture of steam and hot air to the source zone. The mixing increases the contact of the volatile organic compounds (VOCs) with the steam/hot-air and accelerates contaminant removal. To increase VOC removal efficiency and to reduce the soil mixing cost, zero-valent iron (ZVI) is added following steam injection.

A full-scale field demonstration was completed in January 2003 at Cape Canaveral Air Force Station to verify the efficacy of this technology to remove trichloroethene (TCE) and 1,2-trichloro-1,2,2-trifluorethane (Freon 113). Thirty-two test cells, 1300 cubic yards of soil, were treated from a depth of 20 to 55 feet below land surface. TCE concentrations were detected as high as 1,100 milligrams per kilogram (mg/kg) in soil and 510,000 micrograms per liter (µg/L) in groundwater during baseline sampling. Freon 113 concentrations as high as 12,000 mg/kg in soil and 350,000 µg/L in groundwater were also observed. Thermal treatment removed 60 to 90 percent of the initial VOC contamination after 60 to 70 minutes of mixing. ZVI addition increased these removal rates to 90 to 99 percent. Based upon the demonstrated results, full-scale remediation of the 42,000 cubic yard source zone is scheduled for spring 2004. It is anticipated that as a result of this source reduction remediation, the site will achieve cleanup target levels for the extensive dissolved groundwater plume in less than 60 years as compared to several hundred years anticipated without source-treatment.

An Overview of the Hydraulic Testing of the Final 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 are 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 are 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 are 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 and vernal pools) are eliminated.

Methodology for Integrating Direct Sensing Tools With In-Situ Remediation Injection Technology to Facilitate Effective Treatment of Groundwater

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The effectiveness of in-situ groundwater remediation technologies is a function of the delivery of reagents into direct contact with contaminants located in the dissolved, desorbed and NAPL phases. Many in-situ remediation projects move into full-scale without a good understanding of the radius of influence and distribution of reagents that can be achieved.

In order to deliver reagents effectively, the location of contaminant mass in relation to lithology must be determined. The membrane interface probe (MIP) is a direct push applied sensing tool that simultaneously measures soil conductivity and volatile organic compounds. Once contaminant mass has been identified, a reagent delivery strategy is developed to maximize reagent distribution, radius of influence, and injection rates, as well as to optimize project costs.

Delivery of reagents into the saturated zones is accomplished through direct push technology or injection wells. Injection is facilitated through a wide range of injection pumps, technologies, and delivery techniques. Distribution of reagents, radius of influence, and injection rates are directly impacted by the hydraulic conductivity and heterogeneity of the target interval.

Vironex will present a new methodology that utilizes site characterization data obtained with the MIP and integrates this soil conductivity and contaminant mass information into injection strategies, delivery techniques, and equipment selection for a wide range of chemical oxidation and bioremediation reagents, contaminants and site subsurface conditions.

Pilot Engineered Wetland for Treatment of Dilute Waste Streams

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Engineered wetlands are a cost-effective innovative passive technology that can be applied for the treatment of a range of wastewater streams, including stormwater runoff, process wastewaters, groundwater, and landfill leachate. Captured organic contaminants can be degraded by the wetland microbial population; metal contaminants can adsorbed on the wetland soils or converted to insoluble salts. Wetland ponds also store runoff and rainfall, reduce flooding and soil erosion, and purify water by filtering wastes, sediments, and toxic compounds. CRA has designed and is currently operating a pilot engineered wetland system to determine its effectiveness in treating dilute waste streams including leachate, stormwater, and sludge. The results will be used to develop design and cost data for a full–scale treatment system. The system consists of surface and subsurface flow cells designed to operate in either a parallel or series configurations; each cell is approximately 5 feet in width and 15 feet in length (two Surface Flow Cells, A and B, and one Subsurface Flow Cell, C). The elevation of the wetland cells was designed to allow the whole system to operate by gravity flow. The treated effluent is collected and gravity discharged to process sewer. The available results indicate that wetland system is efficient in reducing the levels of biological oxygen demand (BOD), volatile and semi-volatile organic compounds, and organic acids to non-detect levels. Specific conductivity, salinity, and TDS have also been substantially reduced by the wetland treatment. The wetlands continue to be operated so that the maximum loading rates of the wastewater streams and the sludge waste can be determined. In addition, the potential long-term concerns such as air emissions, vegetation stress, the effects of cold weather, and sediment accumulation, are being examined. The presentation will discuss the performance of the wetland treatment system in detail.

Cyclodextrin Enhanced Remediation at Patrick Air Force Base, Florida

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Aggressive approaches to dense-non-aqueous phase liquid (DNAPL) remediation may present a significant interruption to daily operations at active military installations. The use of cyclodextrin has been identified as a low maintenance method to treat DNAPL in-situ, thus avoiding problems associated with more complicated remediation systems. Cyclodextrin is used to increase the solubility of chlorinated volatile organic compounds (VOCs), such as trichloroethene (TCE), in groundwater and subsequently stimulate biological degradation. Moreover, cyclodextrin may serve as a co-metabolite further enhancing bioremediation. Currently this technology is being implemented on a pilot-scale basis at OT-30 in the industrial area of Patrick Air Force Base, Florida.

Cyclodextrin was selected over other enhanced bio-remediation technologies at OT-30 based upon the combination of adding an electron donor while enhancing solubility. Cyclodextrin is a non-reducing polycyclic maltooligosaccharide-based molecule. It is a mild co-solvent and is less likely to mobilize DNAPL than more aggressive co-solvents such as ethanol. Use of cyclodextrin as a co-solvent has been proven to be effective on low polarity VOCs in bench scale analysis and in previous field implementations.

Cyclodextrin was gravity fed into 11 wells within the contaminated zone during two injection events in July and August 2003. The injection zone ranges from 33 to 38 feet below land surface. Baseline and post-injection samples were collected from area wells to evaluate pilot test performance. Mass flux was monitored at four locations down gradient of the source zone. An initial increase in mass flux and TCE concentration downgradient from the injection zone is anticipated based upon enhanced solubility. The dissolved TCE should be more available for reductive dechlorination, and a decrease in concentration should be observed with time. Results from this study will prove that cyclodextrin is effective at treating DNAPL contaminated groundwater at OT-30 and other areas where more aggressive technologies would be undesirable.

Installation Methods for Subsurface Placement of EHC™ (Solid) and EHC-L™ (Liquid) Amendments

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EHC is a solid or liquid (EHC-L) remediation product that combines controlled-release solid carbon and zero valent iron (ZVI). It utilizes a combination of stimulated biological activity and direct reduction of contaminants by ZVI for the treatment of various chlorinated compounds such as carbon tetrachloride, tetrachloroethylene, dichloromethane, and 1,2-dichloroethane. Derivatives of the standard EHC product have also been implemented for treatment of compounds such as pentachlorophenol.

Effective subsurface installation and distribution of soil and groundwater remediation products poses a significant challenge to implementers of these technologies. Numerous methods for installation of the EHC technology have been utilized, and a comparison of the results of the installations is provided.

A description of the installation techniques and a comparison of the resulting subsurface distribution will be provided. These methods will include installation in an open trench and excavation, hydraulic fracturing into highly weathered limestone, direct injection into a sand aquifer, and pneumatic injection into glacial till and fractured bedrock.

In-situ Flushing Selective Phase Transfer Technology (SPTT^{TM}) Cost Effective Soil & Groundwater NAPL Remediation Including NAPL and Chlorinated Solvents

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Selective Phase Transfer Technology (SPTT) involves micro-encapsulation using four mixtures and two processes (In-situ & ex-situ), in the remediation of NAPL contaminated sites.
The LNAPL and or DNAPL molecules undergo a phase transfer as micelle encapsulations at the molecular level, such that they are “dissolved” into the water in smaller, more mobile units. Responding to the complexity of NAPL compound has resulted in SPTT mixtures that are selectively applicable to specific ranges of NAPL compounds (i.e., light-range gasoline, medium-range fuel-oil, heavy range bunker-C, MTBE, and chlorinated solvents). The SPTT molecules are environmentally safe and are highly biodegradable (97% in les than 27 days).

Underground (in-situ) contact between SPTT mixtures and NAPL contamination is accomplished through injection wells or injection galleries. The resulting SPTT-NAPL micelle-encapsulations liberate the NAPL from the soils and or free-phase, than once dissolved can be extracted from the soil and groundwater milieu via extraction wells for on-site treatment. Further, SPTT reduces the NAPL mass that would otherwise be released as vapor emissions. Case studies demonstrate that project goals are achieved at 95% of small to medium size sites in less than 18 months and often within 12 months. Hence, this recently patented technology (ca. 2001) is a proven method to expedite soil and groundwater remediation with significant project cost and time savings compared to many other alternatives available.

The ex-situ application method uses modified roll0off de-water units (25-35 cubic yards) for the soil treatment. The contaminated soil is loaded into the unit, and then submerged with SPTT laden water. The SPTT/Water phase is circulated through the soil bed resulting in rapid liberation of NAPL contamination form the solid (Soil) phase into the liquid (Water) phase in as little as 4 hours. Case studies have demonstrated this to be a portable, scalable, economic soil treatment alternative.

Monitoring Improvement in Water Quality Following Reclamation of Acidic Coal Refuse with Biosolids

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A long-term field study was initiated for the reclamation of an acid-generating coal refuse pile in St. David, Illinois, using ten combinations of six levels of biosolids (0-3,360 Mg ha^{-1}) with/without clay (10.2 cm) and agricultural lime (179 Mg ha^{-1}). The treatments were applied to ten 0.405-ha plots, and five cover crops were planted, followed by mulching. A lysimeter was placed in each plot to monitor water quality monthly over thirteen years, following treatment applications in 1987. Statistical analysis (SAS) of concentrations of twenty-one chemical parameters showed no significant differences ($p \geq 0.05$) among the treatments in acidity, TSS, total P, Al, Cd, Cr, Cu, Fe, Mn, Pb, and Zn. In comparison with the control, there was significant improvement ($p \leq 0.01$) in pH, EC, alkalinity, Cl^-, SO_4^{2-}, TDS, Ni, and all others listed above. Lysimeter samples from the two highest biosolids levels (2,800 and 3,360 Mg ha^{-1}) initially contained NH_4-N, NO_2-N, and NO_3-N at concentrations of 41.4-598, 0.051-1.88, and 474-525 mg L^{-1}, respectively, which decreased 90-99% by the year 2000. Within two years of biosolids application, active acidity in samples decreased 100-fold (pH $3.4 \rightarrow 5.3$), while SO_4^{2-} decreased by a maximum of 96% ($39{,}400 \rightarrow 1{,}500$ mg L^{-1}). This resulted in decreased solubilities of most metals by 1993, and of Ni and Pb by 1997. Acidity, TSS, TDS, EC, Cl^-, and SO_4^{2-} were greatly reduced and attained equilibrium five to six years after biosolids application. Data clearly indicate that the biosolids were exceedingly beneficial in the reclamation of the acidic coal refuse site, resulting in marked improvement in water quality.

Composition, Peculiarities and Methods of Utilization of Oil Wastes

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Oil-and-gas productive industry occupies a leading place in the world economy. Every year the volume of produced and transported oil is increasing in the world. However, this productive industry is one of the largest pollutants of soils, water and air. In oil-producing regions great territories are polluted by spilled oil and oil slime as a result of various failures during the process of oil production and pipeline transportation. Transport losses of oil from oil-trunk pipelines are considerable.

The aim of the work is to determine composition and peculiarities of oil contaminated soils, oil slimes and lake oil from deposits of the Republic of Kazakhstan and on their basis develop methods of utilization.

Physicochemical characteristics of a number of oil wastes and their organic and mineral parts are determined in the work. The increased content of pitches and asphaltenes are typical for organic part of oil wastes that is the result of climatic factors effect on wastes in the process of long-term storage in open storehouse. Therefore, while the developing of rational variants of the processing of organic part of wastes its utilization for production of road-building materials is of a great interest.

Methods of bitumen obtaining from organic part of oil wastes and asphalt concrete mixture preparation by direct oxidation of oil wastes were proposed. Road and building bitumen were obtained by oxidation of organic part of oil wastes. Obtained asphalt concrete mixtures at the oxidation of oil wastes showed values of breaking point of compression 1.5-1.9 MPa and water saturation 0,2-0,3 vol. %. Methods of coke obtaining from organic part of oil wastes and claydite by utilization of oil wastes were proposed.

Reductive Dechlorination of Solvents in Groundwater using Controlled Release Carbon with ZVI

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Adventus Remediation Technologies Inc. (Adventus) has developed a combination of controlled-release solid carbon and zero valent iron (ZVI) particles to yield a highly effective material for stimulating the reductive dechlorination of otherwise persistent organic solvents present in groundwater. The materials are known as EHC™ and can be employed as fill material for permeable reactive barriers or injected into groundwater and contaminant source zones in a variety of ways. Following placement of EHC into the subsurface environment, indigenous heterotrophic bacteria consume the organic component of EHC (processed fibrous organic material) and consume dissolved oxygen thereby reducing the redox potential in groundwater. In addition, these bacteria ferment carbon and release a variety of volatile fatty acids (acetic, propionic, butyric) into the groundwater plume which serve as electron donors for other bacteria, including dehalogenators and halorespiring species. Finally, the small ZVI particles (i.e., between 10 and 100 μm) provide substantial reactive surface area that stimulates direct chemical dechlorination and an additional drop in the redox potential of the groundwater. These physical, chemical, and biological processes combine to create a strongly reducing (e.g., -600 mV Eh) environment that stimulates both chemical and microbiological dechlorination of solvents in groundwater.

Groundwater beneath an active grain storage facility in south central Kansas is impacted by carbon tetrachloride (CT) which was used as a silo fumigant. Chloroform (CF) - a recognized anaerobic biodegradation product of CT - is also present. There is limited evidence for the presence of other CT catabolites such as dichloromethane (DCM) or chloromethane (CM). Significant soil impacts were not observed for any constituent. Remedial engineering and design efforts considered the use of ZVI or EHC^{TM} to support in situ source management (ISSM) and enhanced passive remediation (EPR) for treatment of the groundwater plume. Two conceptualized groundwater remedies (i.e., PRB and source area treatment) using ZVI or EHC were subsequently compared for full-scale field demonstration of their ability to effectively manage a plume of CT and related compounds. Cost factors for EHC, applied at dosages shown to be effective and long lasting, are substantially (i.e., 50%) lower than materials currently being employed for enhancement of in situ reductive dechlorination of solvents. A ZVI PRB (100% iron with dimensions 61 m long x 10 cm wide x 3 m deep) represents a cost-effective approach for managing the VOC plume, if natural attenuation processes are allowed to manage the lowered concentration of CT metabolites. The use of EHC at 2% mass seems more appropriate for source area treatment to affect source removal/flux reduction and accelerate site remediation and closure. Full-scale implementation of the combined approaches is scheduled for spring of 2004.

Modeling the Market for Long-Term Monitoring

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Based on the report "Treatment Technologies for Site Cleanup: Annual Status Report (11th Edition)" (EPA-542-R-03-009), over 1,100 Superfund sites have remedies that may require long-term monitoring of groundwater to ensure their continued effectiveness. These remedies include treatment remedies, such as pump and treat (P&T) of groundwater and permeable reactive barriers, containment remedies, such as capping and vertical engineered barriers, and other remedies, such as monitored natural attenuation and some institutional controls. One of the most common of these remedies, P&T, is being used at 743 Superfund sites. The investment needed for long-term monitoring at these sites will result in a continuing demand for services and technologies that provide better, faster, and cheaper environmental monitoring. Government officials need improved information about the future demand for monitoring services so that they can better prioritize support of technology research and development efforts. Technology vendors, developers, and service providers are also able to identify business opportunities. This presentation provides the results from the first program-wide assessment of long-term monitoring needs at Superfund sites using P&T, including an analysis of the market for long-term monitoring equipment and services. It presents estimates of current costs to the Superfund program for long-term monitoring of P&T systems. It also presents estimated future expenses and trends over time based on anticipated long-term monitoring needs. In addition, it provides the results of a sensitivity analyses of the effects of key variables, such as the introduction of emerging monitoring, sampling, and analytical methods, the use of geophysical and remote sensing technologies, the application of optimization lessons learned and rules of thumb, and changes in sampling and analytical costs. The analysis is based on a cost model developed using standard engineering practice, published information from existing P&T projects, known estimates of long-term monitoring requirements, existing cost models, and EPA databases on P&T applications at Superfund Sites. Preliminary findings for this research are being presented at the Federal Remediation Technologies Roundtable conference on Accelerating Site Closeout, Improving Performance, and Reducing Cost Through Optimization (June 2004 in Dallas, TX).

Design/Build of an Emergency Multiphase Extraction System

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At a bus maintenance garage, routine tank tightness testing (TTT) for a 10,000-gallon diesel underground storage tank (UST) revealed a leak emanating from the conveyance piping between the UST and the diesel dispenser. Investigation activities implemented included gauging monitoring wells on the site, assessing nearby catch basins and manholes for the presence of light non-aqueous phase liquid (LNAPL), and utilizing direct-push drilling techniques to quickly install numerous small-diameter monitoring wells and soil gas monitoring points. Gauging activities revealed a plume of LNAPL over 20,000 square feet covering a portion of the Site and extending in the downgradient direction beneath the adjacent street.

Timely remediation was required since LNAPL had migrated to within 50 feet of the nearby residential area and elevated concentrations of air-phase petroleum hydrocarbons were measured in soil gas. Numerous product recovery techniques were evaluated for implementation at the site including:

- Multiphase extraction utilizing drop tubes
- Multiphase extraction using a total fluids pump and applied vacuum
- Product recovery via pneumatic pumps
- Product recovery via electric product-only pumps
- Product recovery using passive canisters

The design of a product–only recovery system utilizing pneumatic pumps was implemented in the short term with the goal of upgrading the system in the future with groundwater extraction and enhanced product recovery via applied vacuum/soil vapor extraction. Project successes include elimination of potential vapor intrusion to indoor air, product recovery system design, upgrade to a multiphase extraction system, LNAPL recovery of over 3,000 gallons in less than one year and significant reduction in the size of the LNAPL plume.

Overcoming Site Challenges to Optimize an Inactive LNAPL Containment & Recovery System

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An existing LNAPL containment and recovery system located in southeastern Massachusetts was installed following an underground storage tank leak in the early 1990s. The ensuing leak produced an LNAPL plume over 20,000 square feet migrating downgradient underneath an active commuter train line into a wetland. As part of the emergency response actions, an impermeable barrier and recover trench were installed prior to the wetlands. Four product recovery sumps, two located in the recovery trench, two in the source area, and multiple observation wells were also installed at the site.

Numerous logistical and site-related complications had to be overcome to optimize the LNAPL Recovery system that had been inactive for over two years. An active commuter rail line, which presented serious safety concerns, roughly bisected the LNAPL plume. The rail line also complicated the establishment of electrical service for any automated systems since power would need to cross the lines. Also, a high groundwater table and numerous issues relating to flooding/ponding water and breakout of free-phase petroleum product existed. The source area (former UST) is 15 feet above the train line and recovery trench, dropping quickly on a steep slope. Since the current property owner had little available capital, additional monetary resources were limited.

Optimization alternatives were evaluated that incorporated all these site-related and logistical issues to activate/replace the existing system and to increase LNAPL recovery rates. These alternatives included an evaluation of:

- Solar and marine-battery operated LNAPL recovery systems
- Initiating groundwater depression
- Placing sorbent booms in the area of petroleum breakout
- Installing additional product recovery skimmers
- LNAPL flushing technologies (i.e. steam, surfactants, and co-solvents) and
- Upgrade and repair of existing LNAPL recovery equipment

The evaluation was presented and the most cost-effective, logistical alterbative will be selected for implementation.

Useful Design and Cost-Estimation Tool for Air Handling Systems on Temporary Structures for MGP Sites

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The remediation of contaminated manufactured gas plant (MGP) sites can pose solid, liquid and air emission concerns. Depending on technologies selected to remediate the site, one or all of the concerns could come into play. Generally, the solids (soil) can be treated on-site, hauled off site for disposal and thermally treated, or treated in-situ. Rainwater or excavation water can be stored, treated on-site with known activated carbon technologies or hauled to a POTW for treatment. Since MGP sites are generally located in urban settings, toxic air emissions and work-site odors are areas of particular awareness.

An effective solution for control of toxic emission and odor is to cover the site with a temporary structure during remediation activities. These structures are used for covering the workspace and offer advantages such as all weather work, containment of dust and noise abatement. However, a covered site poses additional issues such as release of toxic emissions during opening and closing doors and creating an environment that may require additional protective equipment for workers. The most effective means of controlling toxics and odors is to create a negative pressure inside the structure and treat air prior to release through activated carbon. In addition, fresh air is required to enable working in Level C or D environment.

This paper discusses all the engineering and economic issues that must be addressed before the air purification system can be properly designed. Such things as required air changes, size of building, mode of operation and the need for prefiltration before the carbon adsorber must be discussed.

Also, presented is a technique to quickly and easily determine the cost of a system once the size of the structure and the required number of air changes is known. This information may be used for the purposes of optimizing cost-effectiveness for the alternative design possibilities.

Optimization of a Pump and Treat System at the Massachusetts Military Reservation

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In September 1997, a pump and treat system began operating to remediate the Fuel Spill-12 (FS-12) groundwater plume at the Massachusetts Military Reservation. The contaminants of concern within the FS-12 plume are benzene and ethylene dibromide. The FS-12 plume originated from a fuel pipeline leak in the early 1970s where approximately 70,000 gallons of both aviation gasoline and jet fuel were released to the subsurface. The original design of the remedial system consisted of 25 extraction wells operating at a total design rate of 772 gallons per minute. The extracted groundwater is piped to a treatment plant where contaminants are removed using granular activated carbon filtration. Treated water is returned to the aquifer through 23 reinjection wells. At the time of the FS-12 system start-up in 1997, the plume covered a linear distance of approximately 4,500 feet, the maximum width of the plume was approximately 2,300 feet, and the maximum thickness was approximately 100 feet. Over the past several years, the FS-12 remedial system has been modified through a series of optimization steps to improve plume recovery, reduce cleanup time, and reduce costs. The optimization effort is an ongoing process of evaluation and adjustment of system operation and monitoring and will continue as the vertical and horizontal extent of the plume contracts. Groundwater modeling has proved to be a powerful tool in the system optimization process. The FS-12 groundwater model has been used to determine the best combination of pumping and reinjection rates to more efficiently remediate the plume as its geometry changes. The specific objectives of the optimization are to provide better extraction system efficiency while maintaining hydraulic capture of the plume, lower total flow rates, focus extraction stresses on the most contaminated zones within the aquifer, and minimize the recirculation of treated water.

Evaluating Monitored Natural Attenuation as a Possible Remedial Technology on a Contaminated Site

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Chlorinated hydrocarbons are a widespread class of contaminants found in soil and groundwater. Within this group, perchlorethylene (PCE) and trichloroethylene (TCE) are two of the most common contaminants detected in the environment. Monitored natural attenuation (MNA) is a remedial technology that has been acknowledged by the Environmental Protection Agency (EPA) as a possible cleanup action on Comprehensive Environmental Recovery Cleanup Liability Act (CERCLA), Resource Conservation and Recovery Act (RCRA), and Underground Storage Tanks (UST) sites contaminated with chlorinated hydrocarbons. In a study located on the Chemical, Metal and Pesticide (CMP) disposal pits on the Savannah River Site in Aiken, South Carolina, we are examining an area with a PCE and TCE plume moving through it to determine whether natural attenuation is occurring. Experiments that are currently underway include soil, groundwater, and plants analyses in order to establish whether PCE and/or TCE degradation is occurring. We are also examining the physiochemical conditions of the site to determine if the appropriate environmental parameters are in place for contaminant degradation to occur. Environmental parameters under study include oxygen levels, availability of electron acceptors, redox potential, moisture levels, soil composition, and the presence of PCE and TCE degraders. If at the conclusion of the study we determine that the proper conditions exist on the site, then natural attenuation

Poster Session- Site Assessment

Subtle Sampling Variations for Industrial Air Monitoring
Shannon Bouley, BEM Systems, Inc., Orlando, FL
Susan Sitkoff, BEM Systems, Inc., Orlando, FL

Rapid Hydraulic Conductivity Tests Using Slug Test Accelerator Tool
Joshua Goldowitz, Rochester Institute of Technology, Rochester NY

An Optimization of a Bioassay for Toluene Analogs Using Bioluminescence Reporter Strain KG1206
In Chul Kong, Yeungnam University, Gyungsan-si, Kyungbuk, Korea
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Demonstrating Elimination of Nuisance Odors at Petroleum Contaminated Sites
Steven Low, Shaw Environmental, Inc., Andover, MA
Joanne Perwak, Shaw Environmental, Inc., Andover, MA
Olaf Westphalen, Shaw Environmental, Inc., Andover, MA

Fracture Characterization of Crystalline Bedrock for Groundwater Investigations: An Example from the Marlborough Quadrangle, Massachusetts
Stephen B. Mabee, University of Massachusetts, Amherst, MA
Scott A. Salamoff, Colorado State University, Fort Collins, CO
Joseph Kopera, University of Massachusetts, Amherst, MA
Donald U. Wise, University of Massachusetts, Amherst, MA

A Preliminary Environmental Site Investigation for a Bridge over the Mississippi River at Moline, Illinois
C. Brian Trask, Illinois State Geological Survey, Champaign, IL

LNAPL and Hydrogeological Characterization of a Tidally Influenced Petroleum Bulk Terminal in the Northeast, USA
Andrew D. Walker, Shaw Environmental, Inc., Hopkinton, MA
Lynn Maybury, Shaw Environmental, Inc., Hopkinton, MA

Subtle Sampling Variations for Industrial Air Monitoring

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Mold has been a leading concern for many building owners, prompting for specific sampling plans being developed to test impacted heating, ventilation, and air conditioning (HVAC) systems. New regulations for vapor intrusion have been released by the USEPA, prompting assessment of buildings located in the vicinity of groundwater volatile organic plumes. While there seems to be an overlap for these two types of sampling, there are subtle variations that need to be followed in order to obtain the most accurate depiction of conditions in buildings for each of these concerns.

Mold is most commonly found inside HVAC systems and in areas with previous water damage. Based on these impacts, sampling must occur in the vicinity of the water damage or directly under the HVAC vents. Sampling plans for these concerns are straightforward and require the HVAC plans aided with a site walkthrough. Vapor intrusion requires a more complicated sampling plan. For this scenario, we are concerned with the accumulation of vapors potentially leaching through subslabs. Although the HVAC system plays a part in the sampling plan development, we are required to provide a more thorough evaluation of the potential entry points for these vapors. This paper will discuss the most appropriate sampling strategies for both scenarios for indoor air concerns.

Rapid Hydraulic Conductivity Tests Using Slug Test Accelerator Tool

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Hydraulic conductivity (K) is the most commonly measured hydraulic characteristic on contaminated sites because it is crucial for determining the velocity of contaminated groundwater. A new tool and technique is described which allows for an accurate K measurement in ¼ the time of a state-of-the-practice slug test.

Traditionally K is tested by introducing a solid cylinder (the slug) into a well and lowering it below water table. The well water is displaced upwards, producing a difference in water level (h_o) between the well and the aquifer. The residual difference in water level (h) is then monitored as the volume of displaced water seeps into the aquifer. This is known as a falling head test. The same results are obtained with a rising head test where water is removed from the well. In either case K is determined from the slope of h/h_o Vs. time.

The new tool consists of two coaxial 5’ tubes: the outer tube just fits within a 2” monitoring well and the inner tube is just large enough for the probe of an electric water level meter. The annulus between the tubes is sealed, and the inner tube has sufficient extensions to reach from the top of the well to below the water table. The well is “slugged” by inserting the bottom of the tool 1’ into the water. This produces a 4’ h_o in the inner tube. The test is completed by monitoring h in the inner tube.

The new tool and procedure is more rapid because it produces a large h_o for a given volume of displaced water. Field tests show close agreement between K results using the new tool and traditional slug testing.

An Optimization Of A Bioassay For Toluene Analogs Using Bioluminescence Reporter Strain KG1206

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Volatile organic compounds, such as the BTEX group, are common contaminants in environment throughout the industrialized world, and there is growing interest in the use of microbial processes for biomonitoring of these pollutants. The TOL plasmid of *Pseudomonas putida*, which is able to degrade toluene analogs and intermediates, is an example of a pathway that has been investigated well. The recombination of these with bioreporter genes, such as the *lux* (encoding luciferase) and the *lac*Z (encoding β–galaxtosidase) has become a great asset in biomonitoring of contaminated environments. In this study, a constructed genetically engineered strain of *P. putida* mt-2 KG1206 containing the intact TOL plasmid and a plasmid with the P_m-*lux* gene has been used to bioassay toluene analogs and intermediate in soil system. This type of strain can be used for the biomonitoring of environments contaminated with specific pollutants, and can establish a correlation between specific pollutant concentration and produced bioluminescence from reporter strain. However, the lack of standardization and existence of mixture is a major problem for this work.

In this study, characteristics and the effects of culture conditions on this constructed strain were investigated in the presence of toluene analogs and intermediates. In addition, quantification protocol for pollutant was developed for standardization.

Demonstrating Elimination of Nuisance Odors at Petroleum Contaminated Sites

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Under the Massachusetts Contingency Plan (MCP), characterization of risk to public welfare considers the existence of nuisance conditions; such a condition includes odors of petroleum products and their breakdown products. MADEP acknowledges that guidelines or standards that determine when a petroleum odor constitutes a nuisance condition are difficult to articulate. However, guidance broadly defines a nuisance odor condition in terms of persistence and frequency. A combined approach using assessment, monitoring, and evaluation was used to demonstrate that a nuisance odor condition did not exist at a former retail gasoline site. Risks to human health and the environment had been eliminated at the gasoline-contaminated site. Nuisance odors had been documented at the site prior to remediation. Therefore, site closure required a means of demonstrating that a nuisance odor condition no longer existed. An innovative investigative program was developed that included: focused ambient-air monitoring, field observations of odors at regular intervals, and focused odor testing. Odor testing (via ASTM Method E 679, modified) was performed due to the subjectivity of odor detection and the difficulty in quantifying odors using standard air monitoring equipment. This method utilizes a trained odor panel to evaluate air samples for odor character and average intensity. Using the combination of conventional monitoring, field observations, and the odor panel results, it was shown that no significant risk to public welfare existed, thereby meeting all requirements for site closure.

Fracture Characterization of Crystalline Bedrock for Groundwater Investigations: An Example from the Marlborough Quadrangle, Massachusetts

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Integration of a wide array of structural data with well-field hydrologic testing is increasingly recognized as a critical step in understanding groundwater flow behavior and recharge in crystalline bedrock aquifers (Lyford et al., 2002, Walsh and Lyford, 2002). The Marlborough Quadrangle, about 40 km west of Boston, was selected as a test case of how a state geological survey can most effectively and efficiently collect and present such data in order to better constrain conceptual models of groundwater flow in general and to be of maximum use for hydrologists and consultants working on specific local problems. In this study, 3200 structural measurements were taken by a two-person team over a nine-week period at 68 stations distributed throughout the quadrangle and keyed into a GIS database. Resulting maps include standard geologic map bases overlain by typical rose diagrams and maps showing fracture domains, sheeting distribution, foliation trajectories, bedrock elevations, generalized piezometric surface configuration, and overburden type and thickness with separations into permeability class. Geology of the quadrangle can be separated into three zones: (a) north of the Assabet River Fault (ARF), (b) the area between the ARF and 1.5 km-wide Bloody Bluff Fault Zone (BBFZ), and (c) south of the BBFZ. Generalized foliations in the zones are: (a) 215, 50N, (b) 240, 65N, and (c) 270, 45N. Two pervasive, steeply-dipping (>60º) fracture sets occur throughout the quadrangle: an older 150º set that includes sulfide-bearing veins and fracture surfaces along the ARF and a 015° set of largely unmineralized common joints. Sheeting and unloading joints are generally coincident with shallow dipping foliation in (c) but crosscut foliation in (a) and (b). We believe this approach will provide hydrologists and consultants with basic framework data that will expedite and improve site characterization, the planning of subsurface investigations, construction activities and groundwater exploration.

A Preliminary Environmental Site Investigation for a Bridge over the Mississippi River at Moline, Illinois

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A preliminary environmental site assessment along the alignment of I-74 and its bridge over the Mississippi River was completed by the Illinois State Geological Survey for the Illinois Department of Transportation in 2002. The purpose of the survey was to determine any environmental concerns, both natural and man-made, that the Illinois DOT might encounter during activities to build a new bridge to carry I-74 over the Mississippi River between Moline, IL, and Davenport, IA. A preliminary investigation of the project area from 27th Street in Moline to 67th Street in Davenport, using government lists, Sanborn Fire Insurance Maps, city directories, and a drive-through of the project area, identified a total of 127 sites that were believed to constitute a possible risk to the project. Further investigation was conducted of 37 sites on the Illinois side of the river. Location of the project in part of downtown Moline and long-time development of the Moline riverfront by industrial and commercial operations offered a variety of parcels for investigation, ranging from corner gasoline stations to railroads and foundry sites. The dominant sites comprised current or former underground storage tank and leaking underground storage tank sites, automotive repair sites, and foundries and other sites where metals were handled. Railroads, junk yards, cleaners, and spills made up the remainder of the sites investigated. During a limited subsurface investigation, heavy metals and volatile organic compounds indicative of petroleum were detected at several sites. Examples of some of these sites will be presented.

LNAPL and Hydrogeological Characterization of a Tidally Influenced Petroleum Bulk Terminal in the Northeast, USA

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Characterization of hydrogeologic and site conditions including groundwater flow direction, hydraulic gradient, LNAPL distribution, thickness, and type, and tidal influence was performed on an inactive petroleum bulk terminal in the northeast. The study area encompassed approximately 10 acres located immediately adjacent to a tidally influenced water body with a 10 foot tidal range. Twenty-five monitoring wells were installed and over 30 gauging points were utilized in this study.

Two discrete LNAPL plumes located 350 feet apart were characterized and found to consist of a weathered gasoline-like LNAPL and a No. 6 fuel oil-like LNAPL. Each LNAPL plume was approximately 80 feet long by 40 feet wide.

Groundwater flow at the site was bi-directional, with an east to west divide through the center of the site. In addition, groundwater in two areas of the site flowed radially. Multiple factors were attributed to the flow patterns including, lithology, groundwater infiltrating utilities, and the effects of the surface water body.

Based upon a 24-hour tidal study, the majority of the site was tidally influenced with a maximum observed groundwater fluctuation of approximately 4 feet and an observed tidal influence as far as 320 feet from the surface water. Interestingly, the groundwater response was not directly related to the proximity to the surface water or the tidal stage. This observation likely relates to variations in seawall permeability and lithology. No groundwater flow direction reversal due to tidal influence was observed.

Gradient ranges were calculated and varied considerably throughout the site. Little to no gradient was observed in the upgradient area, which was not expected as the site topographically slopes downward 30 feet towards the surface water. Upon completion of the study, site-specific conditions were well understood. This detailed understanding of the site will facilitate the upcoming evaluation of remedial options.

Poster Session- Training Range Issues

Characterization of Soil Contamination at Former Small Arms Training Ranges Utilizing a Triad Work Strategy

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A Metal Detector Study to Locate Inactive, Un-Maintained Small Arms Firing Range Impact Areas

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Characterization of Soil Contamination at Former Small Arms Training Ranges Utilizing a Triad Work Strategy

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This paper describes the application of a Triad approach at Fort Lewis, Washington. Fort Lewis is a major military facility located approximately six miles south of Tacoma, Washington. The facility consists of approximately 34,875 hectares of cantonment areas, natural prairies, lakes, wetlands, and forests. Weapons qualifications and field training has occurred at Fort Lewis Ranges since around the time the Fort was established in 1917. As part of the Fort Lewis Agreed Order with the Washington State Department of Ecology, Fort Lewis Directorate of Public Works tasked USACE with determining the nature and extent of contaminated soils in three former small arms training ranges. These ranges included a former pistol range (ca. 1929-1944), an infiltration range (ca. 1951-1965), and a skeet range (ca. 1962-1972). The characterization was designed to determine if surface soils contain significant concentrations of metals with the focus on collecting sufficient data for potential future actions (i.e., risk analysis or soil remediation). A Triad work strategy was created in order to conduct sampling in one mobilization and to manage uncertainty around site specific remediation decisions. Concurrent analysis of soil samples during the Demonstration of Method Applicability (DMA) using both field portable X-ray Fluorescence (FPXRF) and laboratory methodologies for the initial sampling period established a correlation between FPXRF and laboratory data. Immediately following the DMA, the site characterization data was collected in the form of FPXRF data and fixed-laboratory soil collaborative sample results to refine the conceptual site model for each site. During the site characterization process, additional sample locations were determined from the analysis and interpretation of real time data, which identified the extent and distribution of contamination. Communication strategies were developed to inform the project delivery team, customer and regulator of real time data and to ensure the effectiveness of the sampling communication and to allow real time decisions.

A Metal Detector Study to Locate Inactive, Un-Maintained Small Arms Firing Range Impact Areas

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Precise locations of older firing ranges at many military bases are often unavailable, because the records for training have either been destroyed or are vague and non-descriptive. We conducted an “environmental forensics study” of a 25-acre site at a large military facility in order to locate impact areas of a Thompson sub-machine gun range that was last used over 50 years ago. Preliminary assessment activities included historical map and aerial photography review, site visits, and interviews with range control personnel, which suggested sub-machine gun training in the general area. However, site visits did not indicate any visual features signifying range use, and the site had been overgrown with vegetation covering all traces of bullets. We used a Garrett Infinium metal detector to successfully locate several small impact areas. The impact rounds were identified, marked, and the location coordinates were identified using GPS. The study was completed in 4 days, and at a fraction of the cost of physical. The characterization will be used in future development of the site.

Wednesday, October 20, 2004

Poster Session- Analysis

Recovery Determinations for Dioxin Analysis with the CALUX® Bioassay

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Ultra High Throughput Microwave Digestion: A novel Breakthrough Approach for Pressurized Dissolutions

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Analysis of 1, 4-Dioxane – Technical Challenges and Observed Results

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A Revaluation of Antiquated Partitioning Coefficients and their Affect on Soil Clean-up Levels

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Using Portable XRF to Solve Field Testing for Environmental Issues Relating to Using Tungsten Munitions.

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Recovery Determinations for Dioxin Analysis with the CALUX® Bioassay

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For quantitative methods such as high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) and bio-analytical methods such as CALUX®, recovery determinations are very important for toxins such as dioxins. Recovery determinations in HRGC/HRMS are performed by spiking isotopically labeled congeners into the sample prior to extraction, with recovery based on the amount of labeled compound recovered. Bioassays do not differentiate between isotopically labeled and unlabeled analytes. Recovery determinations in bioassays can be accomplished with a surrogate sample spiked with a radiolabeled congener of dioxin. We demonstrate here that 1,2,3,4-TCDD, a biologically inactive congener of the dioxin family of chemicals, can be used as an internal spike to determine recoveries of dioxin-like chemicals. Samples were spiked with ^{14}C labeled 2,3,7,8-TCDD or 1,2,3,4-TCDD and submitted to extraction and clean up using Xenobiotic Detection Systems, Inc. patent pending XCARB sample clean up method (acid silica column in series with an XCARB column). The XCARB column is differentially eluted to yield a PCB and PCDD/F fraction. The 1,2,3,4-TCDD spiked samples were resuspended in toluene containing four PCB injection standards, and recoveries determined by gas chromatograph with electron capture detection or scintillation counter. Average recoveries determined by 1,2,3,4-TCDD with paired samples spiked with ^{14}C-2,3,7,8-TCDD indicated that the recoveries determined by the two methods were very similar, 88.5% (± 1.2%) and 87.2% (± 2.4%), respectively. Recovery determinations were also verified by HRGC/HRMS. This procedure allows for quantitative determination of dioxin-like chemicals in various sample matrices. Supported by SBIR Grant from NIEHS ES 08372-03.

Ultra High Throughput Microwave Digestion: A novel Breakthrough Approach for Pressurized Dissolutions

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Microwave digestion over the last 15 years has become a well-accepted technique in use routinely in laboratories around the world. The savings in time and the improvement in digestion quality associated with the elevation of reagent temperature have assumed increasing importance as detection limits for measurement equipment such as ICP and ICP-MS have decreased. However, materials constraints in vessel technology have limited the throughput for pressurized digestions to between 10 and 15 samples per batch, which can offset the savings in digestion time by physically limiting the throughput.

In this paper, a breakthrough in vessel design will be demonstrated which allows a 3 to 4 times increase in throughput per batch for pressurized microwave digestion. Novel temperature sensing methodology will be discussed allowing a ‘connection free’ system with full temperature control of up to 40 pressurized digestions simultaneously.

Data will be presented for dissolutions at temperatures up to 200C of environmental reference materials, organic reference materials and ‘real world’ samples showing within and between batch variation for this novel approach. Particular attention will be given to recoveries of the traditionally ‘volatile’ elements such as As, Se and Hg.

Further results will be presented showing that optimization of an important design criteria – the ‘aspect ratio’ of the vessel - allows a full carousel of 40 samples to achieve regulatory methodologies such as EPA 3051 without requiring a significant increase in available energy.

Analysis of 1, 4-Dioxane – Technical Challenges and Observed Results

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The compound 1, 4-Dioxane has been the subject of increasing concern regarding its potential presence as a groundwater contaminate. Dioxane has many industrial uses, most notably as a stabilizer for chlorinated solvents, raising the specter that it may be present at chlorinated solvent sites. The degree to which dioxane contamination is prevalent in the environment is unknown because historically, there has been very little monitoring for this compound. The compound forms an azeotrope with water, making it a highly mobile contaminate that is also difficult to remediate. The same physical characteristics that make it a threat to groundwater also present many analytical chemistry challenges, particularly concerning the analytical sensitivity required to address 1, 4-dioxane at risk-based concentration levels. In this paper, the authors modified Methods 8260B and 8270C to maximize the analytical performance for this compound. Accuracy, precision and sensitivity data is presented for each method with recommendations for obtaining the best performance from each method.

A Revaluation of Antiquated Partitioning Coefficients and their Affect on Soil Clean-up Levels

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Soil cleanup levels are often set using partitioning modeling to predict contaminant concentrations leaching into groundwater. This modeling typically uses literature values for partitioning coefficients which are based on historic studies and theoretical relationships. An indirect, though critical, parameter affecting the partitioning calculation is the efficiency of the soil sampling/analytical method used. The more efficient the method, the lower the partitioning coefficient needs to be to accurately reflect the amount of contaminant that will actually leach. A recently developed soil sampling method (Method 5035) dramatically improves the efficiency of soil analyses for VOCs (by as much as an order of magnitude). This in turn has affected the development of soil cleanup levels.

In 1994, at a Connecticut Superfund Site, soil cleanup levels were established via leach testing/partition modeling of samples collected using then current methodology. GZA implemented SVE at the site; a few years later, the data indicated that we were approaching the cleanup objectives. However, soil samples collected using Method 5035 indicated significant residual concentrations – greater than what was detected prior to remediation. It was suspected that these increased concentrations were an artifact of the sampling methodologies employed.

To assess the effect of using Method 5035 on the detected soil concentrations and required cleanup levels at the site, we collected soil samples and analyzed them via a modified (to limit losses during sampling and analysis) Synthetic Precipitation Leaching Procedure (SPLP) and Method 5035/8260. A soil-water partitioning coefficient (K_d) was then calculated for each set of samples. Using a multivariate statistical analysis and a one dimensional steady state flow/finite difference transport model we were able to demonstrate that the leachable concentrations in soil were not significant (relative to groundwater goals). These data were subsequently used to revise the site-specific goals for VOCs in soil by an order of magnitude.

Using Portable XRF to Solve Field Testing for Environmental Issues Relating to Using Tungsten Munitions

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The Army has been using Tungsten (W) munitions since the 1990’s when it was determined that lead-based munitions posed environmental and human health issues. However, W munitions have recently been discontinued over rising health and environmental issues. Recent concerns have been raised over potential health hazards and increases in ground acidity at firing ranges which may be caused by W. Since lead (Pb) residue was already present, accelerated corrosion of Pb can occur. This is of particular concern in areas where ground water can become contaminated by lead corrosion. Therefore it is necessary to develop tools and techniques to identify the extent of W and Pb present in soil and ground water.

Some testing has been started in the Massachusetts Military Reservation (MMR) and US Army - Aberdeen Proving Ground in the U.S. Portable X-ray Fluorescence (XRF) Analyzers now provide the means to quickly obtain on-location precise elemental analysis of most metal pollutants. The use of a portable Innov-x XRF Analyzer provides promising results in testing of soils to accurately map locations, determine the amount of Pb and W, quickly survey sites under field conditions.

Designed as “point and shoot” analyzers they can gather data virtually anywhere-- shooting ranges or other locations. They use “Smart Beam” X-ray tube technology and a high resolution Si PiN diode detector that eliminates radioactive isotopes found in most other units. While this removes NRC regulation, costly isotope disposal or travel restrictions, it also eliminates any potential of pollutants from that source.

The software intelligence of a personal PC is built into the analyzer. Users can employ a GPS, add new elements for rapid identification, or perform analytical tasks. Its PDA runs calibration files with up to 25-elements using fundamental parameters, spectral matching and/or empirically-generated data.

Poster Session- Arsenic

Bioavailability of Arsenic to Edible Plants Grown in Poultry Litter Applied Soils

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Bioavailability of Arsenic to Edible Plants Grown in Poultry Litter Applied Soils

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The poultry industry is one of the largest and fastest growing livestock production systems in the world. Poultry is often treated with organo-arsenical feed additives used to control coccidial intestinal parasites, improve feed efficiency, and promote rapid weight gain. Since these arsenic compounds are not readily absorbed by poultry, poultry litter may contain as much as 30-50 mg As kg^{-1}. Approximately, 90% of the 13 million metric tons of poultry litter annually produced in the U.S. is applied as a fertilizer on cropland and pasture. There are already reports of high inorganic arsenic concentrations in rivers close to these chicken farms and chicken litter applied fields during/after storm events. Another important but unstudied aspect of this application is the possible accumulation of arsenic in agricultural plants. This study focuses on the bioavailability of As to various edible plants grown in soils amended with poultry litter. Arsenic speciation changes in the soil and plants over time was also monitored. For comparison, soils were also amended with inorganic As species and differences in plant bioavailability was assessed. In addition, we evaluated the ability of different leach solutions to target the desired As species, as well as a variety of chemical soil extractions to determine their usefulness in predicting plant bioavailable As in soils. Arsenic speciation was conducted using both ion chromatography - inductively coupled mass spectrometry (IC-ICP-MS) and hydride generation - cryogenic trapping - atomic absorption spectroscopy (HG-CT-AAS).

Poster Session- Bioremediation

Bioremediation of Contaminated Soil and Sediment by Composting
Dr. Zareen Khan, Jawaharlal Nehru Technological University, Hyderabad, India
Prof. Y. Anjaneyulu, Jawaharlal Nehru Technological University, Hyderabad, India

Rapid Biological Treatment of Residual DNAPL With Slow Release Electron Donor HRC-X™
Stephen S. Koenigsberg, Regenesis, San Clemente, CA
Anna Willett, Regenesis, San Clemente, CA

The Efficacy Of Oxygen Release Compound (ORC®): A Nine-Year Review
Stephen S. Koenigsberg, Regenesis, San Clemente, CA
Anna Willett, Regenesis, San Clemente, CA

Enhanced In-situ Bioremediation of a Complex Free-Phase Plume of No. 6 & No. 2 Fuel Oils and Motor Oils Below a Permanent Structure: Selecting the Remedy
Patrick Korths, S E A Consultants Inc., Cambridge, MA
William Mallio, S E A Consultants Inc., Cambridge, MA

Field Demonstration of Three Techniques for Bioremediation of Chlorinated Ethenes at Naval Station Treasure Island
Daniel P. Leigh, Shaw Environmental and Infrastructure, Inc., Concord, CA
Tarek Ladaa, Shaw Environmental, Inc., Knoxville, TN
Robert J. Steffan, Shaw Environmental, Inc., Lawrenceville, NJ

Aerobic In-Situ Bioremediation (ISB) of Semi-Volatile Organic Compounds (SVOC) via an Oxygen Gas Injection System
Kenneth L. Sperry, Xpert Design and Diagnostics, Allentown, PA
Omer J. Uppal, Xpert Design and Diagnostics, LLC, Stratham, NH
Dennis Keane, Xpert Design and Diagnostics, LLC, Stratham, NH
Matthew Nelson, Xpert Design and Diagnostics, LLC, Stratham, NH
Jaydeep Parikh, Xpert Design and Diagnostics, LLC, Stratham, NH
John L. Persico, Blasland, Bouck & Lee, Inc., Cranbury, NJ
Joseph J. Tota, United Technologies Corporation, Hartford, CT

Anaerobic Bioaugmentation Approaches for Treating Chlorinated Solvent Contaminated Aquifers
Robert Steffan, Shaw Environmental, Inc., Lawrenceville, NJ
Tarek Ladaa, Shaw Environmental, Inc., Knoxville, TN
Simon Vainberg, Shaw Environmental, Inc., Lawrenceville, NJ
Daniel Leigh, Shaw Environmental and Infrastructure, Inc., Concord, CA

Results of a Successful Enhanced Reductive Dechlorination Pilot Test under the SITE Program

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Stephen S. Koenigsberg, San Clemente, CA
Robert D. Norris, Brown and Caldwell, Golden, CO
Willard Murray, Gloucester, MA

Bioremediation of Contaminated Soil and Sediment by Composting

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Chemical pollution of the environment has become a major source of concern. Bioremediation technologies are today well established for the clean up of chemically contaminated land and many technologies are applied commercially in large scale. Composting matrices and composts are rich sources of microorganisms which can degrade pollutants to innocuous compounds such as CO_2 and water. In the present study composting of contaminated soil and sediment from Patancheru industrial area (Hyderabad, A.P, India) was performed on a laboratory bench scale pile. Fertilizer was added to increase the nutrient content and addition of commercial compost provided a rich source of microorganisms. After maintaining proper composting conditions the feasibility of composting was assessed by monitoring pH, total volatile solids, total microbial count, temperature and hazardous organic concentration. The entire composting process took five weeks resulting in degradation of hazardous organics and production of a compost with a high nutritional content which can be used as inocula for treatment of hazardous waste dumpsites.

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. Case histories describing successful field applications of HRC-X and total project cost will be presented.

The Efficacy Of Oxygen Release Compound (ORC®): A Nine-Year Review

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Oxygen Release Compound (ORC®) is proprietary formulation of intercalated magnesium peroxide that releases oxygen slowly and facilitates the aerobic bioremediation of a range of environmental contaminants, including petroleum hydrocarbons, certain chlorinated hydrocarbons, ether oxygenates (e.g. methyl tert-butyl ether [MTBE]), ammonia, certain herbicides, and arsenic. The history of ORC's introduction and acceptance represents a model for the evolution of an innovative technology. This statement comes by virtue of the fact that, since 1994, ORC has been applied 8,900 times worldwide and has been the subject of an extensive body of literature. This technology, known as a "time release electron acceptor", has now been clearly established as a sensible strategy for engineering accelerated bioattenuation on sites where design, capital, and management intensive options are either undesirable or contraindicated. ORC can be configured as a permeable reactive barrier, applied as a broader plume treatment, and emplaced post-excavation as part of the backfill. This presentation will summarize results from numerous field applications of ORC.

Some guidelines for using ORC have also emerged. It is contraindicated at sites where the BOD/COD load, seasonal or otherwise, is excessive or poorly understood, i.e., the technology is best applied to dissolved phase plumes and moderate levels of residual NAPL, once the majority of the source is removed. ORC was first used for the remediation of BTEX and TPH groundwater contamination, and other applications have since been made for an array of other aerobically degradable compounds such as vinyl chloride, pentachlorophenol, polycyclic aromatic hydrocarbons and MTBE. With respect to MTBE, as early as 1996, consultants using ORC noticed that MTBE concentrations decreased at a higher than expected rate. In concert with published evidence that ethers are aerobically biodegradable, additional field experiments demonstrated that oxygen can indeed enhance the remediation of MTBE; a concept that has since been verified in other quarters.

Enhanced In-situ Bioremediation of a Complex Free-Phase Plume of No. 6 & No. 2 Fuel Oils and Motor Oils Below a Permanent Structure: Selecting the Remedy

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An evaluation of options for heavy-oil remediation was required at a major urban bus terminal. Significant constraints were imposed on selecting a remedy because the terminal operates 24 hours a day, seven days a week, 365 days a year. Based on operational constraints and bench-scale feasibility testing, an enhanced in-situ bioremediation program was selected as a remedy to cleanup a 200’ x 75’ complex free-phase plume of No. 6 & No. 2 fuel oils and motor oils, that partially extends under a permanent structure at the bus terminal. A total of 25 four-inch ID access wells were installed in a 10’ x 10’ grid to allow the periodic inoculation of microbes and nutrients to the subsurface. Soil access ports and groundwater monitoring wells were also installed to allow bi-monthly sampling to monitor and evaluate nutrient levels (i.e., nitrates, nitrites and total phosphorus) and petroleum hydrocarbon concentrations. Remediation is currently ongoing, however initial Total Petroleum Hydrocarbons (TPH) and Extractable Hydrocarbons (EPH) analyses of soil and groundwater samples indicate a substantial reduction of petroleum hydrocarbons. TPH and EPH concentrations decreased at certain sampling locations from above 10,000 parts per million (ppm) to less than 1,000 ppm. The implementation of this bioremediation remedy program has provided encouraging results in the reduction of petroleum hydrocarbons, had minimal impacts on the operation of the bus terminal, and provided the Potentially Responsible Party (PRP) with a cost effective remedial approach, as compared to other possible remedial alternatives (e.g., soil excavation and removal with dewatering). Continued monitoring will assess long-term effects and compliance with closure standards under the Massachusetts Contingency Plan (MCP).

Field Demonstration of Three Techniques for Bioremediation of Chlorinated Ethenes at Naval Station Treasure Island

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Chlorinated ethenes, including tetrachloroethene (PCE) trichloroethene (TCE), dichloroethene (DCE) and vinyl chloride (VC), are a major source of groundwater contamination in the United States. In situ anaerobic bioremediation (ISAB) has been shown to be an effective technology for remediation of chlorinated ethenes. Various techniques have been developed to improve the ISAB process including bioaugmentation, hydrogen amendment and utilization of various substrates. Groundwater at Naval Station Treasure Island (TI) Site 24 has been affected by discharges of PCE at concentrations in excess of 20,000 µg/L. A pilot test was designed and conducted to evaluate ISAB methods to treat the high concentration source area. The pilot test evaluated three separate ISAB techniques including 1) lactate addition alone, 2) lactate and bioaugmentation with the SDC-9 culture and 3) lower concentration of lactate supplemented with hydrogen. The techniques were implemented simultaneously in three adjacent, hydrologically separate groundwater recirculation loops established in the chlorinated ethene source area. Real-time polymerase chain reaction (PCR) analysis was conducted in the field to quantify the dechlorinating organism Dehalococcoides sp (DHC) during SDC-9 injection and after biodegradation. The concurrent pilot tests successfully demonstrated the benefits of each ISAB technique. As anticipated, ISAB with only lactate was demonstrated to be an effective technology for degrading chlorinated solvents. However, bioaugmentation with the SDC-9 culture substantially increased the biodegradation rates and resulted in rapid and complete dehalogenation of chlorinated ethenes to ethene. The distribution of the SDC-9 throughout the bioaugmentation loop was confirmed by the PCR analysis. The addition of hydrogen demonstrated a technique by which the mass of substrate (i.e., lactate) added to support dehalogenation could be substantially reduced. The successful pilot test demonstrated the value of several techniques that will be used in the full-scale remedial design.

Aerobic In-Situ Bioremediation (ISB) of Semi-Volatile Organic Compounds (SVOC) via an Oxygen Gas Injection System

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Aerobic ISB is being evaluated as an alternative to an existing groundwater extraction system for treatment of aniline and nitrobenzene present as a dense non-aqueous phase liquid (DNAPL) at a site in New Jersey. The geology at the site consists of overburden soils overlying the Passaic Formation, a sedimentary rock that consists of interbedded sandstone, siltstone, shale, and conglomerate. Poorly sorted sands with some gravel and occasional silt and clay beds characterize the overburden. The upper portion of the Passaic Formation is highly weathered and fractured.

The basis of design of the ISB system was a field trial conducted between March and August, 2002. Low-flow pulsed injection of oxygen gas was performed for a period of 64 days during which approximately 4,200 pounds of oxygen were injected into the overburden and weathered bedrock via four injection wells. Rapid dispersion of dissolved oxygen was observed in groundwater and SVOC concentrations were reduced by greater than 90% within five weeks. First-order biodegradation rates for aniline and nitrobenzene were calculated to be less than 10 days (expressed as a half-life).

Full-scale implementation of the ISB system is being performed in a phased approach, with the first phase acting as an extended pilot test. The Phase I ISB system consists of an array 32 oxygen injections wells in the overburden and weathered bedrock spaced 40 to 80 feet apart in an area approximate 160 feet wide by 400 feet long and began operation in December 2003. The oxygen supply system is comprised of a 3,000 gallon liquid oxygen storage tank and evaporator and a fully automated oxygen distribution system housed in a portable trailer. Oxygen gas is pulse injected in two-minute intervals every half-hour. Groundwater monitoring results from the first six months of operation of the Phase I ISB system will presented.

Anaerobic Bioaugmentation Approaches for Treating Chlorinated Solvent Contaminated Aquifers

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Chlorinated solvents, including tetrachloroethene (PCE) and trichloroethene (TCE), are major groundwater contaminants throughout the United States. Extensive research and clean-up activities have demonstrated that these compounds can be biologically degraded in situ provided the correct environmental conditions exist and the proper microorganisms are present. In many cases, biodegradation can be initiated and performed by simply adding a supplementary carbon source (i.e., electron donor) to generate reducing conditions and provide reducing equivalents for biological reductive dehalogenation. In other cases, however, the addition of an electron donor alone does not support rapid site remediation, or biodegradation is incomplete. This is often caused by insufficient numbers of effective chlorinated solvent degrading microorganisms. In these cases, bioaugmentation can be used to achieve complete detoxification. Microbial cultures for bioaugmentation can be obtained commercially (i.e., exogenous cultures), or they can be isolated from active areas of a target site (i.e., indigenous cultures) and re-applied into inactive zones. This latter approach eliminates many of the concerns of introducing foreign cultures into resident aquifers, while allowing the use of organisms already adapted to survival in the target environment. We will describe the enrichment, characterization, and application of Shaw's Dechlorinating Consortium (SDC)-18 obtained from Area 18 at Lake City Army Ammunition Plant, and SDC-9 obtained from IR Site 9 at NAS North Island. The cultures enriched from these sites all contain Dehalococcoides sp., and are capable of dechlorinating PCE, TCE, and their daughter products to ethene via halorespiration. Data will be presented on the large-scale growth of SDC-9 for field-scale inoculation, and results of a successful field application of in-situ bioaugmentation at NAS Treasure Island. Special emphasis will be given to the time required to enrich and grow cultures, the challenges of growing large volumes of dehalogenating cultures, and remediation costs of the bioaugmentation approach.

Results of a Successful Enhanced Reductive Dechlorination Pilot Test under the SITE Program

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Hydrogen Release Compound (HRC®) and HRC Primer, a faster releasing version of HRC, were used in a pilot demonstration test to enhance reductive dechlorination of perchloroethene (PCE) and trichloroethene (TCE) in groundwater. A substantial amount of data, including concentrations of volatile organic compounds (VOCs), geochemical species, and organic acids were collected because the project was conducted under the United States Environmental Protection Agency (US EPA) Superfund Innovative Technology Evaluation (SITE) Program. Enhanced reductive dechlorination was selected because of its known effectiveness in treating PCE and corresponding daughter products down to low regulatory levels.

Data was collected for VOCs and geochemical parameters for two transects and a number of other wells over a 4-year period. The data showed that TCE concentrations were reduced by 88 to 98 percent, and cis-dichloroethene (cis-DCE) was produced and then degraded. Additionally, significant amounts of vinyl chloride and ethene were produced. Geochemical parameters responded as anticipated and were consistent with biodegradation patterns. Organic acids and elevated TOC levels were observed across the site and remained elevated through the 27 months of monitoring, as were favorable changes in the geochemistry.

In conclusion, a single application of a combination of HRC and HRC Primer was effective at initiating and maintaining reductive dechlorination of TCE through ethene for at least 27 months. A second addition of HRC may be required to bring remediation to a close and to maintain a barrier for an extended time. The data support observations by others that providing sufficient electron donor for a sufficient period of time can carry degradation past cis-DCE. This presentation will give extensive data showing how enhanced biodegradation and changes in geochemistry occurred across the site and over an extended time period. Total project cost information will also be presented.

Poster Session- Brownfields

Brownfield Site Assessment and Remediation – City of Lawrence Gateway Bridge

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Brownfield Site Assessment and Remediation – City of Lawrence Gateway Bridge

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This paper describes how the Massachusetts Brownfields process was implemented at the Oxford Paper Mill Site in Lawrence, Massachusetts. The paper presents the process for obtaining monies for assessment and remediation of the site, and the interaction of all of the various stakeholders. This project has significant stakeholders that include City of Lawrence, Massachusetts Department of Environmental Protection, Massachusetts Highway Department (MHD), the Environmental Protection Agency (EPA), Mass Development and Community Action Groups. The successful implementation of this complex process has allowed the City to abate contamination, develop a large-scale park and allow for the construction of a Gateway Bridge for the City, which is integral to future development of the city.

The City employed a dynamic process where the community, City and regulators developed a detailed plan to address integration of various stakeholder schedules and to additionally provide the necessary monies to remediate a 2 acre Brownfield site current with development of open space and a new gateway to the City of Lawrence.

Contaminants of concern at the site include asbestos, PCBs and PAHs. Concentrations of PCBs were identified on the site that significantly exceeded the EPA and MCP clean-up goals.

The challenges for this project include assisting the City in obtaining sufficient funding, coordinating with the abutting property owner cleanup of the raceway (man-made waterway) that runs through the site, and coordinating areas of remediation with MHD and the City.

The benefits to the community and the City are tremendous. A dilapidated paper mill site with nine buildings is being revitalized and returned to the City to be used as park land. In addition, this project will provide access for a much needed additional bridge to the city to encourage new business developments.

Poster Session- Chemical Oxidation

Field Pilot Testing for Chemical Oxidation at the Former Nitchequon Meteorological Station
Eric Bergeron, Golder Associates, MontrJal, QuJbec Canada,
Christian Gosselin, Golder Associates, MontrJal, QuJbec Canada
Adriana Peisajovich, Transport Canada, Dorval, QuJbec Canada
Ginette Lajoie, Cree Regional Authority, MontrJal, QuJbec Canada

Case Study on the In Situ Destruction of Contaminants at a Dry Cleaner Site
Sunitha Chavali, Reardon Environmental, Inc., Houston, TX
Thomas R. Liebert, Reardon Environmental, Inc., Houston, TX

In-Situ Chemical Oxidation of Petroleum Contamination by Activated Persulfate - Field Study
Scott C. Crawford, Xpert Design and Diagnostics, LLC, Stratham, NH
Kenneth L. Sperry, Xpert Design and Diagnostics, LLC, Allentown, PA

Expedited Remediation of a Brownfields Site Using the Modified Fenton's Process
Prasad Kakarla, Thomas Andrews and David Zervas, In-Situ Oxidative Technologies, Inc. (ISOTEC^{SM}), West Windsor, NJ

Naphthalene Removal by Pulsed and Peroxide-Coated Microbubble Ozone Injection
William B. Kerfoot, Kerfoot Technologies, Inc., Mashpee, MA
Andrew Brolowski, Streamline Environmental, East Falmouth, MA

In-Situ Chemical Oxidation (ISCO) Applications at MGP Sites
J. David Mannion, Shaw Environmental, Inc., Hopkinton, MA
Duane K. Root, Ph.D., Shaw Environmental, Inc., Knoxville, TN

Strategic Use of In-situ Ozonation to Achieve Expedited Site Closure
Steven D. Schroeder, P.E., RMT, Inc., Greenville, SC

Field Pilot Testing for Chemical Oxidation at the Former Nitchequon Meteorological Station

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Transport Canada used the Nitchequon Site as a meteorological station from 1942 to 1985. The site is located 1600 km north-east MontrJal and is only accessible by hydroplane or helicopter. Several characterizations revealed that the soil was contaminated with hydrocarbons (PH). In situ and ex situ pilot-scale chemical oxidation testing using the following three technologies were investigated: Tecosol in situ process (SOLTEC®), ex situ reactors and in situ passive reactor cells. The main objectives of the study were to evaluate the technical/economical feasibility of using a full-scale chemical oxidation remediation approach for the Nitchequon site and to prepare a preliminary rehabilitation plan including a budgetary cost evaluation and a preliminary schedule for remediation of the Nitchequon site. The in-situ treatment of the Nitchequon soils using the SOLTEC® technology was ineffective. The tests performed in continuous mixed reactors achieved interesting removal efficiencies. The final PH concentration and overall removal efficiency reached in the mixer for the different fractions of PH C_{10}-C_{50} are the following: C_4-C_{10} average final concentration of 1,6 ppm (96% reduction), C_{11}-C_{16} : average final concentration of 690 ppm (86% reduction), C_{17}-C_{34} average final concentration of 243 ppm (33% reduction), C_{35}-C_{50} below detection limit and C_{10}-C_{50} average final concentration of 990 ppm (83% reduction). The mean initial PH C_{10}-C_{50} concentration was 5975 ppm. The results of the passive rector tests will be available only in spring 2004. A preliminary rehabilitation plan has been developed. The proposed approach is to treat the soil with permanganate in horizontals blenders, backfill the excavations with the slurry to complete the chemical oxidations reactions and add a clean cover of soil (0.3 m thickness) over the treated soils. The total budget (excluding taxes) to perform the full-scale rehabilitation of the Nitchequon site is between 3.4 and $5.0 M.

Case Study on the In Situ Destruction of Contaminants at a Dry Cleaner Site

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Soil and groundwater contaminated with Perchloroethylene (PCE) poses a challenge for remediation, as PCE is highly resistant to natural degradation due to its high chlorine content and high specific gravity. Hence powerful oxidizing agents are required to break PCE into benign by products. An operating dry cleaning facility in Longview, TX required immediate remediation of the soil and groundwater contaminated by PCE. Due to the high contaminant levels, Reardon injected a combination of two powerful oxidizing agents: Fenton's reagent with a high oxidant to catalyst ratio to generate superoxide radicals ($O_2^{\bullet-}$) and remediation grade sodium persulfate to generate sulfate radicals ($SO_4^{\bullet-}$). By generating these powerful oxidizing radicals in soil, Reardon was successful in breaking the chlorinated molecule into chloride ions, steam and carbon dioxide. Reardon excavated the highly contaminated parts of soil and treated it in separate roll off bins by injecting the above-mentioned oxidants into the soil under high pressure using its patented injection technology. Sodium persulfate and ferrous sulfate (catalyst) under low pressure will be used initially for groundwater treatment. The contaminant concentrations before and after the treatment will be presented. The challenges faced by Reardon during the remediation of the site like operating problems experienced with the different oxidants and tenant/contractor interface issues, which were solved in the short timeframe for the project and the results will be discussed. The reaction contaminant chemistry in the soil and groundwater will also be discussed in detail.

In-Situ Chemical Oxidation of Petroleum Contamination by Activated Persulfate - Field Study

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An innovative in-situ oxidation treatment using activated sodium persulfate (the X-Ox Process) was field-tested at a site impacted with petroleum hydrocarbons. Persulfate ($S_2O_8^{2-}$) in the presence of naturally occurring or externally supplemented ferrous iron (Fe^{2+}) will react to produce a powerful oxidant known as the sulfate free radical ($SO_4^{-}\bullet$). The X-Ox Process involves the addition of a chelating agent to control the rate of sulfate free radical formation, which can increase the efficiency of the reaction with the target compounds. The site is a former retail gas station where two gasoline underground storage tanks have impacted soils and groundwater. Total BTEX concentrations of 11,370 µg/L and total alkylbenzenes concentrations of 5,000 µg/L have been observed. The geology consists of a fine to coarse-grained sand to a depth of 3.6 meters below surface grade overlying granite bedrock. During a 3-day injection event, a total of 17,269 liters of 60 g/L persulfate solution was injected into the target area (approximately 1,000 Kg of persulfate) with ferrous iron and a chelating agent. The oxidant loading was equivalent to 1.7 grams of oxidant per kilogram of soil. In practice, this is a relatively low oxidant loading. Initial post-injection groundwater data indicates that total BTEX concentrations have been reduced by 26% to 48% after the single oxidant dose. Total alkylbenzene concentrations were reduced by up to 91% in one part of the target area, however, there was significant rebound in the remainder of the target area (i.e., between 84% and 98% of the initial concentrations). Formation of intermediate compounds was also observed, and these intermediate compounds are continuing to degrade with continued contact with the oxidant. Initial results are promising considering a relatively low oxidant loading was used in the preliminary treatment.

Expedited Remediation of a Brownfields Site Using the Modified Fenton's Process

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A Brownfields site in New Jersey is being developed for construction of a new home improvement retail store. Due to high levels of TCE, PCE, VC, and BTEX contamination present over a 32,000 Sq. ft portion of the site, an expedited remedial schedule was established to substantially reduce soil concentrations, which exceeded 2,800 mg/kg for average volatile organic compounds (VOCs). The bulk of the contamination is present from 5 to 15 feet below ground surface (bgs) with the hot spots indicating total VOCs of up to 11,200 mg/kg. Subsurface geology consists of mostly sands with groundwater encountered at depths of 7-8 feet bgs. In situ chemical oxidation (ISCO) using a modified Fenton's reagent was selected to achieve the remedial objectives. The modified Fenton's reagent uses patented chelated iron catalysts and stabilized hydrogen peroxide to promote destruction of contaminants under circum-neutral pH (i.e. pH 5-8) conditions. An existing groundwater pump-and-treat system remained operational at the site during the course of the treatment program. It was hoped that source area soil remediation will reduce the operation and maintenance timeframe of the pump-and-treat system from the currently estimated 100 years to less than 20 years. Therefore, a remedial goal of VOCs less than 5 times the New Jersey Residential Direct Contact (NJRDC) Criteria was set for ISCO.

The currently ongoing modified Fenton's treatment program was initiated in August 2003 using a plurality of permanent injection wells and temporary direct push injection points. An aggressive, multiphase injection approach is being implemented at this site to allow for enhanced desorption and degradation of recalcitrant contaminants. A total of 32 permanent wells were installed at a spacing of 25 feet from one another. Additionally, the injection activities utilized between 60-90 direct push points per event to destroy soil contamination. Desorbed free product was recovered periodically using peristaltic pumps to accelerate the cleanup process. To date, the injection activities have been performed over three (3) 17-18 day events, with two (2) additional events scheduled to be completed by March 2004. A total of up to 16 sampling locations were utilized for performance data collection. Results received to date indicate a 78% destruction of total VOCs in site soils and 88% destruction in site groundwater. Of the soil samples collected, eleven of the 16 locations have indicated reduction to below the NJRDC cleanup criteria following three injection events. Additional results should be available within the next few months in time for the conference.

Naphthalene Removal by Pulsed and Peroxide-Coated Microbubble Ozone Injection

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Naphthalene compounds occur commonly in coal-tar product and weathered heavier oil spills. The compounds are readily oxidized in aqueous or adsorbed phase by microbubble ozone treatment. The authors compared the rate of oxidation of naphthalene during aqueous reaction with dissolved ozone, microbubble ozone, and peroxide-coated ozone. In the Perozone™ system the OH· radical is not transported towards the contaminant; it is continuously generated by the interaction of hydrogen peroxide and ozone injected pulse-wise into saturated soil. The extent of travel in soil of reactive Perozone™ is compared to microbubble ozone. The kinetics of naphthalene oxidation is reviewed and compared to observed rates of removal. Hsu and Masten (1997) raised questions about whether excessive soil oxidative demand (SOD) or self-decomposition would interfere with effective treatment of polyaromatic compounds. Field experience with pulsed ozone has shown low SOD and rapid treatment of naphthalene under a variety of conditions.

In-Situ Chemical Oxidation (ISCO) Applications at MGP Sites

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This paper focuses on two refinements to the application of in-situ chemical oxidants at MGP sites; pulsed ozone technology, and the use of persulfate reagent. Shaw's experience with ozone has led to the development of pulsed ozone technology (patent pending) for the treatment of PAH contamination. Testing with this technique has demonstrated the ability to destroy PAHs using up to an order of magnitude less ozone than traditional continuous application technology. A more recent oxidant alternative to permanganate ion and Fenton's Reagent is persulfate ion. Persulfate ion is a stronger oxidant than permanganate, capable of oxidizing PAHs, and at the same time is typically much less sensitive than permanganate to chemical demand from natural organic and other petroleum (TPH) compounds found in MGP soils. Under these conditions, persulfate reagent may be preferred over Fenton's reagent for treatment. There are potential MGP site applications that may be well suited to the use of these reagent technologies. They include PAH contaminated groundwater and saturated zone soils or potentially shallow soils that can be treated by an infiltration gallery. Chemical oxidant behavior and characteristics are compared to MGP site characteristics to select which, if any, chemical oxidation technologies are appropriate for consideration at a site.

Strategic Use of In-situ Ozonation to Achieve Expedited Site Closure

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Remediation for chlorinated volatile organic compounds (CVOCs) in groundwater often requires several years of time and a continuing influx of funding before meaningful cleanup progress can be achieved. Companies which fund these efforts have strong financial drivers to quickly reduce environmental liabilities, and are becoming increasingly wary of technologies that commit them to years of cost without a reasonable expectation of when, or if, an endpoint will be reached. In-situ oxidation provides an alternative that can be used as a key component to a site-wide remedial approach, which significantly reduces lifetime costs and the time required to achieve cleanup targets. Full-scale site remediation case studies, which use in-situ oxidation with ozone injection, are presented. One case study, highlighted and presented in detail, consists of a federal CERCLA site in South Carolina, where in-situ ozonation is being used as a supplemental remedy for groundwater. After several years of air sparging, CVOCs remained present and in-situ ozonation has been applied to complete remedial efforts. After only eighteen months of treatment, groundwater concentrations in all monitoring points are at or below MCLs, and EPA has granted approval for shutdown of the ozone system. Cost and performance information is also presented for other full-scale site applications where this approach is being successfully employed. For these case studies, the strategy to achieve closure relies on in-situ oxidation to reduce high concentrations of CVOCs in groundwater, to the extent required to facilitate natural attenuation as a final polishing step. As part of implementation, groundwater recovery systems will be removed from service years ahead of projections or never implemented.

Poster Session- Database/ Data Management

Developing a Property Management System in Support of Department of Defense Superfund Remediation

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Developing a Property Management System in Support of Department of Defense Superfund Remediation

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The Massachusetts Military Reservation is a multi-jurisdictional Department of Defense installation comprising 30,000 acres across four towns on Cape Cod. In the past it's size, location relative to large northeastern population centers, and historically sparse population made it a key training and staging area for a variety of Department of Defense interests. Decades of military use, combined with a porous glacial terrain and complicated by a sole-source aquifer, have created a variety of groundwater contamination plumes that have spread from the Reservation. Efforts to remediate the contamination require the acquisition of access agreements with area property owners so that treatment systems may be most effectively sited, installed, and maintained. The Air Force Center for Environmental Excellence (AFCEE) assumed responsibility for the remediation at MMR in 1996, and since then has secured several hundred such agreements with area property owners, mostly in hard-copy format. In 2003 AFCEE, in cooperation with other Department of Defense agencies, contracted with CH2M HILL to develop a web-based data management system to archive existing access agreements and support the process for obtaining future agreements. The property and easement management system is based on commercially available geographic information system (GIS) and relational database management system (RDBMS) development platforms and is designed to compliment other data management systems used on the program. Development of the system has to balance the requirements and interests of different, and sometimes competing, stakeholders and must address such issues as functionality, ERPIMS and SDSFIE standardization, future scalability, and deployment within and outside of the Department of Defense network firewall.

Poster Session- Environmental Fate

The Fate and Behaviour of MTBE and BTEX in the Vadose Zone

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Mobility and Persistence of Petroleum Hydrocarbons in Peat Soils of Southeastern Mexico

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Effects of Surfactants on Gas/Solid Partitioning of Herbicides

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Slow Desorption of Phenanthrene from Silica Particles: Influence of Pore Size, Pore Water, and Aging Time

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The Fate and Behaviour of MTBE and BTEX in the Vadose Zone

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There is wide interest in the environmental fate and behaviour of MTBE and the BTEX compounds because they are major constituents of petrol and hence frequently discharged into the environment as a consequence of accidental spillages. The vadose zone is often the first barrier to these contaminants before they reach the groundwater, where they can become more recalcitrant and subsequently create problems with drinking water supplies. In a range of column studies we observed that the downwards transport, interaction with the soil and evaporation of these compounds could be correlated with their physico-chemical properties. In degradation studies it was found that MTBE was metabolised more rapidly in a mixture with the BTEX than alone ($t_{0.5}$ = 1.7 day alone and 1.1 in mixture). It was also seen that TBA was produced as a direct consequence of this degradation. These data were subsequently used to parameterise the HAZCHEM model and the model predictions compared with the laboratory data.

Mobility and Persistence of Petroleum Hydrocarbons in Peat Soils of Southeastern Mexico

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Spilled crude petroleum from oil wells contains numerous hydrocarbons, some of which are toxic and threaten life. We have studied the mobility and persistence of hydrocarbons in waterlogged soils that contain large proportions of fermented organic matter (Histosols) and large concentrations of dissolved organic carbon (DOC) in the State of Tabasco, Mexico. We sampled soil and phreatic water at sites polluted by oil spills for several decades, as well as at sites that had only recently (few weeks) been polluted, and compared their hydrocarbon contents with those of unaffected sites in the same area. Samples were analyzed for 16 non-alkylated polyaromatic hydrocarbons (PAHs) and n-alkanes from nC9 to nC34.

The spilled hydrocarbons had remained predominantly in the organic surface horizons of the soil where spillage occurred; there was little evidence of movement within the soil. The fraction of low molecular weight compounds was larger at sites of recent spills than where spills happened several decades ago. Nevertheless, sites of old spills still contained large concentrations of hydrocarbons, among which those of low molecular weight represented from 30 to 49% of total PAHs and from 50 to 84% of total n-alkanes, indicating that volatilization or microbial degradation is slow in these soils. In the peat horizons the measured organic carbon partition coefficients (K_{oc}) for the higher molecular weight PAHs were consistently smaller than those estimated by empirical equations by up to two orders of magnitude. The dissolved organic carbon of these peat soils seems to influence this behavior. At sites of old spills, partition coefficients for the PAHs were larger than at sites of recent spills.

Effects of Surfactants on Gas/Solid Partitioning of Herbicides

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Many pesticides have been detected in air samples collected downwind of agricultural regions. However, little is known about the gas vs. particle transport behavior or the influence of surfactants commonly found in pesticide formulations on pesticide volatilization and partitioning with airborne particulate matter. This study addresses these important soil-air exchange processes that can lead to widespread dispersal of pesticides in the environment.

Most herbicides are applied as formulation mixtures that consist of adjuvants (surfactants and solvents) in addition to the active ingredients. The presence of surfactants has been shown to affect pesticide partitioning in soil-water systems, therefore the addition of surfactant is anticipated to influence the partitioning of herbicide in soil-air systems such as in unsaturated soils and airborne soil-derived particulate matter. This study is the first to investigate the effects of surfactants on herbicide partitioning between the soil and air compartments. Seven herbicides from two families — chloroacetanilide and dinitroaniline — and alcohol ethoxylate (AEO) surfactants are being examined.

Desorption kinetics experiments were conducted in soil-gas flow systems at ambient temperature and relative humidity. Herbicide-spiked soil was allowed to dry prior to loading onto a filter in a stainless steel filter holder. A vacuum pump pulled clean and particle-free air through the spiked soil and the polyurethane foam (PUF) plugs that were used to capture gaseous herbicides desorbed from the soil. The PUF and soil samples were extracted by supercritical fluid extraction (SFE) and analyzed by GC/MS to quantify herbicide concentration in the gas and solid phases, respectively.

Preliminary results for metolachlor and pendimethalin showed more rapid release to the gas phase from the soil spiked with the formulated mixture compared to pure herbicides, and also greater overall desorption losses in the presence of the adjuvants. The surfactant effects on partitioning of the other five herbicides are being explored in our on-going research as a function of soil type, relative humidity and temperature.

Slow Desorption of Phenanthrene from Silica Particles: Influence of Pore Size, Pore Water, and Aging Time

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In an effort to better understand the environmental fate and transport of aged petroleum hydrocarbons in aquifer solids, we performed a series of sorption and desorption experiments using phenanthrene as a model hydrocarbon compound and porous silica particles as model aquifer solids. When micro-porous and meso-porous silica particles were exposed to aqueous phenanthrene solutions for various durations it was observed that sorbed-phase phenanthrene concentrations increased with aging time only for meso-porous but not micro-porous silicas. Desorption equilibrium was reached almost instantaneously for the micro-porous particles while both the rate and extent of desorption decreased with increasing aging time for the meso-porous silicas. These findings indicate that phenanthrene can be sequestered within the internal pore-space of meso-porous silicas while the internal surfaces of micro-porous silicas are not accessible to phenanthrene sorption, possibly due to the presence of physi- or chemi-sorbed water that may sterically hinder the diffusion of phenanthrene inside water-filled micro-pores. By contrast, the internal surfaces of these micro-porous silicas are accessible to phenanthrene when incorporation methods are employed which assure that pores are devoid of physi-sorbed water. Consequently, when phenanthrene was incorporated into these particles using either supercritical CO_2 or via solvent soaking, the aqueous desorption kinetics were extremely slow indicating effective sequestration of phenanthrene inside micro-porous particles. A two-compartment conceptual model is used to interpret the experimental findings and assess the bioavailability and risk of aged petroleum hydrocarbons in groundwater aquifers.

Poster Session- Environmental Forensics

Why Sometimes It Is A Good Idea To Bury Your Head In the Sand – A Case Study of Environmental Forensics

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Evaluation of Solvent Plume Discharge to a Wetland Stream using an Innovative Passive Diffusion Sampling Methodology

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Determining the Source of Hydrocarbon Sheen Using Chromatogram Fingerprinting and Biomarker Source Ratio Analysis

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Historical and Chemical Determination of the Sources of PAHs in Soils at a Former Coal-Burning Power Plant, New Haven, Connecticut

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Use of Total Lead Concentrations in Environmental Forensics Age-Dating of Subsurface Gasoline Contamination

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Why Sometimes It Is A Good Idea To Bury Your Head In the Sand – A Case Study of Environmental Forensics

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Imported backfill and topsoil can originate from a number of sources, not all of which are free of contamination. Presented in this paper is a case study of the investigation of questionable topsoil and backfill that was placed on over 900 residential properties over several years as part of landscaping restoration activities associated with a sewer improvement project in the City of Gloucester. The paper presents the development of a forensic approach to determining the source, time period and distribution of the questionable topsoil and backfill used on the project. The approach developed significantly reduced the number of samples needed to identify the problem and evaluate the risk under the Massachusetts Contingency Plan. Polarized Light Microscopy (PLM), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray analysis were conducted to definitively identify the nature of the contaminants. The presentation includes the development of the approach, a presentation of the findings and statistical analysis of the analytical data and selected SEM photomicrographs and EDX spectra. The presentation concludes with practical recommendations for property owners, municipalities and project managers to prevent the use of poor quality topsoil or backfill on their project or property.

Evaluation of Solvent Plume Discharge to a Wetland Stream using an Innovative Passive Diffusion Sampling Methodology

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This paper describes the first phase of a multi-phase project currently underway to delineate a chlorinated solvent (primarily trichloroethylene [TCE]), plume in groundwater downgradient of a former industrial site. The TCE was introduced to the subsurface environment at the site, resulting in a groundwater plume extending from the on-site source to a wetland-stream complex, the primary discharge point for groundwater migrating from the site. To date, the plume has been delineated from the source to the upgradient edge of the wetland via quarterly groundwater sampling through a network of monitoring wells. At the upgradient edge of the wetland, TCE concentrations in groundwater remain elevated, while products of reductive dechlorination are present. Additionally, surface water sampling indicates that the solvent plume is discharging to a stream that drains the wetland.

The first phase of the plume delineation project consisted of a recently completed solvent plume discharge evaluation (SPDE), with the objective of evaluating the locations of solvent plume discharge to the wetland stream. The SPDE was cost-effectively conducted by deploying passive diffusion samplers (PDSs) in the wetland stream sediments at 45 locations along a 1,900 foot length of the stream. Once equilibrium between the PDSs and the sediment pore water was attained, the concentrations of chlorinated ethylenes in the PDS samplers were measured. The analytical results were mapped as a function of stream length and indicate a definitive point of plume discharge to the stream and a possible plume fringe. The results were also correlated with sediment type, water quality parameters, and piezometric measurements obtained during this work. The ratios of degradation products to TCE were greater in the PDS samplers than ratios observed at upgradient monitoring locations, indicating an increasing natural attenuation potential as the plume migrates through the wetland. The results of the SPDE were used to focus the next phase of plume delineation, currently being conducted. Preliminary results of the plume evaluation are compared to the SPDE results.

Determining the Source of Hydrocarbon Sheen Using Chromatogram Fingerprinting and Biomarker Source Ratio Analysis

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During the mid to late 1800's, the predecessor to a major oil company (The Company) operated a refining complex along the banks of the Allegheny River in the Western Pennsylvania. Records indicate that various refining, manufacturing and petroleum storage operations, conducted by other entities, have also occurred at the site since at least 1877. The Pennsylvania Department of Environmental Resources (PADER) notified The Company of the existence of localized oil sheen visible on the Allegheny River.

The sheen appeared to originated from a location along the River that may have been experiencing impact from a variety of sources, including asphaltic tar material buildup on the river bank (resulting from former refinery operations), and an accumulation of non-aqueous phase liquid (NAPL) in groundwater potentially discharging to the River (the result of current bulk storage operations). Determining the actual source of the sheen became critical for allocation of potentially significant remedial costs and future Natural Resources Damages (NRD) between The Company and other Potentially Responsible Parties (PRPs).

This paper describes the sampling strategy that was developed for the sheen and potential source materials, and sampling methods that were developed and employed to provide representative samples. An initial evaluation of the chromatogram fingerprinting and double ratio plot analysis using specific biomarkers (benzothiophenes) was inconclusive. The data were recently revisited to evaluate other paired PAH ratios that have provided more conclusive results.

Historical and Chemical Determination of the Sources of PAHs in Soils at a Former Coal-Burning Power Plant, New Haven, Connecticut

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The English Station power plant in New Haven, Connecticut had operated for nearly 100 years before being decommissioned in 1992. The property is located on a largely man-made island located in the Mill River. Historical records research indicated that almost all of English Station island's land mass above the original mud flats appears to have been derived from dredged spoils from the east and west branches of the Mill River between 1900 and the early 1930's. Soils from the property had been previously shown to contain polycyclic aromatic hydrocarbons (PAH) at concentrations that exceed the state's Department of Environmental Protection's (DEP) acceptable levels for commercial properties. Understanding the source(s) of these PAH was important for future property and environmental management decisions. This study was conducted to assess the industrial use history of the Mill River study area and conduct detailed chemical characterization of the extractable hydrocarbons in soils from the site, particularly the PAH, in order to determine their likely source(s). Soil samples (n=68; surface to 27 ft. below grade) were extracted and analyzed for total extractable petroleum hydrocarbons (TPH) and a subset were then selected for analysis via (1) a modified EPA Method 8270 for an extended suite of PAH (n=35) and/or (2) organic petrology (n=25). The results indicate that most PAH in the soils studied are derived from MGP tar(s) and non-specific, residual petroleum wastes. Synthesis of the industrial history of the study area and the chemistry and organic petrology of soil demonstrated that the dredged sediments used to construct the English Station island contained MGP tar(s) and petroleum wastes discharged from historic MGP and/or other industrial operations on the Mill River. The more recent coal combustion operations on the English Station property have contributed lower amounts of PAH, in the form of particulate coal and bottom ash (clinker), but with a spatially limited distribution.

Use of Total Lead Concentrations in Environmental Forensics Age-Dating of Subsurface Gasoline Contamination

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Forensic age-dating of subsurface gasoline releases in the United States of America using total lead concentrations is being used today to resolve environmental, financial and legal liability disputes in environmental pollution cases. Assumptions originating from U.S. Government regulations governing the U.S. Environmental Protection Agency mandated leaded gasoline phase down promulgated in the 1980s, which are implicit in such methodology, are wrong. Assumptions do not reflect existing chemical data on the composition of leaded gasoline sold in the U.S. over the decades of the 1940s through the 1990s. Review of existing leaded gasoline data in national motor fuel surveys over a 50-year time period revealed that total lead concentrations in leaded gasoline were too variable to be predictable based solely upon the context of U.S. Government regulations. Environmental forensics approaches for age-dating gasoline contamination using total lead concentrations result in highly variable and scientifically unreliable conclusions and must not be used to resolve environmental, financial and legal liability disputes.

Poster Session- Legal Issues

Liability Management at a Fuel Pipeline Release Site

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Liability Management at a Fuel Pipeline Release Site

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A landowner reported a leak in a subsurface fuel pipeline located on remote, uninhabited farmland. The landowner perceived a delay by the company in responding to the release and expressed dissatisfaction. Subsequently, a fire of suspicious origin occurred at the site. The fire and associated safety concerns resulted in extensive emergency response actions by the company. A large area was excavated to isolate and repair the pipeline and prevent product migration via a proximal ditch. However, the excavated, contaminated soils were stockpiled on bare ground without any measures to prevent contaminant leaching or runoff. The landowner filed a lawsuit against the company alleging that the initial response and subsequent actions were intentionally delayed and thus harmed his interests. The lawsuit resulted in further delays as protracted negotiations were required with the landowner and his legal counsel to obtain site access. Meanwhile, the open excavation collected water from several rain events, creating a potential for contamination to migrate and infiltrate. Also, contaminated stormwater now needed to be addressed. As an added complication, the landowner hired a consultant who undertook site and regulatory actions that conflicted with the company's actions. Because of these developments, the agency increased its scrutiny of an already high-profile project. During the site investigations, the landowner's consultant remained onsite to observe and collect split samples. Extensive negotiations were required with the state agency and the landowner's counsel before remedial actions could be initiated. Because the company lacked a plan for expeditiously assessing and addressing potential liability at release sites, it found itself in a reactive mode. Such a lack of liability planning resulted in significant project schedule delays and cost overruns. Had a plan existed to address landowner concerns and undertake prompt action to mitigate contamination expeditiously, issues related to schedule, cost and public relations could have been better managed. The lawsuit and remedial actions are ongoing.

Poster Session- Miscellaneous

Experimental Study of Nonreactive Solute Transport in Fine-Grained soils under Consolidation

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Experimental Study of Nonreactive Solute Transport in Fine-Grained soils under Consolidation

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This paper presents and analyzes results from twelve consolidation tests for non-reactive solute transport in fine-grained soils under consolidation. Kaolinite specimens, 50 mm in diameter and 70 mm in height, were prepared at 55% water content (above the liquid limit). The initial concentration of bromide (the tracer) was 1000 mg/L and 0 mg/L in the upper half and lower half of the specimen, respectively. The consolidation tests were conducted under constant load of 25 kPa with single drainage on the top in the consolidometer. Samples were collected from the surrounding solution during the test for bromide analysis. To determine the bromide profile across the specimen at the end of tests the specimen was sliced into four parts and centrifuge was used to extract the pore water for bromide analysis. Test results confirmed that with an average coefficient of consolidation of 2 × 10. 4 cm 2 /s(0.7cm 2 /hr) consolidation induced advection is the dominant mechanism for the bromide transport during the consolidation process. Further analysis showed that the ratio between diffusion coefficient and consolidation coefficient determines the relatively role they play in the transport.

Poster Session- MTBE

The Half-Life of Gaseous Ozone Pulsed Soil Perfusion for MTBE and Other Oxygenate Removal

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Air Sparging Effectiveness in MtBE Removal from Water, Tested on an Intermediate Scale Laboratory Apparatus

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The Half-Life of Gaseous Ozone Pulsed Soil Perfusion for MTBE and Other Oxygenate Removal

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It is a common misconception that ozone gas has a short half-life. Dissolved ozone, which reacts with water to release hydroxyl radicals, has a half-life of minutes; whereas ozone in gaseous form has a half-life measured in hours or longer. W. S. Sease in "Ozone Mass transfer and contact Systems," stated that at 0°C, the half-life of gaseous ozone is 2,000 years. Ozone-air mixtures placed in sampling VOC vials, checked periodically, showed an initial quick drop (half-life 5-9.5 hours) during which time the gas reacts with other air components (nitrogen and moisture), then a slow half-life of 35 hours commonly exists. Reducing microbubble size has a profound effect on capacity of bubbles to remain in solution, their reactivity, and in transmission through soils. Below 100 micron size, stable solutions of nano to microbubbles can be produced in aqueous solutions. With pulsing at certain frequencies and pressure differentials, the bubble emulsions can be transmitted vertically and laterally for oxidative reactions with target organic compounds, like MTBE. By controlling bubble size, ozone concentration and air/ozone volume released per pulse, the likelihood of fugitive ozone emissions can be reduced or eliminated while oxidation reactions proceed. Laboratory tests were conducted to compare microbubble buoyancy versus diameter for various column diameters. Vertical travel velocities were then compared to columns of sand of differing permeabilities. The effect of pressure differentials in producing significant vertical and horizontal transport were defined and compared to observed field transport. The arrival of microbubbles into monitoring wells could be counted and was correlated with the arrival of wavefronts. The observed rate of removal of MTBE at different release sites from retail gasoline service operations is compared with theoretical mechanics. Observed half-life (pseudo-first order) attenuation coefficients ranged from 3 to 14 days when mean midway ROI values from nano to microporous diffusors are compared. The radial spread must be taken into account when comparing efficiencies of removal from site to site. A modification of Clayton's equation for ozone reactivity can be used for predictive purposes.

Air Sparging Effectiveness in MtBE Removal from Water, Tested on an Intermediate Scale Laboratory Apparatus

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In the last decade the groundwater contamination by MtBE due to fuel spills or leakage from underground storage facilities became a high sensible environmental issue. Among all the in-situ groundwater remediation treatments, aimed to remove MtBE and the other gasoline components, the Air Sparging (AS) has been widely used since it is one of the best established economical and reliable technologies for the remediation of volatile compounds dissolved in groundwater. Nevertheless there are still many uncertainties regarding the airflow distribution in saturated media and the interactions of various physical-chemical processes during AS applications. Thus, the present experimental study was aimed to investigate the effectiveness of AS in dissolved MtBE removal from a saturated media, performing a removal test under confined and controlled conditions in an intermediate scale tank (m 1 x 1 x 1,2). The experimental conditions have been focused to study the stripping process driven by the air injection, since stripping is considered to be the most effective among the removal processes driven by AS, in the short terms of its in situ application. Through data interpretation, several considerations were made to evaluate the effects of geometry, water temperature and bulk water movement on the effectiveness of AS removal from MtBE contaminated water. This study confirmed that in-situ AS has a significant potential in groundwater remediation contaminated by MtBE, showing that the stripping action driven by the air injection give such a strong contribution to the comprehensive removal action of the AS technology. Following this, was also investigated the influence of some factors governing the efficiency of the process of stripping, such as the sparge point screen size and the usage of surfactants to enhance the AS performance.

Poster Session- Pay-for-Performance

High-resolution Baseline Surveys for focusing remediation efforts

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High-resolution Baseline Surveys for focusing remediation efforts

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With the emergence of Pay-for-Performance Contracting, it has become increasingly critical to have better site characterization data in order to create high-resolution and more accurate conceptual site models. Without such clarity, all the risks of the unknown site conditions will be either built into an inflated price proposal or underestimated, causing the selected low bidder to cut corners or request numerous change orders to make up for the unexpected cost overruns. It is in no ones' interest to proceed with insufficient knowledge about site conditions. Currently State Pay for Performance programs are struggling with how best to deal with large spatial data gaps, prior to going out for bid.

Historically, many remediation efforts have failed due to inadequate site characterization and/or over-generalized and misleading conceptual site models. This resulted in costly remediation efforts that do not achieve the clients' expectations or their regulatory goals, cost-effectively, if ever. Today, many older remedial technologies are being reassessed, optimized and in many cases replaced by new emerging, remedial technologies or a combination of technologies are being implemented. In some cases, the redesign still does not have an adequate amount of information for creating an efficient remedial system. This is proving to be costly as well as an ineffective way to do business.

The need for total mass characterization including sorbed, dissolved, free-phase liquid and vapor phase site data both pre and post application of the remedial technology(s) are critical to project success. Fortunately with the emergence of a variety of direct sensing tools such as the Membrane Interface Probe and optical methods (fluorescence) much more information can be collected in a short amount of time and more accurate site models can be built. These tools gather thousands of measurements on the geology, hydrology and nature and extent of the subsurface contaminants. The data can be processed into high definition 2D and 3D images of the site, which provides the bidder with much more detail than is normally available for designing a remediation approach. With this detail, both the bidder and the regulator will be able to determine what areas can be remediated and which cannot, resulting in more realistic expectations of the remediation effort.

To determine the effectiveness of the remediation effort, additional surveys can be conducted post application of the selected technology(s). These surveys reveal not only reveal the success of the efforts but also show where the chemicals may have been mobilized. In some cases, they will show where a subsequent application is necessary. Direct sensing surveys are both time and cost-effective in providing much more realistic assessment of subsurface conditions than a limited number of monitoring wells or discrete samples spread throughout the application area.

Poster Session- Risk Assessment

A Review of Risk Assessment Methods to Demonstrate Potential Risk from Exposure to Asbestos in Soil

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Assessing the Toxic Risk of Polychlorinated Biphenyl (PCB) Congeners Using the Bluegill Sunfish Immune System

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Factors Affecting the Bioconcentration of DDE from Soil By 3 Earthworm Species

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Applying a Spatially Explicit Wildlife Exposure Model to Improve Remedial Efficiency: The SEEM Case Study

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Human Health and Ecological Risk Assessment of a PCB-Impacted Former Radar Station in Atlantic Canada

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A Review of Risk Assessment Methods to Demonstrate Potential Risk from Exposure to Asbestos in Soil

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Standard analytical methods do not exist to measure asbestos fibers in soil. Analytical methods, including Transmission Electron Microscopy (TEM), developed to measure asbestos in bulk material, have been applied qualitatively to the soil matrix to determine the type and degree of asbestos contamination in soil. Current quantitative risk assessment practice relies on TEM analysis of soil samples, in combination with dust generation estimates, to model an asbestos concentration in air, the exposure pathway of concern. However, uncertainty is introduced when modeling TEM results from soil to an airborne asbestos concentration in respirable dust due to the heterogeneity of asbestos types and soil types. As a result, this method may not reliably quantify asbestos exposure points for use in quantitative risk assessment. An analytical method more directly related to exposure and risk assessment for asbestos, the Draft Modified Elutriator Method for the Determination of Asbestos in Soils and Bulk Material (D. Wayne Berman and Anthony Kolk, 2000), measures the amount of asbestos released to the air in respirable dust from asbestos-contaminated soil. These measurements can be used directly to quantify risk from inhalation of asbestos in air thereby eliminating the need to model asbestos soil concentrations to dust. A challenge that risk assessors will meet when applying the Modified Elutriator method to asbestos risk assessments is how to use these estimates to back-calculate an asbestos soil concentration that is protective of human health. Part of this challenge will be to determine how the amount of asbestos released to the air in respirable dust compares to the amount of asbestos measured in soil, given the heterogeneity of both asbestos types and soil types. A comparison of asbestos risk assessment methods is presented.

Assessing the Toxic Risk of Polychlorinated Biphenyl (PCB) Congeners Using the Bluegill Sunfish Immune System

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The immune system, sometimes overlooked as a sensitive and frequently-targeted organ for chemical-induced toxicity, is an essential component in maintaining overall good health of an organism. Any alteration in normal immune function can disrupt homeostasis and result, ultimately, in increased susceptibility to disease. For these reasons, studies examining chemical-induced immunotoxicity in residing species are essential for accurately predicting the health of an ecosystem. The objective of this study was to examine the impact of a widespread aquatic contaminant (i.e., PCBs) on the immune response of a feral fish species to determine its sensitivity for predicting PCB-induced immunotoxicity. The effects of a single intraperitoneal exposure of bluegill sunfish (*Lepomis macrochirus*) to either a potent coplanar (PCB 126) or environmentally-relevant noncoplanar (PCB 153) PCB congener on host immunocompetence was determined by examining non-specific and cell-mediated immune parameters. Cytochrome P-4501A (CYP1A) induction, typically measured as a biomarker of PCB exposure, was also examined. Phagocyte-mediated oxyradical production and mitogen-stimulated lymphocyte proliferation were examined using kidney/spleen cells recovered from laboratory exposed fish on 3, 7, 14 or 21 d post-PCB exposure. While both congeners enhanced extracellular superoxide production by kidney phagocytes 3 d post-exposure, only PCB 153 had significant effects on lymphoproliferation. Proliferation of both T- and B-lymphocytes was suppressed (compared to controls) as early as 3 d and up to 14 d post-PCB 153 exposure. Hepatic CYP1A was only induced in fish treated with PCB 126. Given the lack of CYP1A induction associated with PCB 153 exposure, immunosuppression may prove a more relevant biomarker for predicting exposure to- and health risks from- noncoplanar PCB congeners. Results reveal the sensitivity of the fish immune response for assessing PCB-induced immunodysfunction and demonstrate the utility of such a system for assessing risks to exposed populations, and for predicting ecosystem health.
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Factors Affecting the Bioaccumulation of DDE from Soil by 3 Earthworm Species

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The uptake of pollutants by soil organisms is controlled by a number of biological, chemical, and physical variables. Factors affecting the extent to which a compound such as DDE (a persistent product of the metabolism of DDT) is biologically available are important because knowledge of them could inform the evaluation and management of contaminated sites. We studied the effects of species differences, soil concentration and residence time of the contaminant, and interactions with a plant, on the bioaccumulation factor (BAF; dry-weight ratio of contaminant concentration in the tissue to that in the soil) of DDE for earthworms. In 4 field-weathered soils, the BAF for *Eisenia foetida*, an epigeic species (surface habitat), was approximately 10-fold higher than those for *Lumbricus terrestris*, an anecic species (deep habitat) and *Aporrectodea caliginosa*, an endogeic species (habitat within the soil profile). Within the range tested (82 ppb to 405 ppb), the data indicate that BAF may decline with increasing pollutant concentration in soil. Residence time of DDE did not significantly alter the BAF for *A. caliginosa*, but the BAF for *E. foetida* was lower in weathered soils relative to that in spiked soils. The presence of a single plant also affected the BAF of *E. foetida* and *L. terrestris*. Bioaccumulation by *E. foetida* grown with *Curcubita maxima* was over 3-fold lower than that by the worms grown alone. Growth with *Curcubita maxima* led to a modest decrease in the BAF for *L. terrestris*. These data suggest that risk assessments of contaminated sites should consider the differences in bioavailability of soil toxins to different species and the environmental factors that control uptake by organisms. Total chemical concentration alone is not a reliable indicator of the toxicological significance of a contaminated soil.

Applying a Spatially Explicit Wildlife Exposure Model to Improve Remedial Efficiency: The SEEM Case Study

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The development of wildlife exposure models that incorporate the impact of chemical distribution, habitat distribution and the foraging behaviors of the assessed species, not only insert realism into the risk assessment, but also insure that remedial actions focus on the areas where habitat and chemicals intersect. The Spatially Explicit Exposure Model (SEEM) is being developed for the US Army to improve the realism of wildlife exposure modeling. SEEM tracks exposures for all individuals in a user-defined population rather than evaluating a single representative individual. Foraging for each individual is guided by habitat suitability preferences. As a result, individuals are less likely to forage in areas where the habitat suitability is low. Also, users may select two different foraging strategies, a free-ranging strategy and a static home range strategy. In the free-ranging strategy individuals move across the landscape guided by habitat suitability. Foraging each day is bounded by the home range, however each day that home range boundary shifts based on the path followed the previous day. In contrast, in the static home range strategy, individuals move out from a central location (e.g. a nest) to forage a user-specified number of times bounded by the home range. The home range boundary remains in the same location throughout the modeling period. In both strategies individuals forage a user-specified number of times per day. The model is run for a specified number of days. The model generates population-effects curves. In combination with area-effect curves, users may develop remedial strategies that balance risk reduction with loss of habitat due to remediation and remedial efficiency. SEEM assists in developing remedial strategies that reduce site-wide risk, while avoiding the application of a single PRG to all areas of site. SEEM is being developed for inclusion within the US Army Risk Assessment Modeling System (ARAMS).

Human Health and Ecological Risk Assessment of a PCB-Impacted Former Radar Station in Atlantic Canada

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A human health and ecological risk assessment was conducted on a former remote radar station site that was contaminated with elevated soil concentrations of PCBs. The site is adjacent to a frequently used recreational trail. Adjacent lands include forested habitat and a stream. PCBs were identified as the only chemical of potential concern for the human health and terrestrial ecological risk assessment (ERA). A number of metals, and petroleum hydrocarbons were assessed in addition to PCBs for the aquatic ecological risk assessment. The multipathway human health risk assessment (HHRA) focused on a recreational exposure scenario and included potential exposures from wild berry and game consumption. In the ERA, a variety of ecological receptors, including freshwater aquatic life, small mammals and carnivores were evaluated. Probabilistic exposure analysis techniques were used to estimate PCB exposure in both human and ecological receptors. Results and risk management options will be presented.

Poster Session- Risk Based Cleanup

Status of Gasoline-Related Hazardous Waste Sites in Sensitive Groundwater Resource Areas in Massachusetts

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Status of Gasoline-Related Hazardous Waste Sites in Sensitive Groundwater Resource Areas in Massachusetts

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An analysis of data obtained from the Massachusetts Department of Environmental Protection's (MADEP) hazardous waste site databases was conducted to determine the status of gasoline-related hazardous waste sites (GRHWS) within sensitive groundwater resource areas. Of the 199 identified GRHWS in Massachusetts, *no gasoline service stations* situated in a zone of contribution to a public drinking water supply have achieved regulatory closure. This study raises significant implications with respect to the feasibility for regulatory compliance in Massachusetts under current constraints for site closure. This study was conducted to (1) quantify the number of GRHWS in either a zone of contribution to a public water supply well (i.e., Zone II) or other current or potential drinking water source; and to (2) determine the number of these sites that have been restored to "background conditions" through active remediation or have otherwise achieved a "Permanent Solution" as defined by the Massachusetts Contingency Plan. A search has identified 190 active GRHWS in sensitive groundwater resource areas. As indicated by the reviewed databases, most of these sites are currently undergoing some form of remediation. Nine (9) of the identified 199 GRHWS have achieved some form of regulatory closure; however, only one (1) of these sites is located in a zone of contribution to a public water supply and is not a gasoline service station. This analysis begs the question, whether environmental professionals and regulators are in a difficult position of implementing a mandate that compels PRP's to conduct remedial efforts that, to date, have been unsuccessful. Furthermore, it is probable that the majority of these sites are funded through the State's UST reimbursement program and therefore it is fair to ask whether public resources are being used to implement a policy that cannot work.

Poster Session- Sediments

Site-Specific Equilibrium Partitioning Sediment Benchmarks for PAHs in Sediments at Manufactured Gas Plants

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Monitoring of PCDD/Fs Distribution in Marine Sediments according to Different Particle Sizes

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Preliminary Sediment Sampling at the Big Lost River Sinks

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Effects of Data Sampling in Geostatistical Modeling of Sediment Contaminant Concentrations

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Site-Specific Equilibrium Partitioning Sediment Benchmarks for PAHs in Sediments at Manufactured Gas Plants

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From the 1800s, manufactured gas plants (MGPs) produced byproducts, such as coal tars, that contain high concentrations of polycyclic aromatic hydrocarbons (PAHs). The presence of PAHs in phases such as coal tar or soot that do not partition freely may trigger expensive clean-up actions that are not based on site-specific risks. Sediment quality benchmarks, such as the Equilibrium Partitioning Sediment Benchmarks (ESBs), may be overprotective if the characteristics of the sediment reduce the bioavailability and toxicity. The draft USEPA Bioavailability Procedure uses measured or estimated concentrations of PAHs in porewater to estimate the fraction of total PAHs that are bioavailable. The objective of this study is to examine whether the Bioavailability Procedure can be used to develop site-specific ESBs for PAHs that are conservative predictors of sediment toxicity at MGP sites. Sediments were analyzed for 34 PAHs, total organic carbon, soot carbon, and sediment toxicity. Porewater was analyzed for PAHs and organic carbon. The sum of the ESB toxic units (Sum-TUs) were calculated from: 1) concentrations of PAHs in bulk sediment, 2) concentrations of PAHs in porewater, or 3) concentrations of PAHs and soot carbon in sediment. Results indicate that: 1) Sum-TUs based on concentrations of PAHs in bulk sediment correctly predicted lack of toxicity in sediments with concentrations of total PAHs less than 100 mg/kg, over predicted toxicity at concentrations between 200 to 300 mg/kg, and correctly predicted toxicity at concentrations greater than 300 mg/kg. 2) Sum-TUs based on measured concentrations of PAHs in porewater were somewhat variable, but overestimated toxicity in fewer samples than estimates based on bulk sediment. 3) Sum-TUs estimated from measurements of PAHs in bulk sediment and soot carbon were the most accurate predictors of toxicity. This research demonstrates that the Bioavailability Procedure is useful in assessing impacts of PAHs in sediments at MGP sites.

Monitoring of PCDD/Fs Distribution in Marine Sediments according to Different Particle Sizes

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Marine sediment is an important sink of hydrophobic organic compounds (HOCs) entering from terrestrial and atmosphere. We obtained marine sediments from southeastern coast in Korea and separated into particle sizes. The combination of Pinched-SPLITT (split-flow thin fractionation) technique and high resolution gas chromatograpy/high resolution mass spectrometry (HRGC/HRMS) was used. Separated sediments were processed for HRGC/HRMS analysis using a multiresidue method based on US EPA method 1613. From these analyses, we tried to see the PCDD/Fs distribution in different particle sizes, especially fine particles (< 63 µm); 20-63, 10-20, 5-10, 2-5, < 2 µm. Levels of PCDD/Fs in bulk sediments were similar to previous studies and each sediment sample showed some different homologue profiles due to different environment condition. PCDD/F levels in separated sediments tended to increase as particle sizes decreased. These trends in different particle sizes were related to amount of organic carbon contained in each separated particle. It is considered that small particles have higher surface areas than larger particles and organic carbon can adsorb and capture PCDD/Fs. Fine particles showed higher contamination and this represents the effects of organohalogenated contaminants can be different in particle sizes. Furthermore, the smaller particles have the more potential health risk to marine environments such as deposit-feeder.

Preliminary Sediment Sampling at the Big Lost River Sinks

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One aspect of the effects of nuclear and chemical waste on plants and animals not addressed by the Comprehensive Remedial Investigation/Feasibility Study Ecological Risk Assessment for the Idaho National Engineering and Environmental Laboratory (INEEL) was the magnitude of contaminant transport down the Big Lost River into environmentally sensitive areas such as the Big Lost River Sinks. Transport in river systems is a known route for the movement of non-volatile radioactive and conventional contaminants. Studies of fallout plutonium in rivers have shown that the most important transport pathway is through binding of contaminants to the fine-grained sediment followed by subsequent downstream movement of these particles.

The objective of this project was an initial assessment of contaminant transport in the Big Lost River system to the area of the Big Lost River Sinks, concentrating in the areas of primary sedimentation within the Sinks. The objective was met through the collection and analysis of sediment samples from a cross-section of depositional environments within the area of the Sinks for metals listed in part 264.24 of the Resource Conservation and Recovery Act and gross radionuclides. The first sampling was done to a depth of 30 cm. Additional sediments were collected to one meter (1 m) or refusal for future analysis. Statistical analyses of the various contaminants measured were carried out using nonparametric methods, specifically the Kruskal-Wallace ANOVA for comparisons of multiple sample groups and the Mann-Whitney U test for paired comparisons. Statistical analysis showed that the concentrations of the radionuclides and metals measured in this initial assessment were statistically the same or lower than the background values used, with the exception of aluminum, barium, and chromium.

This presentation will discuss the sample results and statistical analysis, highlighting data limitations and recommendations.

Effects of Data Sampling in Geostatistical Modeling of Sediment Contaminant Concentrations

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Sampling strategies and consequent modeling play important roles in characterization of contaminated sediments. This paper analyses how the sample size and density influence the variogram fitting and the kriging in the aquatic sediment contaminant concentration modeling. Ordinary kriging and ordinary cokriging models are considered for the study. Concentration data of three heavy metals (Cr, Ni and Cd) measured at Duwamish River bottom sediment and the percentages of different sediment soil particles (Clay, silt, and sand) are used in this case study. Three subsets are created from each full data set by randomly picking 25%, 50% and 75% of the full dataset. Each subset is created in a manner to be the subset of any larger set. Whenever a data set is not of normal distribution, either log-normal transformation or Box-Cox transformation is found suitable to pretreat the data before variogram fitting. Micro-spatial correlation is modeled with spherical, Gaussian and exponential variograms with nugget effects. After the transformation, the trend component is fitted and removed from the data, and the residual is used to fit the variogram. The fitted variogram is used in the kriging and the kriged values are cross validated with the data measurements in the subset. Minimization of Root Mean Square (RMS) errors of cross validation result is used as the best model parameter-selecting criterion together with an additional condition of having same spread in measured data and cross validated values. In addition, the model is further validated by using the data that are removed from a full set to make a subset as the testing set for the particular subset. The results show that the model predictions rapidly improve with number of data until a relatively ‘steady’ in the cross validation RMS error is achieved. Cokriging with other heavy metals considerably improve the predictions. While cokriging with the soil constituent percents provides better predictions than those can be achieved in the univariate kriging, these cokriged predictions are much inferior to those obtained with the cokriging with other heavy metals. Results are discussed, and the future research goals are identified.