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ABSTRACT BOOK

University of Massachusetts.

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Advances in Methods to Stage Injection of ORC, HRC and Other Materials

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The discussion will provide a general overview of advances in the actual delivery of ORC, HRC and other remediation compounds in an attempt to provide practical options for real projects and field applications.

How You Inject is Equally Important as what You Inject

The injection of ORC, HRC and other remediation compounds has rapidly become a widely accepted practice for addressing contaminated sites. With the advances in the industry's understanding of the in situ remediation process we are seeing an important question asked regarding the success of a project: "How are you injecting the compound at your site?" In developing your plan, it is crucial not to overlook the obvious: proper execution will contribute to the effectiveness of the outcome. In short: how you inject is equally important as what you inject.

Safety First

First and foremost, safety is the responsibility of everyone involved with the project. This applies to the field crews as well as the engineers and remediation design team. Many remediation compounds are relatively benign; however, there are also those that are potentially very harmful if handled improperly. Accidents are the result of making safety an after-thought to the in situ remediation process. Safety first.

Common Injection Method

A very common method for injecting remediation compounds is to use a single portable pump in tandem with the direct push rig. The DPT operator starts by hammering a single rod chain with an expendable point to the desired depth. The injection hose from the pump is secured to the top of the rod chain. As the rods are slowly retracted, the expendable point falls off into the hole and the compound is injected through the exposed down-hole tip at the bottom of the rod chain. This method has been used for years, however it does not address some of the subtle issues faced in the field relative to the accurate delivery of the compound and creating cost and time efficiencies in the overall execution of the work scope.

Advanced Injection Methods

As with any technology, experience has taught us ways of improving the in situ injection process. Today "dedicated injection rigs" are used in tandem with single or multiple direct push rigs. Specific pumping pressures, specific flow rates and specific temperatures apply to different materials in different media. Injection systems are designed as self-sufficient units that can adapt to site conditions as needed. These units contain single or multiple pumps, an independent water supply, an independent power source, pre-heating tanks, and compound mixing tanks. They are capable of moderating the temperature of the compound, moderating the pressure of the pump(s), and moderating the flow rate of the injections to maximize efficiency in the field. Improvements in the tooling allow us to isolate targeted zones and avoid creating or exaggerating preferential pathways. This tooling also addresses the substantial backpressures created in certain applications. These advances maximize time efficiency between borings, minimize product loss, and present a more professional overall field operation to your client.

"Reinjectable" wells have become the preferred practice on sites where injections are anticipated over an extended period of time. Again this process is designed to create cost efficiencies for the overall remediation project.

Operations and Case Studies

Performance criteria will vary from project to project based on a number of variables, however, general performance parameters for actual delivery of HRC, ORC and other compounds will be covered as a point of reference. Specific Case Studies will be presented to provide perspective on these parameters.

Enhanced *In Situ* Chemical Oxidation Using the PRP System

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The Programmable Release Process (PRP) involves the use of inserts in existing or newly drilled wells to release reagents to contaminated soils and groundwater to affect a three-phased remedial process including: 1. direct oxidation of the contaminants of concern (COCs), 2. modification of the groundwater redox chemistry; and 3. maintenance of the modified geochemistry of the impacted groundwater. In anaerobic plumes, a dilute peroxide solution is gravity released to the impacted groundwater to affect in situ Fenton Reagent reactions to oxidize chlorinated and non-chlorinated VOCs and SVOCs. As the peroxide solution disseminates into the plume, oxygen is released thereby modifying the redox of the plume to enable aerobic biodegradation to take effect. The aerobic state of the plume is maintained by the controlled and continued release of the peroxide solution.

In this paper, two PRP field applications are described including a BTEX/MTBE spill site in Saratoga Springs NY and a former gas manufacturing site in Utica NY impacted by PAHs, BTEX, cyanide and select trace metals. The Saratoga Springs site had been under continued remediation since 1988 using conventional pump and treat technologies. Within four months of the PRP application, oxygen levels reached saturation and the source area BTEX groundwater concentrations were reduced from about 15 mg/L to 20 ug/L.

The range of PRP applications include applications for the smear and vadose zones of contaminated sites. The dilute peroxide solution can be used in existing wells to create and maintain an artificial hydraulic head. The increased head floods the normally unsaturated regions of the site within the immediate vicinity of the well providing a mechanism to degrade smear and unsaturated zone contaminants of concern. By maintaining an elevated head of reagents within the contaminated soils, it is possible to degrade contaminants within the normally unsaturated regions of an impacted site. This PRP application was used to degrade PAH and BTEX-contaminated fill material at the former gas manufacturing facility located in Utica NY. The PRP application also elevated the groundwater dissolved oxygen concentrations within the plume thereby promoting aerobic degradation of the COCs.

LNAPL *In-Situ* Remediation in Difficult Settings

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Free Product Fuel is especially challenging to remediate as it is both an immediate risk to health and safety, and prevents the remediation of dissolved phase contaminants for closure. Environmental Consulting, Inc. (ECI) has extensively used Environmental Business Solutions International, Inc.'s (EBSI) On-Contact Remediation Process® family of in-situ technologies to configure methods to field detect free-product, recovery for disposal when possible and then chemically treat the remaining free-product layer.

Our case studies include live gas stations, under buildings, near live tanks and other difficult settings. The free product treatments start with specialized field testing to delineate the free product's extent and condition along with factoring in additional vectors of cubic volume that are probably impacted but not easily verifiable. Once remediation starts, Propagation Injection Points are installed in a manner as to allow for the recovery of free product at the surface though biased displacement. As the Propagation is installed, being an inerted conductive plane at our sites, the beginning stages of the hydraulic fracturing like technology allows for a quick recovery of free product near the injection point. Once the Propagation is installed it becomes a trap zone for free product and allows both vacuum truck service and in-situ chemical treatment. One Propagation based injection point can reach up to a 60 foot radius and can do the work of 9 to 36 wells. The chemical processes used are specialized for free product and are real-time controlled for efficiency and the suppression of temperature and LEL levels.

The entire set of project steps move along like one continuous mobilization for the customer and has been extremely effective at area sites. We offer this service under pay-for-performance contracting available from EBSI.

In-Situ **Chemical Oxidation of CVOCs in Fill and Saprolite**

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Soil and groundwater remediation via chemical oxidation has been performed at a former industrial site with high levels of chlorinated volatile organic compounds (CVOCs), including trichloroethene (TCE) and its degradation products, as well as a number of non-chlorinated volatile organic compounds. Specific challenges to remediation of this site included: 1) soil and groundwater containing high levels of TCE and other volatile organic compounds and 2) the presence of low permeability soils beneath the Site. Through literature research, the results of a bench scale treatability study, and site operating restrictions, direct oxidation of the impacted media using chemical oxidants with a catalyst was chosen as the remedial strategy. In order to achieve the required distribution of the chemical oxidant in the low permeability soils, and enhance the contact between the contaminants and the oxidant, a hydrofracturing technology was selected. Due to its ability to substantially increase the effective treatment volume in the subsurface, this technology was expected to perform better and more cost effectively than other remedial technologies employed in the treatment of similar constituents in similar geology. Remediation is on going at the site, and the first round of sampling following the hydrofracturing and initial injections of hydrogen peroxide indicated an overall reduction in TCE concentrations in the on-site groundwater of approximately 30%. However, soil sampling results indicated that between hydrofractured horizons, CVOC concentrations remain at or near the original concentration, and that the level of increased permeability due to the initial hydrofracturing is not sufficient to access all targeted areas of the subsurface. Additional hydrofractures were installed and a more persistent oxidant (i.e., potassium permanganate) injected into the subsurface. It is anticipated that the additional hydrofracturing combined with the injection of two oxidants into the subsurface will significantly improve the effectiveness of the remediation at the site.

Minimizing Injection Points and Maximizing Delivery of Oxidants for Dry Cleaner Remediation

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The Whitman Companies, Inc. (Whitman), a New Jersey-based environmental consulting and engineering company, teamed with Environmental Business Solutions International, Inc. (EBSI) to perform in-situ remediation of chlorinated ethenes using chemical oxidation at an active dry cleaning facility located in a strip mall in Tinton Falls, Monmouth County, New Jersey. Soils at the site are described as silty sands with some clay content near grade, and glauconitic, dark green to black silty sands with increasing clay content at depth. The highest concentrations of Tetrachloroethene (PCE) detected in soils and ground water were 1,400 mg/kg and 120 mg/kg, respectively. These concentrations were detected in shallow soil and ground water below the building slab in the location of the former dry cleaning machine. Prior to injection of oxidants, hydraulic fracturing was performed at the site to install subsurface propagations, which form high permeability zones in low permeability material, to maximize efficient delivery of oxidants throughout the impacted area. One (1) deep and two (2) shallow propagations were installed in the interior of the unit to treat soil and ground water below the dry cleaners. Following completion of the fracturing, chemical oxidant injections using EBSI's On-Contract Process® were initiated to treat contaminated soils and groundwater.

As compared to the other methods of applying in-situ chemical treatment, this remedial process required fewer injection points to treat the area of concern, and allowed for greater distribution of oxidants throughout the low permeability soils at the site. Only three (3) injection points to cover the interior of the building and the source area whereas other approaches at similar sites have required 10 to 15 injection points to address the same area and interval. Fewer injection points translates to lower costs to the site owner, less on-site chemical addition time, and less disruption to the dry cleaning operation and surrounding leaseholds.

In-Situ Co-Precipitation of Metals

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Effective treatment of metals in soil and groundwater often requires manipulation of the oxidation-reduction potential (ORP) and stabilization of the pH. The goal of almost all metals treatment is to provide long-term, stable and insoluble species. Depending upon the metallic compound, either reducing or oxidizing conditions may be required to create an insoluble species. There are many soluble reducing or oxidizing agents that can be fairly easily injected. Often metals contamination is associated with low pH (acidic) conditions that have dissolved and mobilized metals of concern. Most metal complexes are least soluble at neutral pH conditions. An essential component of an acceptable metals treatment strategy is the ability to provide long-term buffering of the pH. RMT's proprietary metals treatment chemical, EnvironBlend®, provides long-term stabilization of pH. EnviroBlend® can provide enormous acid neutralization capacity (ANC) to provide long-term pH control. For a recent site, EnviroBlend® was estimated to provide at least 1,000 years of acid neutralization based on a modified USEPA multiple extraction procedure. EnviroBlend® is an insoluble solid at ambient conditions. Hydraulic fracturing and slurry injection has been utilized to provide delivery of the material in low permeability environments. EnviroBlend®-^{As} was recently injected for arsenic treatment under very acidic conditions at a site in South Carolina. With hydraulic fracturing, a 50 weight percent slurry solution was injected into low permeability material at rates up to 25 gallons per minute. Impact was visually observed greater than 20 feet from the injection point. The pH increased to near equilibrium conditions, and arsenic concentrations dropped to regulatory acceptable levels.

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PHYTOREMEDIATION

A Dynamic Feedback Model of Plant-Soil Interactions Affecting Metal Accumulation

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Phytoremeditaion of Persistent Organic Pollutants (POPs) in Soil

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Laboratory Measurements of Storm-Water Quality Improvement in Detention Ponds-Phytoremediation Study

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Global Enzymatic Activies - Potential Tools in Assessment of Phytostabilization Strategies

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Effects of Burrowing Earthworms on Phytoremediation of Pb/Zn Mine Tailings

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Metallophytes: A Unique Biodiversity Resource 'Owned' by the Minerals Industry

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A Dynamic Feedback Model of Plant-Soil Interactions Affecting Metal Accumulation

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A great deal of research effort has been expended to develop predictive models for the determination of phytoavailable fractions of potentially toxic metals in soils. Such a model is useful in screening-level ecological risk assessment and in determining the feasibility of phytoremediation for a site. Much of this research has focused on the physico/chemical aspects of metals' binding and mobility in soil, often as a function of pH and other soil properties. "Supply-side" models considering only metal-soil interactions (including sequential extraction techniques), neglect to consider the dynamic nature of root interactions with rhizosphere soil. It is qualitatively well understood that root exudates, excreted primarily in response to the presence of macronutrients, significantly alter soil chemistry in the vicinity of plant roots. There is overlap in the soil properties that influence metal solubility and plant root responses (*e.g.* pH), but some factors exclusively influence plants (*e.g.* N) and are typically not measured in supply-side models. A dynamic feedback-control model of plant roots, considering soil chemistry, its influence on root exudations, and the resulting quantitative impact of those exudations on metal uptake, was developed as a computer model using Simulink (The MathWorks, Inc.). The model uses principles of both soil chemistry and plant physiology, and was calibrated using data from several plant species grown in field-contaminated soils with and without nutrient amendments. A wide range of soils from three continents, some historically contaminated through biosolids application or other anthropogenic sources, were used. This model allows estimation of the concentration of metals in plant tissues based on soil properties, and when soil properties are altered. For example, phosphorus influences both soluble metal in soil, and plant biochemical pathways. The model predicts changes to the amount of zinc accumulated by Indian mustard (*Brassica juncea*) for differing phosphorus amendments in soil.

Phytoremediation of Persistent Organic Pollutants (POPs) in Soil

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Persistent organic pollutants are of environmental concern because of their toxicity, recalcitrance in natural solids, global distribution, and resistance to remediation. There is evidence that certain plants effectively accumulate these weathered residues from soil, suggesting phytoremediation as a treatment approach. Field experiments were conducted to quantify the uptake and translocation of weathered *p,p'*-DDE and chlordane from soil by a range of plant species. Not suprisingly, crops of different genera varied considerably in their ability to extract POPs from soil. Root:soil concentration factors, defined as the ratio of contaminant (ng/g, dry weight) in the roots to that in the soil, approached 16 for certain species of pumpkin and squash but ranged from 0.5-4 for species of melon, cucumber, spinach, lettuce, alfalfa, mustard, vetch, and rye. Somewhat suprisingly, within single species of squash and pumpkin, individual cultivars of demonstrated greater than an order of magnitude variation in the root:soil concentration factors. Although root tissues routinely contain the highest contaminant concentration, this compartment comprises less than 5% of the plant biomass. Consequently, in many species tested, more than 85% of the contaminant is present in the shoot system. We speculate that the crop observed variability in contaminant uptake results from species-specific differences in root exudation. Low molecular weight organic acids (citric, oxalic, malic, malonic, tartaric, succinic) known to be root exudates increase the abiotic desorption of weathered POPs from soil by up to 50%. These same organic acids also increase the aqueous concentration of extracted polyvalent metal ions (Al, Fe, Mn, Mg, Ca, P) from soil by up to 2 orders of magnitude. We hypothesize that root exudates such as organic acids chelate structural metal ions from the soil, resulting in a partial destruction of the solid matrix and subsequent increase in the availability of previously sequestered contaminants.

Laboratory Measurements of Storm-Water Quality Improvement in Detention Ponds – Phtyoremediation Study

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Urban best management practices are traditionally used to improve water quality in storm-water runoff. Among the storm-water management practices that have been studied, the most promising and best understood are detention ponds and retention ponds. One of the major characteristics of detention ponds is the ability of the plants that are present to effectively remove pollutants from the runoff. In partnership with the Minnesota Department of Transportation, three wetland grass species native to Minnesota (*Scirpus validus*, *Spartina pectinata*, and *Glyceria grandis*) were chosen for analysis of their phytoremediation capabilities. These are long-lived, perennial species that are well adapted to conditions commonly found along roadsides. Analysis of urban storm-water runoff in Minnesota and around the country revealed that zinc, copper, cadmium, and lead were the pollutants of greatest concern and had the greatest potential to exceed EPA and Minnesota Pollution Control Agency guidelines for non-point source discharges, even after treatment by detention ponds. The three selected species were grown in hydroponic nutrient solutions that were spiked with average urban storm-water runoff concentrations of Zn, Cu, Cd, Pb, to determine their ability to accumulate these pollutants in their harvestable biomass. The ability of the plants to remove phosphorus and chloride from solution were also analyzed. Surface waters in Minnesota are particularly susceptible to phosphorus loadings, and the long winters result in the application of large amounts of deicing salts that end up in the runoff. In addition to the hydroponic reactor study, the plants were also grown in flow reactors that simulate detention pond conditions.

Global Enzymatic Activities – Potential Tools in Assessment of Phytostabilization Strategies

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The complexity of environmental pollution reported nowadays all over the world increases the demand for innovative, simple assessment methods in the view of remediation strategy selection and monitoring. Phytostabilization, an emerging technology based on the use of plants to reduce the risk of contaminant migration, relies on the ability of plant species to develop a healthy vegetative cover with good stability in time, when grown on contaminated materials. The success of a field application is rather hard to predict, even after years of greenhouse tests. Due to the strong interrelation between plants and microorganisms, it is expected that any change in the size and diversity of microbial population from contaminated material to accurately reflect the material capacity to support vegetation and the evolution of vegetation in time. This paper discusses the possibility of using several global enzymatic activities (dehydrogenase, phosphatase, urease) from phosphogypsum (PG) tailings in the selection of best plant species and PG treatments for a field deployment of phytostabilization. Several plant species were cultivated on PG with addition of various amendments in the greenhouse. Global enzymatic activities from PG were studied periodically and compared with plant growth intensity and metal uptake. Results over only 6 months of trial showed generally a correlation between plant development and the studied enzymatic activities (reflecting microbial population), but sharp differences between the various species of plants. These results allowed the selection of plants and treatments to be used in the field. Such a deployment was carried out and proved successful in establishment of vegetation on PG stacks, with a good vegetative growth recorded up to date, after more than 3 years. However, it was observed that some plant species with good greenhouse development, but lower enzymatic activities recorded in their rhizosphere area, were not stable in time and perished after 1 year in the field. This work suggests the potential of using global enzymatic activities in assessment and monitoring of phytostabilization strategies.

Effects of Burrowing Earthworms on Phytoremediation of Pb/Zn Mine Tailings

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Difficulties with reclamation of metalliferous mine tailings to soft end-uses are associated with inadequate and extreme soil conditions for plant and animal colonisation, and the risk of dispersion of metals to the wider environment. Establishing trees on these spoils potentially provides an effective, low-cost, low-risk and long-term phytoremediation option. To be confident this is a satisfactory form of reclamation, we need to know whether a developing stand of trees and associated ecological processes either (i) removes mobile pools of metals from contaminated soils or (ii) immobilise these pools, rendering them harmless. One associated process in particular concerns the colonisation of developing soils by earthworms and the effects of their burrowing activities. Earthworms contribute to the development of soil from spoil and, in normal soils, are beneficial to plant growth. Potentially, however, earthworms may change the bioavailability of heavy metals and subsequent ecosystem dispersion. Our project studied the effects of a common tropical burrowing earthworm, *Pheretima guillelmi*, on remediation of Pb/Zn mine tailings by planting an N-fixing woody shrub, *Leucaena leucocephala*. The results showed that *L. leucocephala* could grow successfully on tailings with 25% (w/w) soil amendment. *P. guillelmi* could survive and actively burrow in soils added with as much as 50% tailings, and they significantly increased root:shoot ratio and nutrient (N/P) uptake by *L. leucocephala*, stimulated plant growth and increased dry weight yields. However, *P. guillelmi* increased bioavailable metal concentrations in soil accompanying with a direct increase of metal uptake in plant tissues. This had most effect on establishment of younger plants, but there was evidence that acclimation of *L. leucocephala* to Pb/Zn mine tailings was improved by earthworm inoculation. This evidence shows that modeling the effects of soil animals on metal mobility is a vital component of the remediation process.

Metallophytes: A Unique Biodiversity Resource ‘Owned’ by the Minerals Industry

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Metallophytes are characteristic plants of mineralised areas that support soils heavily loaded with metals, so possessing a potential for mining. Through the ages, these plants have developed biological mechanisms allowing them to tolerate metal concentrations toxic to other plants. Some are adapted variants (ecotypes) of common species but others are species strictly endemic to their particular metal-rich area and are often of very restricted distribution. Their metal-specific adaptations and large diversity (species, families and life-forms) grant metallophytes a unique place in biodiversity and genetic resource conservation. Only the European plants are well known. Tropical and sub-tropical metallophyte taxonomy and ecology lie far behind despite the rising mining activity taking place in these latitudes.

Traditionally, metallophytes have been used as geobotanical indicators as they can be used to delineate metalliferous substrates when prospecting. In the more recent drive towards sustainable development and responsible mine site closure by the industry, two further uses need to be promoted:

- in the revegetation and restoration of former mine sites, especially with the endemic species of the area: ecological restoration.

- in the clean-up of toxic metals or biomining of low grade ore that cannot be processed economically by other techniques, using metal-accumulating plants: phytoextraction

Abandoned mine sites are generally seen as a liability since they remain as scars on the landscape and well after their closure persist as a source of pollution through dust and chemical leakages. If a former mining area and surrounding tailings is naturally recolonised by vegetation, the unwanted legacy can become a resource base of unique genetic materials with unique physiological traits. The vegetation developing directly on mine soil is both likely to support metallophytes and represent the surviving species that covered the mineralised area prior to its development into a mine. The study of metallophytes and their colonisation, behaviour and evolution observable on former mine sites can enhance closure and rehabilitation strategies beyond simple greening of the sites.

At a milestone event sponsored by Rio Tinto plc at the Kew Royal Botanic Gardens in July 2001, experts have drawn up a plan of action whereby the industry was given a major role as benefactor and beneficiary. Cataloguing and conservation is a priority (germplasm-seed banks, living collections and *in situ* protected surfaces). This is to be done not only prior to mining activity but also throughout its lifespan since these plants have revealed a remarkable persistence even in changing metal environments.

HEAVY METALS

Assessment of Methylmercury Risk to Three Species of Wading Birds in the Florida Everglades

Darren G. Rumbold, South Florida Water Management District, West Palm Beach, FL

Contamination Issues and Soil Health in Urban Forestry

Nicholas Dickinson, Liverpool John Moores University, Liverpool, UK
Christopher French, Liverpool John Moores University, Liverpool, UK
Philip Putwain, University of Liverpool, Liverpool, UK

Spatial Distribution of Total and Methyl Mercury in Stream Sediments at Superfund Site

Dorothea Seth Richardson, CDM, South Plainfield
Joseph J. Mayo, CDM, South Plainfield, NJ
Demetrios Klerides, CDM, New York, NY
Thomas Taccone, U.S. Environmental Protection Agency, Region 2,New York, NY

Effects of High pH on Metals Mobility in Groundwater

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Review of *In-Situ* Remediation Technologies for Lead, Zinc, and Cadmium in Soils

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In-Place Closure of Industrial Waste Impoundments: A Case History

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Assessment of Methylmercury Risk to Three Species of Wading Birds in the Florida Everglades

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Mercury contamination is one of the more serious problems facing the Everglades restoration. Currently, the Everglades are under human health advisories for limited or no fish consumption because of methylmercury (MeHg). In the Everglades, high concentrations of MeHg have also been found in top predators like raccoons, alligators, wading birds and Florida panthers. This case study reports on a risk assessment that used both deterministic and probabilistic methods to provide managers with estimates of risk while explicitly quantifying uncertainties. The objectives of this risk assessment were two fold: (1) to provide an Everglades-wide perspective of MeHg risk to wading birds, and (2) to address specific stakeholder concerns regarding possible adverse effects from restoration efforts currently under way in the Everglades. The latter objective was achieved using a well-studied oligotrophic site as a reference site for post-restoration conditions for mercury methylation and bioaccumulation. Exposures were based on measured tissue levels during 1997 – 1999 in fish species known to be consumed by wading birds. Toxicity reference values (TRV) were obtained from the published literature. Results suggest that birds foraging in the central basin were at greatest risk, with 86% of the great egret population expected to exceed the TRV. By comparison, only 46% of the egrets foraging at the post-restoration reference site were predicted to exceed the TRV. Model-predicted egg and nestling feather mercury levels exceeded measured concentrations by a factor of 1.4 and suggest that the Monte Carlo model overestimates mercury exposure to the birds. Together with other lines of evidence, including reproductive studies, these results support the conclusion that the restoration effort will not increase MeHg risks to wading birds to unacceptable levels. Alternatively, MeHg risk to wading birds foraging preferentially in the central basin, particularly when near MeHg "hot spots", are of potential concern and warrant further studies.

Contamination Issues and Soil Health in Urban Forestry

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The context of this paper is how and when we decide if a contaminated urban soil is healthy or not. This is the current focus of our project that contributes to urban regeneration in North-West England through community forestry. Dispersion patterns of metals are described and mapped at a range of urban brownfield sites, variously contaminated with trace elements including As, Cd, Cu, Ni, Pb, Zn and B, and planted in field trials with trees (biomass species of *Salix* and *Populus*, with *Alnus*, *Betula* and *Larix*). Contaminant hotspots were targeted for experimental work; heavy metal mobility was quantified as the tree cover became established and for three growth seasons. Although heavy metals and other trace elements exceeded guideline thresholds, toxicity to plants was seldom an important issue; significant toxicity to plants was only recorded in the cases of extremely high concentrations of B and As. Attention is given to assessing the toxicity of hotspots in relation to working guidelines, and to risks of dispersal of contaminants into the wider environment. Results are presented of efforts to influence hotspots through uptake and harvest of short-rotation coppice and using soil amendments. Mass balance models are compared with datasets for more mature woodlands. Metal mobility is significantly influenced by soil conditions created by plant growth, rhizosphere processes, earthworm casts and the drilosphere (burrow walls). Crude measures of metal concentrations in bulk soil are shown to be an entirely unsatisfactory way to describe soil health. Accurate and realistic ecosystem models of elemental fluxes, and improved knowledge of soil ecology provide the key to recognising healthy soils. We consider this an important step towards using accurate and realistic ecosystem models in restoration of sustainable and healthy soils to brownfield land.

Spatial Distribution of Total and Methyl Mercury in Stream Sediments at a Superfund Site

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From 1955 to 1998, Mercury Refining Company was engaged in the reclamation of mercury from a variety of sources including batteries, thermometers, electrical switches and dental amalgams. The Mercury Refining Superfund Site, New York is located adjacent to an unnamed tributary to Patroon Creek, which flows into a major river approximately 5 miles downstream of the site. In the past mercury from the site has reached the creek from a variety of pathways, including: waste batteries that were dumped over an embankment to the tributary; surface water runoff discharged to the tributary; and fall-out from a fire in the Hand Shop building. A remedial investigation/feasibility study (RI/FS) was initiated by the USEPA to determine the nature and extent of the contamination. This paper focuses on the spatial distribution of total and methyl mercury in stream sediments downstream of the site and at background locations. Mercury methylation ratios were examined to determine the areas of highest methylation occurrence. In general, an inverse relationship between the total mercury concentration and the percent of methylation was observed. Total mercury concentrations also showed strong areal correlations with total organic carbon, but little or no correlation to cation exchange capacity, pH or grainsize. Total mercury also shows little correlation to total organic carbon with depth. Three samples located just downstream of the site, showed higher than expected methyl mercury to total mercury ratios. These data may be reflective of higher sulfate concentrations in the stream water or anthropogenic effects on this portion of the stream system.

Effects of High pH on Metals Mobility in Groundwater

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At the ambient pH in most groundwater systems, metal mobility is limited by solubility and sorption reactions. Anthropogenic releases that dramatically alter the groundwater pH may produce a short-lived mobilization of naturally occurring metals. The presence of metals in groundwater with concentrations exceeding acceptable risk levels may cause a concern to human health and the environment. Natural processes may offer effective in situ treatment of metals in groundwater. Groundwater sampling at the Navy site illustrates the mobilization and slow return to normal in a coastal aquifer.

In 1992, a sodium hydroxide spill occurred at the Neutralization Basin at Naval Station Mayport in Mayport, Florida. Groundwater samples collected during a RCRA Facility Investigation (RFI) in 1994 indicated elevated concentrations of several metals including copper, iron, nickel, and vanadium. As part of the Corrective Measure Study (CMS), Tetra Tech NUS, Inc., evaluated the hypotheses that at high pH, the soil matrix became negatively charged and sorbed metals were mobilized in the form of complex anions. It was further hypothesized that as upgradient groundwater naturally flushes the aquifer, the aquifer would return to more natural pH and the metals in groundwater will either precipitate or sorb to the aquifer solids. The CMS proposed a sampling event to test the hypothesis. The results of the groundwater sampling event conducted in August 2001 indicated that the concentrations of copper, iron, nickel, and vanadium (chemicals of concern determined in the CMS) were lower than the concentrations detected during the RFI. The highest pH measured during August 2001 sampling event was 9.29 SU as compared to 11.4 SU measured during the RFI. The results of the August 2001 sampling event indicate that naturally occurring processes will effectively remediate the site.

Review of *In-Situ* Remediation Technologies for Lead, Zinc, and Cadmium in Soils

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This project, sponsored by the International Lead Zinc Research Organization (ILZRO), involved a comprehensive literature and information search and review to assess the extent of scientific knowledge regarding in-situ remediation technologies for lead, zinc, and cadmium in soils. This presentation will summarize the findings of that review. A comprehensive search of technical and regulatory agency databases resulted in more than 100 documents relevant to the topic. Special emphasis was placed on documented studies of field- and/or full-scale applications. Each of these documents were carefully reviewed and summarized in an electronic database. This presentation will review the most promising in-situ remedial technologies for these metals in soil and will discuss the technologies in terms of their developmental status and data gaps, potential effectiveness to meet various remedial objectives, and advantages and disadvantages. In addition, the influence of site-specific factors (such as the depth and areal extent of contaminated soils, soil type and chemistry, and subsurface heterogeneity) on the successful implementation of the technology will be discussed. Case studies will be summarized for selected technologies, along with performance and cost data. Finally, general guidelines for technology selection based on site-specific factors will be discussed.

In-Place Closure of Industrial Waste Impoundments: A Case History

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A manufacturing facility located ¾ miles from the shore of Lake Erie, in southeast Michigan, was the site of 52 acres of sludge impoundments containing electroplating sludge (a listed hazardous waste) and millwater treatment sludge. Some areas of the impoundments were also filled with foundry sand, slag, and non-sludge wastes. The site has been used for industrial purposes since 1927. The site consisted of a number of diked impoundments, underlain by a native clay layer. Below the clay, a confined water-bearing stratum of limestone/dolomite bedrock exerted uplift pressure on the clay. In the years since waste placement, the impoundments had become covered by surface water, and native and voluntary vegetation had become established. The site was home to many species of wildlife, including the American Bald Eagle. High-voltage transmission lines had also been constructed through the center of the impoundment area.

The waste, which varied in thickness up to 21 feet, had very low strength and would not support the weight of investigative or construction equipment. The waste constituents of concern were cadmium, copper, lead, nickel, and zinc, which exceeded Michigan's risk-based criteria for unrestricted land use and for the interface between groundwater and surface water. Although the sludge was a listed hazardous waste (F006), analytic testing showed it did not exceed regulatory criteria for hazardous waste. Two of the impoundments were regulated by RCRA interim status regulations; the remainder of the site was covered by CERCLA.

The site was successfully closed by removing outlying sludge deposits and consolidating them into two discrete containment units, solidifying the sludge, installing a soil-bentonite-fly ash perimeter cutoff wall around each unit, and constructing a composite cover over the solidified sludge. This paper presents a summary of the challenges involved in designing, permitting, and constructing the in-place closure for the site.

MTBE

In-situ Remediation of MTBE and other Petroleum Hydrocarbons by Iso-Gen™ Technology

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MTBE, TBA, and TAME Removal with Microbubble Ozone Injection

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Effectiveness of Air Sparging and Soil Vapor Extraction for Methyl-Tert-Butyl Ether (MTBE) Removal

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Is The Transect Method For Determining the Mass Flux of a Contaminant “Junk Science?”

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Removal of Methyl-t-Butylether from Water Using Synthetic Adsorbents

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Phytoremediation of MTBE with *Ceratopteris richardii*

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Strategic Pumping to Divert MTBE and BTEX Plume From Municipal Water Supply Wells

Evan T. Johnson P. E., LSP, Tighe & Bond, Westfield, MA

Full-Scale MTBE Biobarrier - Presentation of Final Results form a 3-year ESTCP Demonstration at Port Hueneme, CA

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In-situ Remediation Of MTBE And Other Petroleum Hydrocarbons By Iso-Gen™ Technology

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H_2O Technologies has developed Iso-Gen™ as a new *in-situ* process using electrolysis to generate high concentrations of dissolved oxygen (DO) in water.   The technology uses electrolysis to disassociate water into hydrogen and oxygen and by use of a specific set of metallurgical and electrical conditions Iso-Gen™ enables the oxygen to go into solution in water as stable dissolved oxygen (DO). The DO is available for microbes to utilize and degrade MTBE and other petroleum hydrocarbons and additives. Iso-Gen consists of an in-well unit and an external controller that provides power and communication with the in-well unit(s). The Iso-Gen™ technology uses vertical recirculation mechanisms to distribute the DO laden groundwater throughout the aquifer without pumping any water to the surface. The downhole pump creates a 360-degree recirculation pattern into the aquifer. Iso-Gen has been applied successfully on 8 MTBE contaminated sites to date. Results from the field sites show that MTBE is consumed by microbes when high concentrations of DO are introduced by Iso-Gen™ over a broad area. Bacterial studies for MTBE degraders have been done on groundwater samples 90+ days after Iso-Gen application that show very robust populations of microbes capable of thriving with MTBE as their sole carbon source. Further observation of field sites indicate that DO is a lagging indicator, increasing after petroleum hydrocarbons have been reduced, presumably by microbial consumption.

MTBE, TBA, and TAME Removal with Microbubble Ozone Injection

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When microbubble ozone is injected into the saturate zone, MTBE and other oxygenates are stripped into the bubbles to react with ozone. When microbubble ozone comes in contact with MTBE, two breakdown products are hydrogen peroxide and oxygen. A peroxide/ozone film is then formed to increase the efficiency of the decomposition reaction with later MTBE entering the bubbles. The fine micron bubbles are shown in laboratory tests to strip MTBE, TBA, and TAME from aqueous solutions. Analysis of a clean-up on a retail gasoline outlet is conducted. The stoichiometric demand of MTBE, TBA, and TAME are computed. The rates of decay observed in the field are compared with the Clayton model of simplified radial transport. All oxygenates exhibited substantial decay. Reductions of MTBE ranging from 75% to over 99% were observed during the test period of 3 months. Although TBA attenuation was similar to MTBE, TAME appeared to reduce at a faster rate. A close correlation was present between computed theoretical oxidant demand and the observed rates of decay.

Effectiveness of Air Sparging and Soil Vapor Extraction for Methyl-Tert-Butyl Ether (MTBE) Removal

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Although specialized technologies are being developed to treat MTBE due to its unique characteristics, it should be noted that in some cases significant removal can be achieved with conventional treatment technologies such as in situ air sparging with soil vapor extraction (IAS/SVE). The U.S. Navy performed an interim remedial action consisting of IAS/SVE to reduce gasoline concentrations in soil and groundwater at the Department of Defense Housing Facility (DoDHF) Former Underground Storage Tank (UST) Site 957/970 in Novato, California. The project was funded by Southwest Division, Naval Facilities Engineering Command in San Diego, California through the Naval Facilities Engineering Service Center (NFESC) in Port Hueneme, California. The system initially focused on four zones where maximum concentrations of benzene, ethylbenzene, toluene, and total xylenes (BTEX) had been detected in groundwater; however, the concentrations of MTBE in both groundwater and the extracted vapor stream were also monitored closely during system operation. As remedial activities progressed, MTBE became a greater concern among the scientific and regulatory community; therefore, its removal became more central to the specific remedial objectives at the Site. Although the IAS/SVE system was designed to remove elevated levels of BTEX compounds, results showed that the system effectively removed significant MTBE mass. The MTBE removal was confirmed by the presence of MTBE in the extracted vapor stream and by the reduction of MTBE groundwater concentrations. In addition to significant groundwater concentration reductions during system operation, MTBE concentrations did not rebound and continued to decrease for two years after system operation stopped. The aggressive treatment of “hot spot” areas resulted in treatment to levels below those required to be protective of human health for the intended future site use.

Is The Transect Method For Determining the Mass Flux of a Contaminant "Junk Science?"

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When creating a computer model to make predictions about the fate and transport of contaminants and assess the risk to water supplies posed by the migration of groundwater contamination, the modeler must enter a value for the "source term" of the contaminant. A relatively new method under development for purposes of quantifying the threat of the contaminant source term is to estimate the amount of mass migrating within a contaminant plume past a transect which is perpendicular to the direction of groundwater flow. Most attempts to estimate mass discharge in Canada and the United States have been based on the use of transects of single-screened or multi-level wells which are periodically sampled which requires reliable estimates of groundwater velocity distribution and interpolation between locations for which data are available. Clearly the methodology has promise, but relatively few peer reviewed articles have been published on the subject and there is no current published standard for applying the transect method and judging the accuracy of mass flux measurements using it. Recent field studies suggest that dense sampling grids and many site-specific measurements of groundwater velocity are typically needed to reduce the uncertainty in the process to an acceptable level. In recent litigation in California, a trial court found that the transect methodology "when properly applied" is generally accepted in the scientific community, but precluded from admission mass flux estimates produced in a way which the court found did not properly apply the method. The decision highlights that if the results of a scientific study are intended for use in court, careful consideration must be given to the legal standards applicable to the admissibility of such results. This presentation will include an analysis of both the scientific and legal issues presented to the California court and the scientific and legal significance of the court's decision to the consulting profession.

Phytoremediation of MTBE with *Ceratopteris richardii*

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The phytoremediation of methyl-tertiary-butyl-ether (MTBE) using *Ceratopteris richardii* (C-ferns) was investigated. Concentrations of MTBE (vol/vol) were studied at 100 ppm up to 15,000 ppm. The growth and development of C-fern spores in nutrient agar was observed as was the plant development of C-ferns. Growth and development were observed by leaf and rhizome development. Development of spore growth in nutrient agar was studied for a period of 63 days or until agar nutrient was depleted.

A direct correlation of plant growth to concentration of MTBE in agar medium was observed. Control agar medium and low levels of MTBE (100, 500 ppm) utilized all agar medium after 40 days. The agar medium remained essentially unchanged with robust plant growth in direct proportion to higher concentrations of MTBE.

Data developed leads to the speculation that the C-ferns are utilizing MTBE as a primary source of nutrient before reverting to the nutrient based agar as a secondary nutrient source.

Transplanted C-ferns in soil indicate direct correlation also with level of MTBE concentrate.

We are now investigating additional studies for elucidation of mechanisms involved.

Strategic Pumping to Divert MTBE and BTEX Plume From Municipal Water Supply Wells

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Three underground storage tanks were installed as part of the opening of a new convenience store in Palmer, Massachusetts in 1989. Shortly after installation, the tanks indicated low product volume. Rather than believing there was a leak from the new tank, the store owner ordered a second delivery of fuel to refill the tank. However, upon removal, it was determined that the tank had been damaged during installation. In total, it is estimated that over 12,000 gallons of gasoline containing MTBE was released from the storage tank. Shortly after the release was detected, a consulting firm was hired to install a soil vapor and product recovery system on the property. Several borings and monitoring wells were installed to evaluate hydrogeologic conditions and determine the limits of the gasoline release. The data indicated that a variable thickness LNAPL layer measuring 120' x 90' was present beneath the facility, that groundwater was at a depth of 20 feet, and that groundwater elevations fluctuated by as much as 10 feet seasonally in the area. The water supply wells for Palmer Water District #1 (a shallow tubular well field and a deep gravel pack well) are located approximately 1500 feet immediately downgradient of the gasoline release.

The initial data from the treatment system installed at the convenience store indicated that the LNAPL area was decreasing and that the gasoline plume had been contained on the site. However, samples from downgradient monitoring wells installed as part of the VOC investigation revealed that an MTBE and BTEX plume had migrated beyond the original release site. Continued monitoring indicated that the MTBE and selected BTEX compounds were migrating at a rapid rate through a deeper soil unit than the one in which the fuel had originally had been released. Given the concern for the municipal supply wells, a pumping well was installed between the release point and the municipal wells to divert groundwater flow from the well field. Despite initial success with the single recovery well, subsequent monitoring indicated that the plume was continuing to migrate toward the well field. Therefore, an additional five recovery wells were installed. Following negotiations with the state Department of Environmental Protection (DEP), approval was obtained for discharging the recovery well flow to an adjacent surface water body for discharge. The DEP ruling was predicated on the fact that the concentrations of MTBE and other BTEX compounds were well below surface water standards and that the benefits to the municipal well field outweighed any minor impacts to surface water.

In 2000, the responsible party, the tank manufacturer, filed bankruptcy and completed their response actions at the site. Site remediation and oversight has been taken over by the DEP with assistance from a state contractor. Recovery wells continued to discharge to the river and recent monitoring data collected by both the state and the Water District indicate that the municipal wells have yet to be impacted by MTBE or BTEX compounds. The system will continue to operate as part of a long-term remedial plan at the site.

Full-Scale MTBE Biobarrier - Presentation of Final Results from a 3-year ESTCP Demonstration at Port Hueneme, CA

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***Paul C. Johnson** and **Cristin L. Bruce**, Arizona State University*

For the past three years, the ESTCP program has sponsored a full-scale MTBE-BTEX biobarrier demonstration at the Naval Base Ventura County, Port Hueneme, CA. This passive flow through biobarrier system was designed to biodegrade MTBE, TBA and other dissolved hydrocarbons leaving the downgradient edge of a residual gasoline impacted source zone. This site is somewhat unique in that the dissolved MTBE plume is approximately 500 feet wide and about a mile long. Upgradient MTBE concentrations are as high as 10 mg/l, and the BTEX concentrations are as high as 1-2 mg/l.

Data from the first 2 years of operation will be presented. MTBE, TBA, and BTEX concentrations are each being reduced to less than 0.005 mg/l downgradient of the biobarrier. Quarterly sampling results have indicated no evidence of clogging of the biobarrier. Results from microcosm studies conducted in the air only, oxygen only, and bioaugmented zones of the biobarrier will also be presented. In addition to the performance data, the design and O&M costs of this system will be presented in comparison with a pump and treat containment system operating at a different location in the same dissolved plume.

SEDIMENTS I

Microbial Characterization of Contaminated Sediments Using Dual Stain Flow Cytometry

Cyndee Gruden, University of Michigan, Ann Arbor, MI
Anna Khijniak, University of Michigan, Ann Arbor, MI
Peter Adriaens, University of Michigan, Ann Arbor, MI

Enhanced Solid-Phase Bioremediation of PAH-Impacted Dredged Marine Sediments from the Tar Site in Sidney, Nova Scotia, Canada

Alan G. Seech, Grace Bioremediation Technologies, Mississauga, Ontario, Canada
Geoffrey Bell, M.Sc., Grace Bioremediation Technologies, Mississauga, Ontario, Canada
James Mueller, Ph.D., URS/Dames & Moore, Rolling Meadows, IL

The Effect of Plants on the Dynamics of Heavy Metals in Wetland Sediments

Shangping Xu, Princeton University, Princeton, NJ
Peter Jaffe, Princeton University, Princeton, NJ

Results of Interspecies Toxicity Comparison Testing Associated with Contaminated Sediment Management

Meg R. Pinza, Battelle Marine Sciences Laboratory, Sequim, WA
Jeffrey A. Ward, Battelle Marine Sciences Laboratory, Sequim, WA
Nancy P. Kohn, Battelle Marine Sciences Laboratory, Sequim, WA

Biological Effects Associated with Sediment Contamination in San Francisco Bay

Dr. S. Ian Hartwell, NOAA/NOS, Silver Spring, MD
Dr. M. Jawed Hameedi, NOAA/NOS, Silver Spring, MD

Sediment MTBE Interactions at a Full Scale Site in Montana: Natural Attenuation and Toxicity

Ronald C. Sims, Utah State University, Logan, UT
Aaron Swank, Utah State University, Logan, UT

Potential for Dehalogenation of Dioxin in Marine and Estuarine Sediments

Donna E. Fennell, Rutgers University, New Brunswick, NJ
Young-Beom Ahn, Rutgers University, New Brunswick, NJ
Lee J. Kerkhof, Rutgers University, New Brunswick, NJ
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Microbial Characterization of Contaminated Sediments Using Dual Stain Flow Cytometry

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The successful design and scaling of bioremediation applications depends on the accurate qualitative and quantitative demonstration of causal relationships between the control strategy and enhanced microbial presence or activity. Microbial sensing in sediment environments is a challenging endeavor due to (among others) matrix interferences and ecological complexity. The advent of sensitive molecular techniques has afforded new opportunities to overcome these challenges by taking advantage of general or specific genetic probes to quantitatively detect and determine activity of biodegrading populations. A biostimulation approach using low-level hydrogen gas amendments was applied to enhance the dechlorination of halogenated aromatics (hexachlorobenzene, dibenzo-p-dioxins) in estuarine river sediments. Prior sediment characterization had indicated the microbial potential for natural dechlorination activity, but the causative microbial populations had not been determined. Using a redox-active stain (CTC, a tetrazolium compound) specific for the hydrogenase enzyme complex, a direct relationship between hydrogen concentration and enzyme activity, as well as an optimal range for enhanced dechlorination activity, was established. Using flow cytometric techniques, the elevated hydrogen and dechlorination activity were shown to correspond to the emergence of a previously recessive populations. Preliminary data indicated no statistically significant difference (two-tailed t-test; $\alpha = 0.05$) between direct counts (EPM) and flow cytometric quantification (1×10^4 to 1×10^8/mL) or metabolic activity assessment (~ 3-90%) of indigenous sediment bacteria using a non-specific stain (Picogreen), CTC, and a membrane integrity stain (propidium iodide). These demonstrations indicate the wide applicability of molecular tools to help establish the causal relationship between control strategies and microbial activity, and to increase the confidence in applying bioremediation techniques to decontaminate natural environmental systems.

Enhanced Solid-phase Bioremediation of PAH-impacted Dredged Marine Sediments from the Tar Ponds Site in Sydney, Nova Scotia, Canada

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A solid-phase bioremediation technology offered by W.R. Grace under the trade name DARAMEND®, has been applied successfully to soils and sediments containing PAHs, chlorinated pesticides, and organic explosive compounds at several sites in North America. For removal of PAHs, the technology utilizes organic (DARAMEND products) and inorganic (i.e. nutrients, pH modifiers) amendments to optimize the aerobic activity of microorganisms indigenous to a soil or waste resulting in enhanced destruction of organic contaminants. In January 2002, GRACE began an ongoing bench scale treatability investigation using PAH-impacted dredged sediment from the Tar Ponds site in Sydney Nova Scotia, one of the largest contaminated sites in Canada. It is estimated that more than 500,000 tons of sediment at the site are in need of remediation. In addition to PAHs, the sediment contains PCBs, petroleum hydrocarbons, and heavy metals. The treatability investigation was designed to evaluate five different treatment protocols and a moist, biotic control. Treatments consist of different DARAMEND applications, or combinations of DARAMEND with inorganic nutrients. The mean initial PAH concentration of the sediment used in the treatability work was 4,386 mg/kg. The sediment was spiked with ^{14}C-phenanthrene to enable estimation of the rate at which this PAH was mineralized. Radioactive CO_2 produced by mineralization of the phenanthrene was captured using caustic (2N NaOH) traps and measuring the amount of radioactivity in the traps with a Beckman LS6500 Liquid Scintillation Counter. Volatilization of PAHs from sediment in the microcosms was monitored using traps containing activated carbon. Extractable concentrations of PAHs are being measured throughout the treatability investigation. Completion of the ongoing study is expected by September of 2002. The results will be presented in detail.

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The Effect of Plants on the Dynamics of Heavy Metals in Wetland Sediments

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Toxicity and mobility of heavy metals in sediments are controlled by their speciation. In wetland sediments, heavy metal speciation is governed by the spatial redox profiles that are determined by the sequential utilization of various electron acceptors during the biodegradation of organic materials. In addition to the redox reactions some heavy metals may undergo (e. g., Cr(VI) ⇔ Cr(III) where the former is more mobile and toxic), sulfide produced through sulfate reduction in anaerobic environments can sequester a variety of heavy metals. In aerobic environments, Fe(III) and Mn(IV) hydroxides are good sorbents that could immobilize heavy metals. However, when these hydroxides are reduced, heavy metals could be released into the dissolved. Wetland plants could control the redox profile and hence the dynamics of heavy metals through transport of oxygen to the rhizosphere, organic exudation, evapotranspiration, and uptake of nutrients like nitrate. The objective of this research is to obtain a mechanically based understanding of heavy metals dynamics in sediments in the presence of plants. Experiments are being conducted where a solution containing nutrients, various electron acceptors (nitrate, Fe(III) and sulfate), acetate, and chromium is pumped into microcosms with and without wetland plants. At the bottom of the microcosms, water is drained at a constant rate. Vertical profiles and dynamics of important redox species such as sulfide and iron are monitored voltametrically with gold-amalgam microelectrodes. Concentration of Cr(VI) is determined via a spectrophotometric technique. Dynamics of chromium, its relation with important redox species and the presence of plants are then analyzed. A reactive transport model has been developed, to aid in the interpretation of the experimental results.

Results of Interspecies Toxicity Comparison Testing Associated with Contaminated Sediment Management

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Contamination of marine and estuarine sediment by polynuclear aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs), and tributyltin (TBT) is a serious concern for the management of sediment in Puget Sound. Many studies have been conducted in the Puget Sound confirming that these contaminants are present in sediment at varying concentrations. Because many of these contaminants produce sublethal effects following chronic exposure, there is concern that current toxicity tests approved by the Puget Sound Dredge Disposal Analysis (PSDDA, 1988) may not be sufficiently sensitive to adequately assess the environmental risk posed by these persistent chemicals when they are present at low to moderate concentrations. This is especially important if bioassay testing is used in pre- and post-characterization to support remediation activities. This project focused on the use of field-collected sediment from Puget Sound to determine the comparative sensitivities of two standard toxicity tests (10-day amphipod mortality, and the juvenile polychaete growth test) with the recently developed, 28-day *L. plumulosus* chronic test (measuring mortality, growth, and reproduction). The experiment was performed using sediment contaminated to varying degrees with a mixture of persistent contaminants. Sediment from eight field sites was collected, composited, and submitted for chemical analysis. Based on the chemical screen, five sites were chosen for toxicological evaluations. The toxicity experiments followed the EPA protocol for the 28-d full-life-cycle chronic *Leptocheirus plumulosus* test (EPA/600/R-01/020) and the PSEP protocols for the10-d acute amphipod sediment toxicity test with *Eohaustorius estuarius* (PSEP 1991) and the 20-d growth test with *Neanthes arenaceodentata*. The results from each of the three toxicity tests were compared to determine the relative sensitivity of each species and the different endpoints to the field-collected sediment.

Biological Effects Associated With Sediment Contamination in San Francisco Bay

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In 2000, NOAA initiated a 2-year comprehensive study to describe biological effects associated with sediment contamination in San Francisco Bay. The objectives of the study are to; (1) estimate the spatial extent and patterns of chemical contamination, toxicity, and macrobenthic community structure, (2) identify the incidence and severity of sediment toxicity, (3) estimate relationships between toxicant concentrations and measures of sediment toxicity and, (4) describe spatial associations among sediment contaminants, toxicity test results and, macrobenthic assemblages. The study area extends from the Delta to the Golden Gate to Guadelupe Slough using a stratified-random design. The technical basis for stratification, the apportionment of sampling effort into the strata, and their sizes and dimensions were determined collaboratively with study partners and coastal resource managers. In 2000, sediment and biological samples were collected from 86 sites. An additional 96 sites were sampled in 2001. Preliminary analyses of samples indicate that chemical contamination is widespread throughout the estuary. Elevated contaminant levels in tributaries and harbors/marinas were site specific with locally very high concentrations. Source and deposition patterns were contaminant-specific. Open water sites had marginally higher concentrations of contaminants in southern San Francisco Bay than in San Pablo or Suisun Bays. Aggregate toxicity index results correlated with ERM quotients. Benthic community response to contaminants was confounded with salinity and bottom type, but correlations with contaminant levels were evident. Introduced species were the dominant biota at many sites, which complicated analyses. Additional analyses will be conducted when YR2001 data are available.

Sediment-MTBE Interactions at a Full Scale Site in Montana: Natural Attenuation and Toxicity

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The study site for this project is a gasoline station on the Flathead Indian Reservation in Ronan, MT that leaked methyl tertiary-butyl ether (MTBE) from an underground storage tank in 1993. MTBE has moved 450 m from the source area to Spring Creek, and biodegradation has been observed in the groundwater/ surface water interface (GSI) zone. The Montana Department of Environmental Quality is interested in an evaluation of the potential application of monitored natural attenuation (MNA) for treatment of the contaminated aquifer. Research at the UWRL has focused on two specific aspects of MTBE MNA at the Ronan site: (1) toxicity of MTBE and metabolites, and reduction in toxicity as a result of biotransformation, and (2) rate of biotransformation of MTBE as affected by seasonal changes in temperature at the site. The measured Microtox Acute toxicity EC50 value for MTBE was 12 mg/l; for the intermediate tertiary butyl-alcohol was 3,580 mg/L. MTBE concentrations at the site range from 80 mg/L near the source area to ppb levels near Spring Creek. The Bio-Noble flash assay was also used to determine the toxicity of aquifer sediments, and all sediments near and within the GSI zone exhibited no toxicity to the test microorganisms. Results indicate a detoxification pathway for the transformation from MTBE to TBA. Bio-kinetic values were determined for MTBE biodegradation over the temperature range typical for the Ronan site, and this information was used along with ground water velocity values to evaluate the effect of temperature and flow on the rate and extent of MNA. Results demonstrated that MNA for MTBE at the Ronan site is influenced by toxicity and by temperature and ground water flow.

Potential for Dehalogenation of Dioxins in Marine and Estuarine Sediments

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The ability of native microbial communities to transform dioxin congeners was investigated in sediments from San Diego Bay, CA and Arthur Kill, NY/NJ, among others. We tested various electron donors and alternate halogenated substrates—“haloprimers”—to determine their relative effectiveness for stimulation of the dehalogenation of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs). Substrates with analogous chemical structures to the dioxins, e.g. halophenols, halobenzenes, and haloanisoles were used as haloprimers. The haloprimers have far greater solubilities than that of dioxin and could serve to selectively stimulate a population of dehalogenating bacteria that could, in turn, dehalogenate PCDD/Fs. Stimulation of dehalogenation was attempted under methanogenic and sulfate-reducing conditions. Dechlorination of PCDD proceeded to a much greater extent under methanogenic conditions than sulfate-reducing conditions. Enrichments supplied with haloprimers showed more extensive dechlorination than those without haloprimers did. Addition of haloprimer plus electron donor resulted in more rapid onset of dioxin dehalogenation than addition of electron donor alone. Furthermore, the structure of the haloprimer had a significant impact on the time required for onset of PCDD/F dehalogenation. Bioprocess modeling and biomolecular community structure analysis are being used to further our understanding of the microbial populations responsible for the dehalogenation in these systems. In the future, a combination of in situ treatment, natural attenuation, sequestration/capping, and dredging of hotspots will most likely accomplish sediment restoration. In situ bioremediation of PCDD/Fs may offer one alternative for cleanup of contaminated areas.

RBCA

Summary of Toxicological Benchmarks and Soil Remediation Goals to be Protective of Environment

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Assessment of, and Risk Based Cleanup Approach for, a Large Volume Jet Fuel Spill

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Undertaking Risk-Based Remediations in Brazil

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Summary of Toxicological Benchmarks and Soil Remediation Goals to be Protective of Environment

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Establishing soil cleanup goals to protect human health and the environment is a key remediation issue. However, because of the complex nature of soils and limited knowledge of the contaminant’s toxicological effects on the environment, there is no general consensus on the ecological soil remediation goals. A series of toxicological benchmarks have been published by the Risk Assessment Program Oak Ridge Health Science Research Division (Oak Ridge) for wildlife, terrestrial plants, and soil and litter invertebrates, etc. Oak Ridge, USEPA, Canada, Ontario, and the Netherlands have proposed soil screening/remediation goals for certain chemicals. Although these published benchmark values and remediation goals can provide a readily available source of soil quality standards, the specific applicability of the benchmark values or remediation goals to a particular site is uncertain, due to differences in geography, ecological receptors, and pollutant bioavailability. This presentation compares the published benchmark values with the soil remediation goals and reviews the approaches used to derive the remediation goals. In addition, the presentation proposes consideration of affected populations in setting up soil remediation goals. Finally, an example of site-specific soil remediation goals that are protective of the environment is presented and compared to the published benchmark values and remediation goals.

Assessment of, and Risk-Based Cleanup Approach for, a Large Volume Jet Fuel Spill

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Due to corrosion, a large volume of Jet Fuel (JP-8) spilled from a 14-inch, high-pressure subsurface pipeline. The spill was detected during routine overflight and reported to Federal, State, and Local authorities. The product was initially contained in a small area, until a 10-inch rain carried it to surrounding wooded and swampland, creeks, and roadside ditches, threatening nearby federal marshlands. Government authorities were preparing to federalize the site and assume site oversight. To prevent federalization and assist in cleanup, a professional spill management team was mobilized. This team gained site control and enhanced ongoing product recovery. Critical pathways were continuously monitored for product flow. Permits were obtained in record time and structural controls were installed to inhibit migration. These actions prevented federalization. The authors developed a Data Quality Objectives- and risk-based assessment and closure plan, and negotiated regulatory approval. Based on data from site visits, aerial photographs, and maps, a Conceptual Site Model identified media, release pathways and mechanisms, and receptors. The authors developed an exposure-based sampling plan using a "weighted grid" pattern based on visible evidence of product. The objectives were to delineate lateral and vertical extent of contamination to State risk-based standards, and obtain data for use in risk-based closure. A separate plan was developed to sample landowner water wells, ponds and yards. By fingerprinting the released product, BTEX, MTBE, Naphthalene, and TPH were identified as critical contaminants. This plan was implemented and soil, sediment, surface water, and groundwater samples were collected from approximately 20 acres of affected land. Thiessen Polygons were drawn using preliminary analytical results to identify patterns of contaminant flow and evaluate the need for additional assessment. Human health and ecological risk assessments are being conducted to evaluate potential residual risks and develop bases to support remedial decisions, regulatory closure and NRDA action.

Undertaking Risk-Based Remediations in Brazil

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Like a number of other countries in Latin America, Brazil is currently in the process of developing a formalized regulatory system (*i.e.* regulations, guidance documents, generic risk-based cleanup standards, *etc.*) to manage and remediate hazardous waste sites. In the interim, responsible parties have some flexibility in making decisions from state to state using an informal system that currently exists. In general, the Brazilian agencies are accepting risk-based cleanup plans developed either using the risk-based framework developed by the Dutch environmental agency or by the United States Environmental Protection Agency (US EPA). This presentation will discuss: 1) current risk-based remediation approaches being used in the states of Sao Paulo and Rio de Janeiro; 2) the similarities and differences between Dutch and US EPA risk-based remediation approaches (*e.g.* risk targets, toxicity factors, default exposure assumptions, *etc.*); and 3) the potential implications of selecting either the Dutch or the US EPA approach on cleanup levels and remediation.

REGULATORY

Developing Soil Re-use Criteria in California for the Alameda Corridor Project

Carl Peter Ripaldi, *URS Corporation, Los Angeles, CA*

Asbestos in Soil: An Owner's Perspective

John M. O'Donnell, P.E., Division of Capital Asset Management, Boston, MA
Mark Roberts, P.E., Division of Capital Asset Management, Boston, MA

Immediate Response Actions to Address Impacts to Residential Receptors

Janine Commerford, Massachusetts Department of Environmental Protection, Boston, MA
Millie Garcia-Surette, Massachusetts Department of Environmental Protection, Lakeville, MA
Laurel MacKay, Massachusetts Department of Environmental Protection, Willmington, MA
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Army and Commonweatlth of Massachusetts: Partnership for Compatible Training and Sustainable Environmental Protection in Cape Cod, Massachusetts

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Emerging Water Contaminants: Technical, Legal and Policy Challenges

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Developing Soil Re-use Criteria in California for the Alameda Corridor Project

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In California, there are ample regulations regarding the management and disposal of hazardous and contaminated soils as waste under the jurisdiction of CalEPA's Department of Toxic Substances Control (DTSC) and the Regional Water Quality Control Board (RWQCB). However, there is a lack of specific guidelines for contractors to use when it comes to evaluating the suitability of soils for re-use as fill. Impacted soils may have trace amounts of contaminants that are not considered hazardous but may be regulated under these agencies depending on the circumstances.

In some cases background levels of heavy metals or petroleum hydrocarbons may exceed waste discharge criteria (WDRs) established by the regulatory agencies presenting the possibility that native soils can't be legally re-used as fill. This presents a great dilemma to the construction industry regarding the establishment of acceptable re-use criteria for soils used as fill. Typically, soil brokers check the soils only to see if they are below hazardous levels for the criteria pollutants established by the agencies. It also presents scenarios in which millions of tons of soils being re-used as construction fill may exceed acceptable contaminant levels resulting in the potential of cross contaminating building sites with soils believed to be clean but unacceptable under currently established regulations. Such actions open up the possibilities of enforcement actions, penalties and fines under federal and California law. They further cloud the acceptability of such sites for redevelopment by a skeptical general public.

The Alameda Corridor Transportation Authority (ACTA) dealt with these issues as it struggled with the need to re-use thousands of tons of impacted soils as construction fill within the project. This became both a cost and schedule consideration. Following considerable investigations, the establishment of background levels for metals and fuel hydrocarbons in native soils, the interpretation of existing regulations and waste criteria, and agency negotiations an acceptable criteria was established allowing for the re-use of considerable amounts of soils within the project confines.

The ACTA experience merits careful consideration by other projects in order to avoid regulatory actions, conserve resources, and facilitate construction.

Asbestos in Soil: An Owner's Perspective

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Most major construction sites in urban areas encounter contamination due to past industrial, retail, and/or residential uses of the property. Typically, evaluation of contamination at these urban sites has focused on Polycyclic Aromatic Hydrocarbons (PAHs), petroleum and metals. However, there has been an increased focus on asbestos in soil/fill due to historic demolition and urban contamination (e.g., automotive brake dust). As contractors and developers gain experience in this area, they are testing for and identifying asbestos in the soils and fill on these properties. As such, the presence of asbestos can have major cost and schedule issues for construction projects in urban environments. The authors will present an overview of asbestos issues in soil and recount two case studies to illustrate the Commonwealth of Massachusetts, Division of Capital Asset Management's experience in redeveloping urban properties in Massachusetts.

The paper will discuss the regulatory framework that relates to asbestos fibers in soil/fill and will include a discussion of applicable Massachusetts Contingency Plan (MCP) and waste prevention regulations and policies. Case studies will be used to illustrate discrepancies between the programs. Analytical methods available for testing of asbestos-containing materials in soil and the potential inaccuracies of these methods will also be discussed, as well as a risk-based approach to developing site-specific risk values. The paper will address these issues through case studies on actual urban construction projects. Finally, the paper will identify areas that may need to be further evaluated or considered by the regulatory and regulated communities to improve addressing asbestos in soil.

Immediate Response Actions Designed to Address Impacts to Residential Receptors

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If Potentially Responsible Parties (PRPs) are unable or unwilling to conduct the response actions, the Massachusetts Department of Environmental Protection (MADEP) may undertake or arrange for response actions as it reasonably deems necessary. In cases where significant evidence exists of an Imminent Hazard (IH) condition to public health, safety, welfare, or the environment from oil and/or hazardous materials at/or from a disposal site, the MADEP is required by statute to immediately ensure that action is taken to control the potential for health damage, human exposure, safety hazards and environmental harm through the appropriate measures. These measures may include, but not be limited to, limiting access to the site; evacuating the area or relocating residents; providing alternative water supplies; or taking other similar temporary action that will remain effective until other comprehensive remedial measures can be implemented by the PRP.

Based on this requirement, the MADEP employs a standard approach to conducting IRAs to address residential receptors using state funds. This approach considers the circumstances under which the MADEP initiates the work, the types of response actions likely to mitigate the specific exposure, criteria by which the MA DEP would provide alternative housing (with re-entry strategy) and an exit strategy designed to outline when the MADEP completes the state-funded response actions. This presentation highlights selected case studies where the MADEP has initiated or conducted response actions to address impacts to residential receptors, including private water supply wells, indoor air and soil.

Army and Commonwealth of Massachusetts: Partnership for Compatible Training and Sustainable Environmental Protection in Cape Cod, Massachusetts

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Historically, there has been much controversy over contamination of groundwater supply in the Upper Cape and the effects of past military training. The need for military training and environmental protection led to divisiveness between the military and the communities located adjacent to the Massachusetts Military Reservation (MMR). Realizing the need to minimize these tensions or face losing a vital training area, the Department of the Army (the Army) and the Massachusetts Army National Guard (the Guard) developed a partnership-based plan with the Commonwealth of Massachusetts to ensure continued military training that does not harm the Cape's natural resources.

The first tier of the Guard's two-tiered plan is an Environmental Impact Report (EIR) that articulates Environmental Performance Standards (EPS) for training that exceed current regulatory requirements but that still accomplish the military's training mission. The second tier is a Memorandum of Agreement (MOA) with the Commonwealth of Massachusetts for long-term environmental management of the MMR. This MOA created a three-member Environmental Management Commission (EMC) to oversee training on the base to ensure environmental compatibility, an Environmental Officer to work daily with the military, a Community Advisory Council (CAC) and a Scientific Advisory Council (SAC).

This presentation will describe how this MOA was developed and signed by Department of the Army and Commonwealth officials, including the Governor. This partnering approach is being touted as a national model that meets the needs of the military and the environmental constituencies alike.

Emerging Water Contaminants: Technical, Legal and Policy Challenges

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Approximately 120 new chemicals are created each year due to ever-improving industry and technology markets. Releases of new contaminants into the environment can occur during production, use and disposal of these chemicals thereby leading to potential contamination of water supply sources. Very few emerging contaminants are regulated. In addition, knowledge gaps regarding emerging contaminants include lack health effects, occurrence (either because these compounds are not measured or because concentrations are below detection limits of readily available analytical techniques) and fate and transport in the environment especially with regards to mobility and persistence. The sources of these compounds are numerous. One source is treated wastewater, which is re-injected into groundwater aquifers for indirect potable reuse purposes. Emerging compounds of concern can be classified in various classes. This presentation will focus on contaminants which have emerged in the last 10 years including pharmaceuticals (antibiotics/drugs), personal care products (polycyclic musks), pesticides/herbicides, industrial solvents (1,4-dioxane), gasoline additives (MTBE), disinfection byproducts such as NDMA (N-nitrosodimethylamine), and inorganic compounds such as perchlorate and arsenic. This presentation will present technical, legal and legislative challenges posed by the presence of these contaminants in water. Background information including chemical's history of use, sources in the environments, nationwide occurrence, physical and chemical properties, behavior in the environment and technologies for removal from soil and water will be presented. In addition, case studies on MTBE, pharmaceuticals and personal care products, 1,4-dioxane, arsenic and NDMA will be discussed.

ENVIRONMENTAL FORENSICS I

The Types and Weathering States of PCB Mixtures in New Bedford Harbor Sediments Revealed by Environmental Forensic Methodology

Stephen Emsbo-Mattingly, Battelle Memorial Institute, Duxbury, MA
Helen Douglas, Foster Wheeler Environmental Corporation, Boston, MA

VOCs Measured in Sodium Bisulfate and Methanol Preserved Samples (Method 5035) and Risk Characterization Impacts

Patrick P. King, GEI Consultants, Inc., Winchester, MA
Michael D. Walters, Polaroid Corporation, Waltham, MA

Evaluation of Light Non-aqueous Phase Liquid Weathering Rates at Various Fuel Release Sites

Daniel R. Griffiths, Parsons, Denver, CO
Bruce M. Henry, Parsons, Denver, CO
Douglas C. Downey, Parsons, Denver, CO
Jerry E. Hansen, AFCEE/ERT, Brooks AFB, TX

Chemical Fingerprinting of Weathered Middle Distillate Fuels Using Bicyclic Sesquiterpanes

Scott A. Stout, Ph.D., BATTELLE, Duxbury, MA
Kevin J. McCarthy, BATTELLE, Duxbury, MA
Allen D. Uhler, Ph.D., BATTELLE, Duxbury, MA

MTBE and its Degradation Products: Molecular Modeling Study

Krishna L. Bhat, Philadelphia University, Philadelphia, PA
Seth Hayik, Philadelphia University, Philadelphia, PA
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Environmental Fate and Transport Modeling of Explosives and Propellants in the Saturated Zone

Christopher Abate, AMEC Earth & Environmental, Westford, MA
Al Laase, AMEC Earth & Environmental, Westford, MA
Jacob Zaidel, AMEC Earth & Environmental, Westford, MA
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The Types and Weathering States of PCB Mixtures in New Bedford Harbor Sediments Revealed by Environmental Forensic Methodology

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Environmental forensic tools describe well the types and weathering patterns of PCB mixtures in the environment. The forensic approach assists many projects historically governed by conservative assumptions about PCB composition, because the site-specific PCB type(s) and weathering processes (anaerobic dechlorination, dissolution, and volatilization) can affect the toxicity and remediation endpoints. For example, the anaerobic dechlorination of a PCB mixture, like Aroclor 1242, can 1) selectively remove more toxic PCB congeners, 2) generate less toxic PCBs, and 3) promote the net reduction of PCBs through dissolution and evaporation. This paper presents forensic methodology for identifying and interpreting site-specific PCB compositions.

Recent PCB measurements of approximately 1000 samples (sediment, water and air) collected from New Bedford Harbor, Massachusetts (NBH) will illustrate the forensic approach for identifying the types and weathering states of selected Aroclor mixtures. These data were generated by high resolution gas chromatographs (GC) equipped with several PCB detectors. These detectors included a low resolution mass spectrometer (LRMS), high resolution mass spectrometer (HRMS), and electron capture detector (ECD). The forensic analytical tools featured in this presentation include PCB congener and homologue fingerprints, principal components analysis (PCA), and diagnostic ratio plots. These techniques were used to compare and contrast recent data with historical studies of weathering at NBH and other PCB contaminated sites, like Hudson River, NY and Silver Lake, MA.

VOCs Measured in Sodium Bisulfate and Methanol Preserved Samples (Method 5035) and Risk Characterization Impacts

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Order of magnitude differences in volatile organic compound (VOC) concentrations were measured in split-samples collected in accordance with EPA Method 5035 and preserved using sodium bisulfate and methanol. Resolving these concentration differences was critical to the assessment of human health and ecological risk at two example sites.

Soil and sediment samples were collected from two sites and duplicate portions were preserved with sodium bisulfate and methanol. VOC concentrations measured in the methanol preserved portions were often more than an order of magnitude higher than VOC concentrations measured in the sodium bisulfate preserved portions of the samples. By giving consideration to what these different data represented, these differences were addressed in the risk characterizations prepared for each of the sites. The greater extraction efficiency of methanol preservation yielded a better measure of the total contaminant mass while, under some circumstances, sodium bisulfate preservation provided a more direct measure of the contamination available to receptors. Tools for predicting VOC concentrations for sodium bisulfate preserved samples using data from methanol preserved samples and vice-versa are presented.

Evaluation of Light Non-aqueous Phase Liquid Weathering Rates at Various Fuel Release Sites

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Large-volume environmental releases of fuels have contaminated and continue to contaminate soil and groundwater at many government and commercial sites across the United States. Uncontrolled catastrophic or chronic releases of fuel products can result in large volumes of fuel being released to the subsurface. Fuels released to the subsurface typically persist as both residual and mobile light non-aqueous phase liquid (LNAPL). Mobile LNAPL is often targeted for remediation as the primary source of contaminant mass and because mobile LNAPL can be remediated to a limited extent. Residual LNAPL trapped in the subsurface is extremely difficult to remediate and continues to act as a secondary source of contaminants to soil, soil vapor, and groundwater as long as the residual LNAPL persists. Of the fuels related contaminants, benzene, ethylbenzene, toluene, and xylenes (BTEX) are of primary importance because of their relatively high solubility and mobility in groundwater, and their relative toxicity (particularly benzene). Little information is available regarding natural weathering rates of the BTEX components from mobile fuel LNAPLs. As a result, contaminant source term reduction rates in contaminant transport models are left to professional judgment with little, or no, scientific basis. The application of overly conservative LNAPL weathering rates negatively impacts the feasibility and cost of implementing monitored natural attenuation (MNA), while the application of inflated weathering rates can lead to an overly optimistic forecast of MNA performance. Parsons and the Air Force Center for Environmental Excellence (AFCEE) have analyzed and calculated natural LNAPL weathering rates for BTEX compounds at multiple sites contaminated with mobile LNAPL. Calculated first order weathering rates for benzene and total BTEX are often as high as 20 percent per year. Results of these analyses will be presented in order to improve the scientific basis of, and defensibility for, BTEX source reduction rates.

Chemical Fingerprinting of Weathered Middle Distillate Fuels Using Bicyclic Sesquiterpanes

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Recognizing distinct types or sources of middle distillate fuels in environmental matrices after weathering has left little more than a non-distinctive ‘hump’, or unresolved complex mixture. This paper describes weathering resistant compounds known as bicyclic sesquiterpanes, which occur in middle distillate fuels (boiling between approximately 240^{o}C to 285^{o}C). These compounds can provide specific information about the nature of these fuels, even after environmental weathering has occurred. Bicyclic sesquiterpanes are, as their name implies, bicycloparaffins containing approximately 15 (‘*sesqui*-’) carbons. These compounds (i.e., C_4 to C_6-decalins) have molecular weights ranging from approximately 194 to 222 amu. Analysis of liquid petroleum products or petroleum-impacted soil extracts by gas chromatography-mass spectrometry (GC/MS; full scan or selected ion monitoring) reveals these compounds on the *m/z* 123 mass chromatogram, due to production of a strong $C_9H_{15}^+$ fragment. Data are presented which reveals the variety of sesquiterpane patterns that can exist in distillate petroleum products. These differences are reasonably attributed to the differences in the crude oil feedstocks used in the production of these different fuels, although some influence of distillation can affect sesquiterpane patterns, depending on the end-boiling points of the petroleum product. Data are presented that demonstrate the consistency in the distribution of sesquiterpanes over a wide range of weathering over environmental timescales. Finally, a case study is presented in which the sesquiterpanes are used to unravel the source of weathered diesel fuel #2 impacting soils on adjacent properties.

MTBE and its Degradation Products: Molecular Modeling Study

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MTBE is the most commonly used fuel oxygenate because of its high octane rating, the ability to dilute undesirable gasoline components, low production costs, ease of blending with gasoline, and ease of transfer and distribution. While much is known about the biodegradation of many gasoline components under both aerobic and anaerobic conditions, the pathway(s) responsible for biodegradation of MTBE have not been fully elucidated. We have examined computationally the thermodynamics and kinetic parameters for several reactions that are involved in the biodegradation of MTBE ultimately leading to the formation of carbon dioxide and water. The results of semiempirical, molecular orbital and density functional theory calculations on MTBE and a variety of its possible degradation products will be presented. These calculations employed the modeling packages CAChe, Spartan, and GAUSSIAN 98 and were performed on Silicon Graphics workstations.

Environmental Fate and Transport Modeling of Explosives and Propellants in the Saturated Zone

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Fate and transport modeling of explosives in the Cape Cod sand and gravel aquifer was conducted at the Demolition Area 1 site on the Massachusetts Military Reservation. The objectives of the modeling were to (1) assess the future groundwater plume configuration and (2) conduct capture zone analysis to assess various remedial alternatives. MODTMR was used to develop a subregional model for Demolition Area 1 from a regional model of Western Cape Cod. Saturated zone flow modeling was conducted using MODFLOW with particle tracking conducted using MODPATH. Transport simulations were conducted using MT3D. Preliminary results indicate (1) the mobility of dissolved explosives and propellants can be simulated by conventional saturated zone modeling techniques, (2) innovative optimization approaches can be applied to remedial design for a mixed plume, and (3) reasonable values of major transport parameters for RDX were obtained from laboratory experiments and the literature.

MGP SITE CLOSURE

The EPRI Nationwide Background PAH Program Results – Just the Beginning

Andrew Jay Coleman, Ph.D., Electric Power Research Institute, Palo Alto, CA
David Mauro, Meta Environmental, Inc., Watertown, MA

MGP Sediment Management Concerns and Approaches - Observations/Considerations

Raymond D. D'Hollander, PE, ENSR International, Syracuse, NY

Designing and Implementing Perimeter Air Monitoring Programs for MGP Site Remediations

Leo Gendron, ENSR International, Westford, MA
Anthony Sacco, ENSR International, Westford, MA
Ishrat Chaudhuri, ENSR International, Westford, MA

Risk Based Action Levels for Perimeter Monitoring Programs at MGP Sites

Lisa J.N. Bradley, PhD, DABT, ENSR International, Westford, MA
Kelly Sullivan, ENSR International, Westford, MA

Comparison of Regulatory and Enforcement Programs at MGP Sites, Northeastern United States

Scott T. Saroff, CPG, Earth Tech, Inc., Syracuse, NY

NYSDEC Strategy for Investigation and Remediation of Manufactured Gas Plants

Robert W. Schick, P.E., New York State Dept of Environmental Conservation, Albany, NY

The EPRI Nationwide Background PAH Program Results – Just the Beginning

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Polycyclic aromatic hydrocarbons (PAHs) are pandemic in the environment from a number of natural and anthropogenic sources. Electric Power Research Institute (EPRI) has started national program to collect background PAHs throughout the United States. EPRI has recently completed studies in the States of Illinois and New York, which show that concentrations of PAHs are higher than previously suspected in background samples. Several studies in the U.S. and Europe have indicated that the concentrations of PAHs in urban surface soils can range from the low parts per billion to hundreds of parts per million (EPRI, 2000) depending on the proximity to and contribution from PAH sources. Literature references concerning the presence of PAHs in environmental media, including surface soils show that there is a lack of consistent data on distributions and concentrations of PAHs in surface soils because of varying sampling and analytical methodologies. EPRI conducted a consistent nationwide assessment of PAHs in urban surface soil from hundreds of sites using a random sampling scheme. Samples have been collected from two depths, 0 - 2.54 cm and 2.54 – 15.2 cm, and analyzed for 40 PAHs and alkylated PAH groups by gas chromatography with mass spectrometry (GC/MS). Resulting data is being used to better understand how these concentrations compare to concentrations found in the soils from industrial facilities of interest, including former manufactured gas plants. The findings from both Illinois and New York were useful for gaining insight into the concentrations that can be expected in urban areas. The EPA residential risk-based-concentration (RBC) was exceeded for at least one PAH at every site sampled. In addition, there was no apparent difference in concentrations with depth and the concentrations of PAHs found had a lognormal distribution.

MGP Sediment Management Concerns and Approaches – Observations and Considerations

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This presentation will focus on some of the practical considerations that need to be addressed in sediment remediation at MGP sites. In particular, the impacts of non-aqueous phase liquids (NAPLs) that may be present will be discussed. The significance of hydraulic gradients, both natural and remediation induced, on remediation methods will be presented.

The influence of vertical hydraulic gradients has been underappreciated as a mechanism for redistributing PAHs. Tidal and other mechanisms that cause rapid lowering of the water surface cause significant upward gradients that disperse NAPLs through the sediments. The upward gradients can also bring NAPLs directly to the sediment surface and water column. These mechanisms are critical in designing capping and containment remedies.

Removal remedies often use “dry excavation” techniques. These removal actions often put significant hydraulic stresses on the sediment system. These hydraulic conditions are often ignored during the remedial design causing delays and additional expenditures in the removal action. Measures to reduce these impacts are discussed.

Various remedial approaches to sediments impacted by coal tar and other MGP related constituents will be presented.

Designing and Implementing Perimeter Air Monitoring Programs for MGP Site Remediations

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ENSR International has been designing, installing and operating perimeter/fenceline ambient air quality and meteorological programs for over 30 years. ENSR's more recent experience includes numerous perimeter and fenceline monitoring programs around hazardous waste sites, landfill excavation projects and MGP site remediation projects. The paper focuses on and presents general guidance on the development and implementation of perimeter air monitoring programs for MGP site remediation projects. Topics include: site-specific perimeter monitoring and data quality objectives; parameters to be measured; determination of action levels for the various parameters; types of instrumentation available; number and placement of fenceline monitoring locations; frequency of sampling; data telemetry and reporting alternatives; routine field operations and equipment QC protocols; perimeter monitoring program conceptual design and regulatory review; and monitoring plan generation.

Risk-Based Action Levels for Perimeter Monitoring Programs at MGP Sites

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ENSR International. Fenceline air monitoring programs increasingly are required at MGP remediation sites. Risk-based action levels (RBAL) for the fenceline monitoring program should adequately address both project needs and the protection of human health. Issues to be considered and addressed in the development of risk-based action levels include the following. 1) Receptors. Off-site receptors should be identified, and appropriate receptors should serve as the basis for the fenceline air standard. 2) Timeframe of remediation. RBALs for a fenceline program should be developed within the context of potential human exposure periods. In toxicology, appropriate exposure periods to consider are: Acute – less than 24 hours up to 3 months; Subchronic – 3 months up to 7 years; and Chronic – greater than 7 years. RBALs should be developed to address each of these exposure durations, depending on the intended length of the remediation. Potential noncarcinogenic health effects should be considered for each exposure duration, however, chronic exposure durations are generally not anticipated for a remediation project. Potential carcinogenic effects are most appropriately considered for the chronic exposure duration, however, they can also be considered for the subchronic exposure duration. 3) Toxicity values. Appropriate chemical-specific toxicity values from the USEPA should be employed in the RBAL calculations. This includes the use of subchronic toxicity values. For benzene, the range of toxicity values provided by USEPA for addressing the potential carcinogenic effects at a given target risk level should be used in developing the RBALs; ideally a range of standards should be developed for benzene where any air monitoring data within that range would be considered to have not exceeded the RBAL. 4) Point of Exposure. Where potential receptors are not at the fenceline, air modeling should be used to calculate an RBAL to be protective of the receptors at the point of exposure.

Comparison of Regulatory and Enforcement Programs at MGP Sites, Northeastern United States

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With heightened community interests of the presence of old former manufactured gas plant (MGP) sites in residential and commercial areas, and increasing potential risk and exposure concerns, various states and USEPA have developed specialized regulatory departments and enforcement programs to oversee the management of these former MGPs. MGPs have unique features with potentially multiple sources of contamination that can migrate differently and have different risk factors. Some of these former MGP properties have undergone redevelopment, and MGP constituents may remain. Many of these MGPs are being used for various purposes and/or are located in areas undergoing redevelopment or being considered for redevelopment. This presentation will provide a review of each of the northeastern States and USEPA regulatory and enforcement programs, and how common MGP constituents, such as coal tar, polycyclic aromatic hydrocarbons (PAHs), and cyanide in soil and groundwater are treated with respect to remedial management. This review will also include the applicability of technical impracticability of aquifer restoration evaluations for ARAR (and state equivalent) waivers, and expected requirements if these waivers are granted, especially for Brownfields redevelopment. Understanding the regulatory closure process and expectations of regulatory agencies is important when planning regulatory closure, Brownfield redevelopment, property reuse, and/or exposure protection.

NYSDEC Strategy for Investigation and Remediation of Manufactured Gas Plants

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The New York State Department of Environmental Conservation (NYSDEC) estimates there are over 250 former Manufactured Gas Plants (MGPs) across the State. Since 1994 the State has been working with the utility industry to develop comprehensive programs to address the former MGPs for which they are responsible. To-date, approximately 190 utility MGPs have been identified and are either in the program or involved in negotiations to bring them in. NYSDEC, in conjunction with the New York State Department of Health, is charged with identifying and addressing the threats these sites may pose to public health and the environment. To accomplish this, investigations are designed and implemented to determine the nature and extent of contamination in the soils, groundwater, surface water and sediments, which may be impacted by these sites. Remedies are then selected to eliminate or mitigate these threats to the public heath and the environment, which may be attributable to the former MGP. NYSDEC strategies for the investigation and remediation of these MGP sites will be discussed.

BIOREMEDIATION

Degradation of 1,1,1-trichloroethane in Groundwater by Indigenous Microorganisms under Anaerobic Conditions

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Sandra Dworatzek, University of Toronto, Toronto, Ontario, Canada
David Major, GeoSyntec International, Inc., Guelph, Ontario, Canada
Peter Zeeb, GeoSyntec Consultants, Boxborough, MA

Enhanced Bioremediation of DNAPL in Clay Formation

Willard Murray, Harding ESE, Wakefield, MA
Diana Tremaine, Harding ESE, Wakefield, MA
Maureen Dooley, Regenesis, San Clemente, CA

Cost and Performance of Vegetable Oil Injection for Enhanced *In Situ* Bioremediation at Two Air Force Sites

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Daniel R. Griffiths, Parsons, Denver, CO
Allison M. Love, Parsons, Denver, CO
Peter Guest, Parsons, Denver, CO
James R. Gonzales, AFCEE/ERT, Brooks AFB, TX

A Bioremediation Case Study: Butane Biostimulation for the Remediation of Petroleum Contaminants

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Joseph Longo, Horsley & Witten, Inc., Sandwich, MA
Felix A. Perriello, Global BioSciences, Inc., North Attleboro, MA
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Facilitated Desorbtion and Incomplete Dechlorination: Observations from 350 Applications of HRC

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Degradation of 1,1,1-trichloroethane in Groundwater by Indigenous Microorganisms under Anaerobic Conditions

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Results from a microcosm study using groundwater and soil from a Massachusetts Industrial Site (Site) show that indigenous microorganisms are capable of sequentially dechlorinating 1,1,1-trichlorethane (TCA) to 1,1-dichloroethane (1,1-DCA) and then to chloroethane under anaerobic conditions. Degradation of co-disposed TCE in microcosms required augmentation with a microbial consortium containing dehalococcoides ethenogenes. Waste chlorinated solvents were discharged to a drywell at this facility for approximately 10 years. Compounds detected in groundwater at the Site include: 1,1,1-TCA, trichloroethene (TCE), associated biotic and abiotic degradation products as well as chlorobenzenes. Shallow and deep groundwater zones are defined by a 7 to 20 foot thick semi-confining silt layer through which chlorinated solvents have migrated. Aerobic and anaerobic microcosms were constructed using approximately 60 grams (g) of soil and 100 to 120mL of groundwater. Both the aerobic and anaerobic microcosms were run in triplicate with active and intrinsic controls. One set of aerobic microcosms was amended with methane. One set of anaerobic microcosms was amended with methanol, ethanol, acetate and lactate (MEAL) and a second set was amended with MEAL and augmented with a non-pathenogenic microbial consortium known as KB-1. The aerobic active control and methane amended microcosms showed 25 and 50% losses, respectively, of 1,1,1-TCA that is attributable to co-metabolic degradation, volatilization or adsorption. The MEAL amended microcosms showed decreasing concentrations of 1,1,1-TCA and TCE with concomitant production of 1,1-DCA, and cis-1,2-DCE. 1,1-DCA was further degraded to chloroethane, however vinyl chloride was not detected. The KB-1 augmented microcosms degraded 1,1,1-TCA, TCE, 1,1-DCA and cis-1,2-DCE faster in comparison to the electron donor-only amended microcosms, with complete dechlorination of TCE to ethene.

Enhanced Bioremediation of DNAPL in Clay Formation

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DNAPL in clay is one of the most challenging environments to remediate. In this presentation results from a full-scale enhanced bioremediation program will be presented from a site with reduced permeability that has shown evidence of DNAPL. The site is located in Tennessee and is a clayey aquifer characterized by elevated levels of tetrachloroethene (PCE) and trichloroethene (TCE). Concentrations of PCE and TCE have been detected above 100mg/L in the source area and at lower concentrations (20mg/L) in the plume. A pilot test was conducted using Hydrogen Release Compound (HRC) to enhance biological degradation of the chlorinated solvents. The pilot test included HRC injection into both a source and plume test area. Complete destruction of PCE and TCE was observed in two test areas. Biodegradation products dichloroethene, vinyl chloride and ethene were detected, and initially the total mass of ethenes increased suggesting an HRC-enhanced desorption effect. It was apparent that the residual PCE and TCE located in the source area were continually being degraded to DCE and VC, which both remained at elevated concentrations. The highest concentrations of DCE observed (greater than 200 mg/L) are equivalent to approximately 270 mg/L of TCE (25% of TCE solubility) and would be equivalent to a PCE concentration greater than its solubility. These facts indicate that there is residual dense non-aqueous phase liquid (DNAPL) within the aquifer in the source area. In the plume area, where PCE/TCE levels began at 20mg/L, DCE levels increased, then decreased. Little to no vinyl chloride was detected over the time course of the study and a reduction of greater than 90% in the total mass of ethenes was observed. Based on these data a full-sale remedial was designed to treat both the source and plume. The program was implemented in the Spring 2001 and results from the full-scale remedial effort will be presented.

Cost and Performance of Vegetable Oil Injection for Enhanced *In Situ* Bioremediation at Two Air Force Sites

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Remediating chlorinated solvents dissolved in groundwater to regulatory criteria is one of the United States' greater environmental challenges. Reductive dechlorination is known to degrade the common chlorinated solvents including tetrachloroethene, trichloroethene, carbon tetrachloride, and trichloroethane. Many organic substrates have been used to stimulate reductive dechlorination of chlorinated solvents dissolved in groundwater. Vegetable oil has been selected as a low-cost alternative and injected into the subsurface at over 15 sites across the country. However, the technology is still being evaluated for its effectiveness and the physical and chemical properties of vegetable oil require careful design of the remedial application. Therefore, performance and cost data are being collected to demonstrate its effectiveness under varied site conditions. Cost and performance results from two large-scale Air Force technology demonstrations are evaluated for this study. Both sites have over 18 months of post-injection monitoring, but vary significantly in terms of lithology and baseline geochemical conditions. Performance monitoring indicates that in both cases, concentrations of chlorinated ethenes have declined significantly. In addition, changing molar fractions of chlorinated compounds (i.e., sequential degradation of parent to daughter compounds) indicate that reductive dechlorination to ethene and ethane is occurring. The cost of applying vegetable oil as an organic substrate at these sites is provided in terms of the cost of the substrate and the cost for emplacing the vegetable oil in the subsurface. It is anticipated that only one full-scale application of the substrate will be required for remediation at these sites. Therefore, operations and maintenance costs are limited to biannual groundwater monitoring.

A Bioremediation Case Study: Butane Biostimulation for the Remediation of Petroleum Contaminants

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A remediation system developed by Global BioSciences (GBI) of North Attleborough, Massachusetts was applied to the cleanup of a fuel oil contaminated site in Fairhaven, Massachusetts using GBI's innovative Butane Biostimulation Technology™ including Butane Biosparging™ and Butane Bioventing™. Eight underground storage tanks originally installed in the 1930s were removed from the site in 1989. A recent investigation at the site identified contaminant concentrations exceeding applicable Massachusetts risk based standards for petroleum hydrocarbons and discovered floating product in one location. Butane Biostimulation™ was selected as the preferred remedial alternative. This patented bioremediation process stimulates naturally occurring butane-utilizing bacteria to metabolize and cometabolize pollutants. In the Butane Biosparging treatment system, butane and air are introduced into the groundwater via a specialized gas delivery system, the *Butane Injector 2000™*. This system injects low volumes of butane gas at a predetermined rate into the air stream from an air compressor. The butane/air mixture is distributed into the groundwater via a set of injection wells. The butane dissolves into the groundwater and provides a food source for butane and petroleum degrading bacteria, and along with increased dissolved oxygen, stimulates an increased biomass and treatment by direct metabolism of hydrocarbons and cometabolism of more recalcitrant compounds such as MTBE. Above the water table, the Butane Bioventing system degrades contaminants in the unsaturated zone. The system provides soil treatment by circulating butane and air through the contaminated area and promoting the growth of butane-utilizing bacteria. Baseline sampling for contaminant concentrations, dissolved oxygen, and the microbial community was completed before system startup. Analyses of groundwater samples have documented system effectiveness by achieving groundwater remedial goals within seven months of system start up.

Facilitated Desorbtion and Incomplete Dechlorination: Observations from 350 Applications of HRC

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The use of a variety of electron donors to accelerate natural attenuation is becoming a standard procedure. As the frequency of use of these protocols increases, certain issues are surfacing and becoming the subject of more intense examination. Two that are identified herein are 1) the ability for electron donor enhancement to facilitate the desorbtion of residual DNAPL and, 2) incomplete dechlorination. Observations with Hydrogen Release Compound (HRC®), a time-release electron donor, at over 350 sites can contribute to the discussion of these issues. Among other things we find that the two subjects are linked insofar as facilitated desorbtion of DNAPL can generate the false appearance of incomplete dechlorination during the early phases of site evaluation.

Clear evidence that enhanced bioremediation is facilitating the desorbtion of DNAPL is not abundant in this venue, because HRC is intended mostly for dissolved phase plume management. Nevertheless, in a relevant sub-population of sites with DNAPL (about 5%), essentially discovered after the fact, there is evidence that enhanced bioremediation facilitates desorbtion. The basis of this conclusion is that parent and daughter products cycle through reduction and replenishment in ways that cannot be explained by changes in plume dynamics and belie the notion that a fixed mass is present.

Regarding incomplete degradation of daughter products it is apparent that reductive dechlorination can slow down and appear problematic on many sites. The important thing, however, is to differentiate the degrees of slowdown so that the sites that are truly recalcitrant and require further intervention can be identified. Often the early accumulation of DCE has nothing to do with inhibition phenomenon, but gives that impression. What may be happening is all or some of the following: 1) unknown sources are providing a constant feed of parent material, 2) rates of degradation of parent compounds are faster than those of daughter compounds ("kinetic disparity") leading to accumulation and 3) differences in solubility from parent to daughter products make the latter more prevalent in the dissolved phase. Once these issues are examined then it is appropriate to search for valid inhibition phenomena; to that end we can cite both the biological explanation (absence of necessary microorganisms) and the lesser recognized geochemical explanation (elevated reduction of iron which blocks electron flow to DCE).

Based on the above reference data set we believe that a truly problematic inability for DCE to degrade further is only present on 7% of the sites given "enough time and enough electrons". We find 1) the geochemical inhibition is often transient as competing electron scavenging reactions run their course and, 2) the microbial insufficiency can often be corrected naturally unless there is complete absence of requisite dechlorinators.

In terms of solutions, with biological limitations one can bioaugment, or, for both biological and/or geochemical limitations, if the pool of DCE is present without significant parent material then a switch to aerobic conditions can be made – thus outflanking the problem. All of these solutions are "second tier", because overall we are coming to a very important conclusion that the vast majority of sites displaying a sluggish pattern of DCE attenuation may simply need "more time and more electrons."

SEDIMENTS II

Validation of a Feasibility Study Foot Print at a Sediment Site Using a Weight-of-Evidence (WOE) Approach

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Monitored Biotransformation of RDX in a Saturated Soil: Alternative e^- Acceptors Alter Microbial Community Structure and Function

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Metabolic Biomarkers for Detecting Anaerobic PAH Biodegradation in Groundwater and Sediments

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Bacterial Degradation of Polycyclic Aromatic Hydrocarbons in Surface Sediments of Coastal Ecosystems

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Remediation of PCB-Contaminated Sediments Using Colloidal Zero-Valent Iron

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Pilot-Scale Demonstration of In-Pile Thermal Destruction of Chlorobenzene Contaminated Soil and Sediments

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A Toxicity Assessment Approach for Evaluation of In-Situ Bioremediation of PAH Contaminated Sediments

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Validation of a Feasibility Study Footprint at a Sediment Site using a Weight-of-Evidence (WOE) Approach

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The primary objective of this study was to more clearly define the extent of sediments that pose an unacceptable risk to the environment and require evaluation in a Feasibility Study (FS). Three lines of evidence (sediment chemistry, toxicity bioassays, and bioaccumulation studies) were used to validate a preliminary remedial footprint developed for the offshore sediments at this site. Data for the three lines of evidence were evaluated using a WOE framework modified from an approach developed for the State of Massachusetts (Menzie et al. 1996). The WOE approach comprises the following five steps: (1) *Determine the weight of the endpoint*. This study considered four equally weighted endpoints: sediment chemistry, toxicity to amphipods, toxicity to echinoderm larvae, and bioaccumulation. (2) *Determine the nature (i.e., whether the finding is positive or negative) and magnitude of the result*. Numeric scores were assigned for various WOE categories based on consensus criteria developed with regulatory agencies. (3) *Integrate the weight, finding and magnitude for a given endpoint result*. The weight, finding and magnitude for each endpoint result were integrated to determine (a) whether or not the result for that endpoint validates inclusion in the FS footprint, and (b) the level of certainty associated with that conclusion. (4) *Integrate all endpoint results for a given sample location.* All endpoint results for a given station were integrated to determine if the location (a) should remain in the FS footprint, (b) should be excluded from the FS footprint, or c) required the consideration of additional inputs to make a determination (i.e., the WOE results were equivocal, resulting in a "gray" area). (5) *Map WOE results from Step 4.* The WOE results for all stations were mapped to provide an illustration of the preliminary FS footprint.

Monitored Biotransformation of RDX in a Saturated Soil: Alternative e^- Acceptors Alter Microbial Community Structure and Function

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Past actions taken by the Environmental Protection Agency (EPA) with regards to the Massachusetts Military Range (MMR) highlights the importance of examining the fate of explosives contamination on military training ranges. The bio-treatability of a cold region military training facility surface soil contaminated with hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) was recently determined. Two critical parameters were examined in the establishment of laboratory microcosms, soil moisture tension and the use of alternative e^- acceptors in treating the saturated soils. Throughout the biotreatability study, RDX loss, intermediate formation and the associated microbiology were monitored. RDX became non-detectable within three weeks of study initiation under the saturated condition whereas RDX remained near the original concentration following 5-weeks of incubation at field moisture. The microbial community occurring under the saturated condition showed an increased percentage of PLFA indicative of facultative anaerobic Gram-negative heterotrophs. The addition of Fe^0 and SO_4 accelerated the rate at which RDX was lost whereas a NO_3 addition significantly impaired RDX biotransformation/biodegradation. Each e^- acceptor supplement induced the formation of a unique microbial community and associated catabolic function. Results from this study suggest that RDX remediation can be accelerated (in this cold region soil) via the addition of specific alternative e^- acceptors and that the effectiveness of the treatment can be monitored through the associated microbiology.

Metabolic Biomarkers for Detecting Anaerobic PAH Biodegradation in Groundwater and Sediments

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In order to implement biodegradation protocols for remediating contaminated groundwater and sediments, it is critical that to be able to monitor the biological activity taking place *in situ*. By understanding the mechanisms of specific biodegradation pathways it has been possible to identify unique metabolic products that can be used as biomarkers for the biodegradation process of interest. Studies of anaerobic naphthalene, methylnaphthalene and phenanthrene metabolism have determined that a direct carboxylation of the aromatic rings is the initial step in degrading these small PAHs. Carboxylation is followed by sequential reduction reactions before ring cleavage occurs. These pathways result in the formation of several unique metabolites that may be used as biomarkers for monitoring *in situ* PAH biodegradation. For instance, 2-naphthoic acid (2-NA), tetrahydro-2-naphthoic acid (TH-2-NA) and hexahydro-2-naphthoic acid (HH-2-NA) are all intermediate metabolites generated by sulfate-reducing bacteria degrading naphthalene. Similar metabolites are produced during methylnaphthalene and phenanthrene. We have developed methods for detecting these biomarkers in groundwater, and have validated their usefulness at a well-characterized field site. Groundwater samples were taken from wells distributed throughout an anaerobic, creosote-contaminated aquifer in Stockton, CA. Each sample was extracted, derivatized and analyzed by gas chromatography coupled to a mass spectrometer. All four of the anaerobic metabolites were detectable in various samples from the site. The concentration of 2-NA at each monitoring well was quantified and correlated to the zones of naphthalene contamination. Presence of the other biomarkers in the same wells as 2-NA was used as confirmation that the anaerobic pathways were indeed active at this site. Taken together with measurements of the aquifer's physical characteristics, this biomarker data was used to describe the spatial extent of naphthalene biodegradation at this site. These same techniques are being modified to detect PAH biodegradation in polluted harbor sediments from Norfolk, VA.

Bacterial Degradation of Polycyclic Aromatic Hydrocarbons in Surface Sediments of Coastal Ecosystems

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Anthropogenic inputs of aromatic hydrocarbons are a common stress to coastal ecosystems. Petroleum-derived compounds can accumulate in surface sediments and change the associated biota. Elevated hydrocarbon concentrations can provide a selective pressure for strains that can metabolize these compounds, but the response of the assemblage can also be affected by environmental factors. We examined the effect of various chemical and physical conditions on bacterial production and aromatic hydrocarbon mineralization in surface sediments of five coastal ecosystems that have significant anthropogenic impacts. The data were gathered during thirty-eight research cruises over the past four years in Pearl Harbor, San Diego Bay, Charleston Harbor Estuary, Chesapeake Bay, San Francisco Bay and Delaware Bay. Sediment from temperate coastal systems had large seasonal variation in mineralization rates and turnover times of sentinel aromatic hydrocarbons (i.e. naphthalene, phenanthrene, and fluoranthene), though there was little correlation with temperature. Aromatic hydrocarbon mineralization, as measured using ^{14}C-radiotracer additions, was dramatically reduced when bottom water dissolved oxygen saturation was below 70%. Ambient hydrocarbon concentration below 10 μg g^{-1} sediment did not appear to support bacterial assemblages capable of rapid mineralization of the hydrocarbons. Hydrocarbon mineralization rates generally ranged from 10^{-6} to 10^{0} μg C g^{-1} sediment d^{-1} in both temperate and tropical systems but were highest in chronically impacted sediments in Charleston Harbor (7.0×10^{-1} μg C fluoranthene g^{-1} sediment d^{-1}) and Pearl Harbor (1.21×10^{-1} μg C fluoranthene g^{-1} sediment d^{-1}). In many ecosystems, high PAH concentration correlated with low bacterial production though this was not seen in Pearl Harbor. In this tropical ecosystem, production generally increased with PAH concentration, as did PAH mineralization. Understanding environmental factors that control hydrocarbon metabolism by the natural bacterial assemblages may help us determine the capacity for estuarine sediments to assimilate contaminants as well as identify areas that are at risk of ecological damage.

Remediation of PCB-Contaminated Sediments Using Colloidal Zero-Valent Iron

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Chemical transformation of halogenated organic compounds (HOCs) by colloidal zero-valent iron (ZVI) is one of the latest innovative technologies in environmental remediation. This research project is developing and evaluating a treatment technology that uses colloidal elemental iron to effect the reductive dechlorination of PCBs to biphenyl. The objective of this work is to develop a robust technology to remediate PCBs in marine and fresh water sediments under ambient conditions in a cost-effective manner.

Experiments are being conducted using PCB-contaminated sediment from the Housatonic River and New Bedford Harbor, both in Massachusetts, under conditions approximating those in the sediment pore water. Extensive laboratory batch studies are underway, in which iron type, concentration, and number of applications are being investigated. A mass balance is being developed to determine the breakdown mechanisms and if, in fact, the PCBs are being reduced to biphenyl.

Results have shown that PCBs can be reduced by 63% in a fine-grained, organic-rich marine sediment and by 95% in a sandy river sediment in approximately one day with one application of 3% ZVI to sediment. Rate constants for dechlorination were estimated to be 0.1422 d^{-1} and 3.2871 d^{-1}, respectively. Adding a greater concentration of ZVI did not increase removal proportionally, and no substantial reduction took place after one day. It was concluded, therefore, that more than one application of ZVI is necessary to reduce the PCBs to lower levels due to the fast corrosion kinetics of the iron. Preliminary results also indicate that higher chlorinated PCBs do indeed dechlorinate to lower chlorinated PCB congeners upon reaction with colloidal ZVI.

Pilot-Scale Demonstration of In-Pile Thermal Destruction of Chlorobenzene-Contaminated Soil and Sediments

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At the Eastland Woolen Mill Superfund site in Corinna, Maine, decades of textile manufacturing led to contamination of approximately 75,000 cubic yards (57,300 cubic meters) of soil by mono-, di-, and trichlorobenzenes, which were components of the dyes used to add color to wool. Roy F. Weston, Inc., under the direction of the U.S. Army Corps of Engineers (USACE) pursuant to an Interagency Agreement with USEPA, is charged with implementing a Non-Time Critical Removal Action (NTCRA). Under the NTCRA, TerraTherm, Inc. performed a pilot test and evaluated the applicability of its In-Pile Thermal Destruction (IPTD) technology for treatment of contaminated soils in an aboveground soil pile. 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. In IPTD, as with ISTD, 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.

The pilot test was conducted in two 55-gallon (208 L) drums. Drum 1 was filled with contaminated soils from the site and Drum 2 contained clean fill. During the treatment phase of the pilot test the drums were connected in series with clean air entering Drum 1 and the vapors flowing from Drum 1, through Drum 2, and then on to the AQC unit. The second drum was pre-heated to the target treatment temperature prior to initiating heating of the first drum. The primary objectives of the pilot test were to demonstrate whether the soil in the pre-heated drum, representing a treated soil pile, could serve as an effective vapor pre-treatment medium; and if the exhaust from the pre-heated soil drum has low levels of emissions. The pilot test indicated that TerraTherm's IPTD technology is potentially capable of removing chlorinated benzenes from the soils at the Eastland Woolen Mill site and ultimately meeting the remedial target soil concentrations. A mass balance performed on the data from the pilot test indicated that 60 to 75 percent of the original chlorobenzenes were destroyed by IPTD. The majority of the destruction likely occurred in Drum 1 after the steam drive. The chlorinated benzenes that were steam-stripped from Drum 1 during the steam drive were largely transported through Drum 2 and removed effectively by the GAC canister. Vapor emissions from the GAC drum indicated that TerraTherm's IPTD would be capable of attaining the applicable emissions standards. Although the overall performance of the pilot test was promising, design and operational limitations prevented a true evaluation of the feasibility and effectiveness of using a heated/treated soil pile for pre-treatment of the vapors. The pilot test did demonstrate that in situ distillation and steam-stripping processes can effectively remove chlorinated benzenes at temperatures below their boiling points. It is believed that if the vapors produced during the distillation and steam-stripping phase had passed through a typical superheated region around a heater/vacuum well (soil temperatures of 400-500°C), very high in-situ destruction efficiencies (e.g., 95-99%) would have occurred.

A Toxicity Assessment Approach for Evaluation of In-Situ Bioremediation of PAH Contaminated Sediments

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Freshwater and marine sediment toxicity tests were used to measure baseline toxicity of sediment samples collected from New York/New Jersey Harbor (NY/NJH) (with traces of PAHs) and East River (ER) (PAH contaminated) sediments. The tests were undertaken to determine how effective were the developed biotreatment strategies in reducing ecotoxicity of the contaminated sediments and to provide a measure of biotreatment efficiency based on ecotoxiciy values. The objective of running the tests was to relate the reduction of contaminant concentration to the reduction of ecotoxicity (lethal, sublethal or bioaccumulative endpoints) based on biological assay points.The four freshwater toxicity tests were: (1) Amphipod, *Hyaella azteca* mortality and growth tests : a standard 10-day USEPA method using 100 ml sediment and 175 ml overlaying water and two 7-day exposure methods (the EMAP method.using 40 ml sediment and 160 ml overlaying water and a reduced volume method, developed by us, that uses 17 ml sediment and 30 ml overlaying water); (2) a 7-day aquatic worm, *Lumbriculus variegatus*, mortality and budding test; (3) a 7/8 embryo larval survival and teratogenic test with *Pimephales promelas* (fathead minnow) (FHM-EL) USEPA method that uses 40 ml sediment and 60 ml overlaying water and (4) a 4-day vascular or aquatic plant, *Lemna minor*(Duckweed), a frond number/growth/chlorophyl test that uses 15 ml sediment and 2 ml overlaying water. Two marine tests were also used: (1) a marine amphipod , *Ampelisca abdida*, 10-day mortality test that uses 200 ml sediment and 600 ml overlaying water and (2) a sheppshead minnow, *Cyprinodon veriagata*, embryo-larval sediment(SHM-EL) mortality test. The reduced freshwater amphipod test was developed and used in this study since existing volume requirement of USEPA standard methods exceeded the amounts available from the enhanced biotreatment studies.To determine the cause the of toxicity in these sediments, five sediment manipulations were performed: (1) a sediment purge procedure, where 2 to 4 volumes of lab water were replaced over the sediment in a 24-hr period: (2) a sediment aeration procedure, where sediment samples(80 ml of sediment (140 g) to a 250 ml glass graduated cylinder and 120 ml of overalaying water) were aerated for 24-48-hr period.; (3) an Ambersorb treatment procedure, where sediment samples were tretaed with 2 types of resins (Ambersorb 563 (AS 563) and Ambersorb 572(AS 572) for removal of organics and (5) an Amberlite treatment procedure, where an inorganic (metal) removal resin , Amberlite IRC -178 was mixed with the sediment. ER sediment was found to be highly toxic to all freshwate and marine organisms tested while the NY/NJH sediment showed no significant toxicity to the marine amphipod but was slightly toxic to the freshware worm and to freshwater and marine fish larvae. For all tests ran on ER sediment with the freshwater organisms and the one marine amphipod, no survival was found

except for one freshwater amphipod test (55%). The ER sediment significantly reduced frond production (58.3%) and chlorophyl a levels (35.4%) in the freshwater duckweed test.

Results from the five sediment manipulation studies showed that freshwater amphipod survival was improved with sediment aeration procedure, with 8% AS 563 and AS 572 as well as with AL IRC-718 treatments. Toxicity can also be reduced with the sediment dilution techique (100 fold). These manipulations and analyses for the specific inorganic and organic contaminants revealed that hydrogen sulfide, PAHs and metals were factors in ER sediment toxicity. Results from Hyalella azteca toxicity tests using ER and NY/NJH sediments treated by aerobic biodegradation slurry approaches showed reductions in toxicity to *H. Azteca* equal to or greater than that achieved through chemical or mechanical manipulations of the sediment samples. *H. azteca* survival after various aerobic bioslurry treatments of ER sediment ranged from 35% to 65%, compared to survival of 20% in ER sediment tested by aeration and addition of 8% AS 572.resin.

REMEDIATION - SOILS

Evaluation of the Dynamic Operation of a Large-scale Active Soil Gas Collection System

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In-situ Remediation of TCE in Clayey Soils Using the Lasagna Process

Chris Athmer, Terran Corporation, Beavercreek, OH

Controlled Environmental Biopiling for Contaminated Land Treatment

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Electrical Resistance Heating for Remediation of Chlorinated Solvents in Low Permeability Soils

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Beneficial Reuse of Diesel-Impacted Soil from Pipeline Release on Tribal Land

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Characterization and Remediation of a Former Drop Forge

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Evaluation of the Dynamic Operation of a Large-scale Active Soil Gas VOC Collection System

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The former Raymark Industries and its predecessors manufactured brake linings and related parts from 1919 to 1989 on a 34acre parcel in Stratford, CT. The site was identified as a federal Superfund site due to past on-site disposal of chemical and asbestos- related waste products, and is currently under the management of the CTDEP. Extensive remediation work performed by the Army Corp of Engineers and its contractors to address contamination from historic on-site waste disposal practices included the installation of a clay and flexible membrane liner, an above-liner drainage system, and conventional and enhanced soil gas collection systems. Treatment systems installed at this site include a DNAPL recovery system, a gas vent sand layer with perforated horizontal gas conveyance collection piping (conventional), vertical air injection and vapor extraction wells (enhanced), and soil gas treatment systems employing thermal oxidation and activated carbon. Currently, a retail shopping complex is being constructed on the site.

The treatment systems have been in operation since 1997 and a significant set of operational data has consequently been produced. This work evaluates this five-year set of operational data. The data include groundwater and soil gas monitoring data, and soil gas and DNAPL recovery data. Multi-level groundwater monitoring wells are sampled for geochemical parameters, VOCs, SVOCs, PCBs, and metals. Air flow-rates, soil gas concentrations, and the vacuum underneath the protective site-wide cap are monitored. The data show decreasing contaminant concentrations in soil gas and in several of the groundwater wells, with concomitantly increasing methane concentrations in the soil gas. The efficiency of the thermal oxidation system has increased by transitioning the enhanced soil gas treatment system from the originally designed full-time operational scheme to operating the system in cycles. Finally, using this data set, additional variations of the soil gas treatment system and groundwater monitoring program are currently under evaluation.

In-situ Remediation of TCE in Clayey Soils Using the Lasagna™ Process

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The remediation of solvent contaminated low permeable soils poses a significant problem for many facilities. A consortium of industrial partners (Monsanto, Dupont and GE), the USEPA and the DOE jointly developed a technology that integrates electrokinetics with in-situ treatment of chlorinated organics to address this problem. The process, called Lasagna™, utilizes a DC electric field to move pore water and contaminants uniformly through the soil mass to treatment zones emplaced within the contaminated area. The emplacement is performed using common piling technologies and results in little or no wastes. The treatment materials emplaced are typically iron, coke and kaolin.

After two field demonstrations, a full-scale Lasagna remediation system was implemented at the DOE facility in Paducah, KY. The system was installed and operated over a two-year period by CDM Federal Programs, Kevil office. The process was shut down in December 2001 after meeting the cleanup target of 5.6 mg/kg specified by the ROD for the site. A description of the Lasagna process will be presented as well as the full-scale system design, operations, costs and results.

Lasagna is a registered trademark of Monsanto Company, St. Louis, MO.

Controlled Environment Biopiling For Contaminated Land Treatment

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TerraNova is an EU Fifth Framework project for the remediation of polluted lands in Europe to prevent groundwater contamination. The Aim is to develop an accelerated ex-situ soil bioremediation system. The degradation takes place in a totally contained vessel to prevent further pollution propagation. In addition to oxygen supply and the biopile's regular inoculation with fresh microorganisms from a NovaCell^{TM} fermenter, a novel aspect of TerraNova is the soil temperature control via inserted pipe matrixes. The leachate is returned via the NovaCell to promote the bacterial cocktail's adaptation to the pollution. Prior to bioremediation, the polluted soil is mixed with BioGel^{TM}, which contains the same microorganisms, along with nutrients to promote rapid initial growth. Preliminary laboratory tests suggested that very high initial bacterial activity occurs when the microorganisms are degrading the provided nutrients. Heat generation due to bioremediation resulted in high temperatures (up to 57^{o}C) in bench scale which totally incapacitated the micro-organisms. A temperature control system was implemented to a 3m^3 pilot-scale TerraNova. The soil was polluted with 10g/kg of 60% creosote, 30% diesel and 10% lube oil. The pollution was reduced by 68% after seven weeks. As expected, a heat generation peak occurred at the start of the remediation and was contained by the temperature control system. These encouraging bioremediation results suggest that efforts should now focus on improving our understanding of the other key processes governing biodegradation. A comprehensive model of the TerraNova process is currently been developed using a Finite Element Method. While this model will be used for simulation and optimisation of the bioremediation, it will also support the design and tuning of model-based controllers for parameters such as soil temperature and moisture content. The project's ultimate target is to develop a stand-alone ex-situ bioremediation plant to allow SME's to remediation European polluted lands.

Electrical Resistance Heating for Remediation of Chlorinated Solvents in Low Permeability Soils

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Electrical Resistance Heating (ERH) is being utilized to treat chlorinated solvents in soil and groundwater at a former Navy Dry Cleaning facility site. Electrical resistance heating is an in-situ technology that uses commonly available electricity and applies it into the ground through electrodes. These electrodes can be installed either vertically to any depth or horizontally underneath buildings, operating facilities, and in the presence of buried utilities. The technology is equally effective in soil and groundwater. ERH is a Thermal Enhancement for Soil Vapor Extraction that is effective in removing volatile organics by boiling groundwater in-situ over an extended period of time at a controlled rate resulting in volatilization and steam stripping of sorbed compounds. Tetrachloroethene (PCE), a typical dry-cleaning solvent has been released at the site and sequential dechlorination products of PCE have been detected in soil and groundwater several orders of magnitude above regulatory standards. PCE has migrated vertically downward as a dense non-aqueous phase liquid through subsurface soil and into the shallow groundwater (3 to 5 feet below ground surface) until encountering a clay unit ranging from 8.5 to 13.5 feet below ground surface across the site. DNAPL has not been observed in groundwater samples but is suspected to be present based on analysis of dissolved phase PCE in concentrations up to 120,000 ppb. The objectives of the ERH implementation are to achieve between 90% to 95% reduction in groundwater concentration of the total chlorinated solvent concentrations in the target treatment area (16,525 square feet, 6700 cubic feet) and to achieve removal of any DNAPL residual or pool(s) to the extent practicable.

Beneficial Reuse of Diesel-Impacted Soil from Pipeline Release on Tribal Land

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A pipeline failure on tribal reservation land in 1987 resulted in the release of approximately 162,000 gallons of diesel fuel. The fuel spread over and within an alluvial fan deposit up to 400 feet from the release point. Emergency response efforts terminated the release and partially remediated the site through trenching and excavation, burning, and free product recovery. Subsequent site investigations and remedial activities characterized the extent of the release in alluvial sediments consisting mostly of sand, gravel, and silt. Groundwater impacts were limited to the area just downgradient of the release point. Soil and groundwater remedial systems selected for the site included an active bioventing system, free product recovery wells, and monitored natural attenuation. A source assessment showed that although these remedial systems were reducing diesel concentrations in soil, the estimated time for remediation was excessive. A remedial alternatives analysis included excavation and disposal at a landfill, in-situ or ex-situ thermal treatment, and an engineered in situ bioremediation. Through the combined cooperation of several entities both public and private, another alternative was discovered which became the most cost-effective and timely solution for site soils. Coordination between state agencies, tribal environmental and cultural branches, and Yellowstone Pipe Line was achieved to excavate and use over 130,000 cubic yards of impacted and unimpacted soil as road base for a local highway project. Soil with relatively low impacts was used as basecourse and traffic gravel, while more impacted soil was isolated by placement in a single 6-inch lift directly beneath the asphalt cap. Crushed gravel from the site was used to manufacture asphalt and chip seal. The mining and subsequent reclamation were completed within one year, and the site is currently under a vegetation management program to control noxious weeds.

Characterization and Remediation of a Former Drop Forge

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In 1987, a release of petroleum was identified at an undeveloped property downgradient of a former drop forge. The drop forge operated from approximately 1900 through 1979. Subsequent delineation of the release determined that the source was within the industrial building area housing the drop forge. In August 1990, nine fuel oil underground storage tanks (USTs) were removed from the industrial complex. While installation dates are not clearly documented, the tanks may have been installed as early as 1909. During the removal, large holes were identified in the USTs where gauging sticks had punctured the bottom of the tanks.

The site is surrounded by water on three sides and throughout the investigations sheens have been observed on the surface water. In 1992, three 36-inch recovery wells were installed in two areas of the site to prevent future outbreaks of fuel oil to the adjacent surface water. In the 1990's, a detailed hydrogeologic investigation was completed to identify the presence of preferential pathways and provide data for the design of a comprehensive hydraulic and physical barrier. An extensive soil boring program, including the use of a cone penetrometer, was undertaken. The results of the investigation indicated that the majority of contaminant transport is occurring through a sand and gravel layer.

In 1997, seven additional recovery wells were installed in one area of the site to prevent additional outbreaks to the adjacent ponds and canal. However, very low groundwater removal rates were obtained due to the minimal thickness of the sand and gravel layer across this portion of the site.

In 1999, a Waterloo® Barrier was installed in a V-shaped pattern to prevent outbreaks to the surface water bodies and provide a pooling-effect to assist the recovery wells in removing petroleum-impacted groundwater from the area. Following the barrier installation, soil excavation was conducted to remove petroleum-impacted soil from the downgradient side of the barrier. To-date very few recurrences of sheens have been observed on the adjacent canal and ponds and the pumping rates have significantly increased in this area of the site.

CHEMICAL OXIDATION

Chelated Native Iron in Fenton-Like Oxidation of BTEX and PAHs in Soils

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Treatment of PCB Contaminated Sediment by Persulfate Oxidation with Pozzolanic Reaction

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The Adsorption of Chromium to Hydrous Manganese Oxides Produced during In-Situ Oxidation using Permanganate

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In-Situ Chemical Oxidation Misfires and Recent Innovative Improvements

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Chelated Native Iron in Fenton-Like Oxidation of BTEX and PAHs in Soils

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This paper presents the feasibility of using chelated native iron as catalyst in a Fenton-like oxidation of BTEX and PAHs in soils. The catalysts selected for the decomposition of hydrogen peroxide consist of iron-aminopolycarboxylate chelates, specifically iron-ethylene diamine tetraacetic acid (Fe-EDTA) and iron-diethylene triamine pentaacetic acid (Fe-DTPA). DTPA is a stronger chelating agent than EDTA consequently its metal-complexes have a higher stability in alkaline conditions. Carboxylate-ligand complexed iron decomposes hydrogen peroxide to free radicals that oxidize hydrocarbons and chlorinated hydrocarbons. The iron for the chelated-iron complexes (Fe-EDTA and Fe-DTPA) is extracted from the native soil using EDTA and DTPA. Chelate-extractable metals such as calcium (Ca) and magnesium (Mg) are also detached from mineral surfaces through dissolution and desorption. A series of batch tests are conducted using different BTEX and PAH impacted soils and aqueous solutions with various concentrations of EDTA and DTPA as well as various concentrations of hydrogen peroxide. To simulate groundwater in equilibrium with the soil, the aqueous phase is adjusted to the soil pH before it is mixed with the soil for approximately 24 hours. The final pH, conductivity, alkalinity, DOC, and Fe, Ca and Mg-concentrations are determined in the supernatant. The stability of Fe-EDTA and Fe-DTPA complexes is affected by pH and the Ca and Mg activity that develops as a result of the formation of anionic complexes with metal ions. The effectiveness of EDTA and DTPA to extract Fe and remain stable for the decomposition of hydrogen peroxide in circum-neutral solutions is evaluated. The effectiveness of hydroxyl radicals diminishes in the presence of free radical scavengers such as carbonate and bicarbonate that develop as a result of Ca, Mg-carbonate dissolution. The effectiveness of Fe-EDTA and Fe-DTPA to generate a sufficient free radical activity for the oxidation of sorbed BTEX and PAHs in circum-neutral conditions is evaluated. A comparison of the conventional Fenton oxidation with the iron-chelate catalyzed Fenton-like oxidation in different soil compositional environments is also presented.

Treatment of PCB Contaminated Sediment by Persulfate Oxidation with Pozzolanic Reaction

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Cleaning up the environmentally persistent poly chlorinated biphenyl (PCB) contaminated sediment and further transforming them into a monolithic structure has been the motivation behind developing effective treatment technology. Highly reactive free radicals generated as a result of photolysis or heat decomposition of persulfate ions in aqueous phases have been found to be able to mineralize many organic compounds including PCBs. In this study, we have investigated the feasibility of combining the chemical oxidation of sodium persulfate ($N_2S_2O_8$) and the stabilization/solidification by lime for the treatment of PCBs sediment and soils.

The study was conducted by using two sets of laboratory scale experimental systems: completely mixed aqueous batch (containing PCBs, water and persulfate) and soil slurry batch (containing PCBs sediment and persulfate solution with/without lime). The aqueous batch experiments conducted in 100-mL zero headspace syringe at 40°C resulted in 94% decrease in PCB concentration within 56 hrs, with a decrease in pH from 4.5 to 1.5 at a persulfate concentration of 10 g/L. In the slurry phase experiments, desorption of PCBs from the organic layer was observed till 12 hours followed by a decrease in PCB concentration at 40°C and 50°C. However, PCBs were not significantly degraded. More experiments were then conducted in a stirred tank reactor setup with excess persulfate and at a temperature of 80°C for a duration of 168 hrs with/without the presence of lime. This resulted in a 95-99+% decrease in PCB concentration levels to as low as 1 PPB. The control experiments showed the final concentration greater than that of the initial concentration. This indicated that the sorbed PCBs that were not otherwise detected were released from the organic layer in the sediment.
The study shows that heated persulfate effectively degraded PCBs in aqueous and soil slurry media under the experimental conditions. Increase in degradation was observed at higher temperatures and also with the presence of lime. Degradation can be improved by increasing persulfate concentration and duration of the reaction.

The Adsorption of Chromium to Hydrous Manganese Oxides Produced during In-Situ Oxidation using Permanganate

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Potassium permanganate ($KMnO_4$) is commonly used for in-situ oxidation at sites contaminated with chlorinated solvents such as trichloroethylene (TCE) and perchloroethylene (PCE). Metal mobility is a concern at some sites where in-situ oxidation is employed. Chromium can exist naturally in the trivalent form {Cr(III)} which is relatively insoluble. However, Cr(III) can be oxidized by potassium permanganate or hydrous manganese oxides (HMOs) to hexavalent chromium {Cr(VI)}. Cr(VI) is relatively soluble (and therefore mobile) and is a known toxin. Since large amounts of HMOs are formed during the in-situ treatment of TCE/PCE contaminated sites, the interaction between HMOs and mobilized Cr(VI) is of interest. The present study addresses the rate and extent of Cr(VI) adsorption to HMOs under representative remediation conditions. Samples containing 0.25, 0.75, and 3.0 g of HMOs were exposed to 1 mg/L of Cr(VI) and monitored over a 21 day period. This experiment was done in solutions adjusted to pH 6.5 and pH 8.5. Results showed that aqueous chromium levels decreased significantly in the presence of HMOs for both pH values, with 3.0 g adsorbing the most chromium. The most significant decreases in aqueous chromium levels occurred within the first 5 days. An equilibrium experiment was also conducted in which 0.5 g of HMOs were exposed to chromium dosages ranging from 0.1-5.0 mg/L of Cr(VI) for 24 hours (ambient temperature, pH buffered to 7). The equilibrium chromium levels were readily predicted using a Freundlich isotherm model. The hydrous manganese oxides used in these experiments were carefully synthesized and treated so that they simulated what is formed at remediation sites. The purpose of this work is to provide a quantitative basis for predicting subsurface chromium levels following in-situ permanganate oxidation.

In-Situ Chemical Oxidation Misfires and Recent Innovative Improvements

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The paper presents an overview of ISCO projects gone bad with a review of recently developed methods to avoid mistakes of the past. A brief overview of each project with pictures, where available, will be presented along with a discussion of the factors leading to failure. In-situ chemical treatment of soil and groundwater at contaminated sites has become increasingly accepted as a feasible, cost-effective, and timely method of site remediation. Laboratory-scale testing has clearly demonstrated the effectiveness of a wide-range of common, often times food-grade, chemicals in transforming or enhancing the transformation of many contaminants. While lab results show success, field application is less predictable due to naturally occurring chemical interferences and site limitations due to the lithologic and hydrogeologic setting. The key difficulty in implementing site treatment to achieve cleanup goals has been the ability to cost-effectively deliver treatment chemicals such that treatment chemicals come in contact with site contaminants prior to degrading or participating in un-wanted side reactions. Projects to be discussed include: an explosion in Wisconsin, an explosion in North Carolina, and many examples of significant volumes of injected fluids exiting at surface grade, sometimes damaging property and harming personnel. The paper is concluded with an overview of the steps that can be taken and the methods that can be used to safely and successfully apply ISCO for site remediation and in some cases, site closure.

TRAINING RANGE RESIDUES

Environmental Fate and Transport Modeling of Explosives and Propellants in the Vadose Zone

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Development of a Field Analytical Platform for Energetic Residues in Soil and Water

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Sampling for Explosives-Residues at Fort Greely, Alaska

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RangeSafe: Meeting the Environmental Challenges of Small Arms Training Through Innovative Technology Application

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Environmental Fate and Transport Modeling of Explosives and Propellants in the Vadose Zone

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Fate and Transport modeling of explosives was conducted at the Massachusetts Military Reservation. The objectives of the unsaturated zone modeling were to (1) determine the likelihood that explosives would migrate to the water table and (2) determine the appropriate soil action level for explosives that migrate to the water table. Unsaturated zone modeling was conducted using the Seasonal Soil Compartment Model (SESOIL). Model results indicate the mobility potential of the explosives and propellants vary depending on the chemical structure. A key fate and transport variable is the dissolution of explosive and propellant particulates which is not accounted for in SESOIL. Several approaches were identified to incorporate these variables into the SESOIL model.

Development of a Field Analytical Platform for Energetic Residues in Soil and Water

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A large amount of site characterization work has yet to be performed at DOD military ranges, ammunition plants, and depots throughout the United States and abroad. The detection criteria and sampling and analytical is a significant challenge and expense at these large sites. Furthermore, the technology and procedures currently available are not able to perform chemical analysis at required detection levels needed for appropriate decision-making in the field. Thus, there is a distinct need for a low-cost, rugged, and accurate field analytical system that will produce repeatable assay results for all energetic compounds and their degradation products. The availability of such a system would enable DOD to create a consistent protocol for the rapid assessment and inventory of such facilities contaminated with energetic compounds. The accepted fixed-base laboratory method for analyzing explosives using a HPLC following the EPA Method 8330 has been enhanced by complementing the traditional UV detection with electrochemistry. The results yield 1 to 2 orders of magnitude lower detection limits, better speciation and greater quality control than current field methods. In addition, results indicate that this modified method which can be used in the field generates comparable results to fixed-base laboratory results. This approach only requires a relatively small sample volume totaling 1 to 3 grams (soil) or 1 to 3 milliliters (water) yielding a significant increase in productivity. Thus, rapid site assessment to determine the nature and extent of the explosives in soil and groundwater can be performed using conventional or innovative vertical profiling methodologies. It is anticipated that this procedure can be used to process up to 40 samples per day of soil or water, collected using either field sampling technique. Such a system will yield more complete, real time data, directly on-site if desired.

Sampling for Explosive-Residues at Fort Greely, Alaska

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Fort Greely, Alaska has an extensive complex of weapon training and testing areas. These areas are located on lands withdrawn from the public domain under the Military Lands Withdrawal Act (PL106-65). The Army has pledged to implement a program to identify possible munitions contamination. Because of the large size (85,042 acres) of the training areas, characterization of the contamination levels will be difficult. We have begun a multi-phase sampling program where we first sampled locations most likely to be contaminated at one impact area to identify locations that have the greatest potential to contaminate adjacent water. We focused our sampling on surface soils and collected multi-increment and discrete samples at locations of known firing events and from areas on the range that had cratering, pieces of munitions, or a designation as a firing point. Firing events included tests of 81-mm mortars, Tube-launched Optically-tracked Wire-guided (TOW) missiles, 40-mm high explosive cartridges, and Sense and Destroy Armor (SADARM). We detected explosives-residue in 48% of the 107 soil samples we collected. RDX was the most frequently detected explosive (39%). Of the samples above the detection limit, median RDX concentration was only 0.021 µg/g. Low order detonations accounted for four of the five highest RDX concentrations. TNT was the second most frequently detected explosive (21%). Median TNT concentration in samples where TNT was detected was only 0.004 µg/g. Low-order detonations produced the highest TNT concentration we found. The amino-dinitrotoluene transformation products of TNT were detected in about 10% of the samples. HMX was found in 11% of the samples. The analytes 2,4-DNT and NG were detected at a firing point. High explosive projectiles that function properly appear to leave little residue in the surface soil. Low order detonations, where only part of the high explosive filler detonated leaving solid explosive composition in contact with surface soil, produced the highest soil concentrations. Firing points are sources of NG and 2,4-DNT. The greatest threat of contamination of ground water would be high numbers of low-order detonations or heavily-used firing points located in ground water recharge areas.

RangeSafe: Meeting the Environmental Challenges of Small Arms Training Through Innovative Technology Application

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Small arms training is essential to maintaining DoD readiness. However, traditional small arms projectiles are predominantly a lead/antimony alloy with a copper jacket. When subjected to bullet-to-bullet impacts or a harsh environment, migration of toxic heavy metals from the range berm may occur. Previous studies testing stabilization methods on active berms without particulate metal removal were ineffective, and in some cases, made the problem worse.[1] Picatinny Arsenal engineers are addressing these issues under a new program called RangeSafe. RangeSafe was established by the Army to help commercialize emerging environmental technologies targeting the management, recovery and remediation of residual contaminants generated throughout the life cycle of armament systems. The RangeSafe concept was initially developed as a companion to the Green Bullet Program, which has successfully developed lead-free small arms ammunition for subsequent deployment.
The RangeSafe approach involves physically removing the lead from the soil prior to green bullet conversion. To accomplish this, placer mining techniques are employed in a soil washing process to remove the particulate metals, which are subsequently recycled. If additional ionic metals removal is required after soil washing, phytoremediation is used. The cleaned soil is then returned to the range for Green Bullet usage. This two step approach eliminates toxic metals from berm soils, allowing for green bullet conversion without costly disposal or the long-term liability of leaving the lead in place.

During a successful RangeSafe demonstration at Range 24 at Fort Dix, New Jersey, lead levels in the range soils in excess of 38,000 mg/kg were reduced to below residential standards. This range is typical of the Army's roughly 3,000 outdoor ranges that have become heavily contaminated with lead bullets and fragments after decades of use, and implementation of the RangeSafe program could save hundreds of millions of dollars nation-wide.

References

[1] "Environmentally Redesigned Small Arms Range Field Demonstration", Mark L. Hampton, Dr. Bonnie Packer, Presented at the NDIA 25th Environmental Symposium & Exhibition, March, 1999

BIOMARKERS FOR CONTAMINATION: HIERARCHICAL APPROACHES

Interpretation of Vitellogenin Gene Expression and Protein Production as Predictors of Exposures to Xenoestrogens and Potential Adverse Reproductive Effects in Fish

Patricia Cline, Golder Associates, Gainsville, FL
Bob DeMott, Exponent, Tampa, FL

Biosensors and Bioanalytical Microsystems for the Rapid and Specific Detection of Pathogenic Organisms

Antje J. Baeumner, Cornell University, Ithaca, NY

An Overview of Ecological Indicators: Putting Biomarkers and Bioindicators in Context

James R. Bernard, Environmental Management Consulting, Harpswell, ME

Residue-effect Relationships as Indicators of Ecological Stress

Ed Zillioux, FPL Environmental Services, Juno Beach, FL
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Sediment Characterization Data as Indicators for Dredged Material Disposal Suitability

Ann B. Shortelle, Harding ESE, Gainsville, FL
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Biomonitoring Environmental Contaminants Near a Municipal Solid-Waster Combuster: A Decade Later

Darren G. Rumbold, South Florida Water Management District, West Palm Beach, FL
Mary Beth Mihalik, Solid Waste Authority Palm Beach County, West Palm Beach Fl

Museum Specimens as Historic Biomarkers and their Utility in the Interpretation of Current Site Contamination

Jim Newman, Pandion Systems, Gainesville, FL
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Interpretation of Vitellogenin Gene Expression and Protein Production as Predictors of Exposures to Xenoestrogens and Potential Adverse Reproductive Effects in Fish

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Plasma vitellogenin (Vtg) in male fish is a frequently measured biomarker to evaluate potential exposure to xenoestrogens in aquatic systems. Vtg is the egg yolk precursor protein, produced in the liver in response to estrogen with concentrations in females fluctuating with spawning and seasonal cycles as Vtg is produced and deposited into eggs. The protein is rather long lived; lasting from 2-6 weeks in the plasma of males exposed to estrogenic compounds and can accumulate with repeated exposures. Elevated Vtg in males or reduced levels in females may be considered biomarkers of exposure to estrogenic or anti-estrogenic compounds respectively.

In the liver, the Vtg protein is produced after the estrogen binds to the estrogen receptor, activating Vtg gene expression. This promotes the synthesis of mRNA, which is then translated into the protein. The mRNA, which could be detectable before the protein has accumulated, has a much shorter half-life (on the order of days). The Vtg mRNA and protein represent different potential exposure regimes. The measurement of these biomarkers and their correlation to adverse impacts on reproduction was evaluated based on fathead minnow exposures to estrogen and anti-estrogen.

Biosensors and Bioanalytical Microsystems for the Rapid and Specific Detection of Pathogenic Organisms

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Research in the Bioanalytical Microsystems and Biosensors Lab at Cornell University focuses on the development of biosensors for the detection of pathogens in the environment, food and for clinical diagnostics. Several biosensor strategies are being developed, all of them involve the use of liposomes as instantaneous signal amplification system.

The simple single-use, inexpensive and rapid optical biosensors are designed for field-tests. While they demonstrate fantastically low detection limits, they also are extremely easy to use. Signals are generated in less than 20 minutes with limits of detection in the range of a femtomol. When combined with Nucleic Acid Sequence Based Amplification (NASBA) single cell detection is possible. Biosensors under investigations focus on the detection of *Cryptosporidium parvum*, Dengue virus, *B. anthracis* and *E. coli*. They will find their application in routine drinking water testing, environmental water testing, food analysis and in clinical diagnostics.

More sophisticated microfluidic devices are developed, that will transfer the technology of the simple strip biosensors into more automated and sophisticated microchannel designs. The same biological principles are used, however, novel sample preparation systems, novel molecular biology amplification chambers, and intricate hybridization channel patterns are being developed: for example, a laser-induced cell lysis system that allows that instantaneous and effective lysis of bacterial, yeast and mammalian cells. Electrochemical detection is accomplished using ultramicroelectrode arrays that allow an even more sensitive detection. This research aims toward the creation of an easy-to-use but sophisticated micro-Total Analysis System.

We present today the principles and techniques of our different biosensor systems, the simple optical biosensors and the more complex microfluidic-based sensors. We demonstrate the application of the optical biosensors for the detection of pathogens in real-world samples and provide an out-look regarding the impact of microfluidic-based biosensing systems on the detection of pathogens in food, the environment and for medical diagnostics.

An Overview of Ecological Indicators: Putting Biomarkers and Bioindicators in Context

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Often management objectives are stated in broad terms such as "sustaining environmental quality" or "maintaining historical biological integrity." These broad statements need to be more explicitly defined so that they can provide a clear focus for ecological risk assessment activities. During the problem formulation stage of risk assessment, risk assessors and managers determine what is to be protected, establish what information is needed, and plan the assessment, including the selection of indicators. Specifically, each of the ecological resources of concern needs to be identified (e.g., salmon) and the specific attribute that is of interest (e.g., numbers in a spawning run in a particular stream) should be stated. The combination of resource and attribute is called an assessment endpoint. Assessment endpoints, or *bioindicators*, are identified based on their relevance to management objectives, their susceptibility to stressors, and their ecological relevance.

It is important to differentiate between *bioindicators* and *biomarkers* in the context of ecological risk assessment. Bioindicators are multiple measures of organism health related to environmental stressors that include several levels of biological organization and time scales of response. Multiple measures of health are needed in order to identify and separate the effects of human-induced stressors (e.g., contaminants) from the effects of natural stressors (e.g., food and habitat availability). Bioindicators can range from biomolecular/biochemical responses to population and community-level responses.

Biomarkers of exposure are biochemical or physiological changes which indicate that an organism has received an internal dose of a chemical (Suter, 1993). Biomarkers can be considered as bioindicators if they are causally linked to ecologically-relevant endpoints (McCarty and Munkittrick, 1996). The fundamental difference is that biomarkers concentrate on measurement attributes, while bioindicators require validation in addition to measurement (McCarty, et al, 2002). Biomarkers are generally used to indicate exposure of organisms to contaminants at lower levels of biological organization while bioindicators are typically used to reflect effects of stressors on biological systems at higher levels of organization (ORNL, 2000).

Residue-effect Relationships as Indicators of Ecological Stress

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Environmental concentrations of contaminants are of increasing ecological concern whether these concentrations are at "background" levels or significantly elevated. However, toxicological and regulatory endpoints are more often set in accordance with human health concerns and their corresponding endpoints. Monitoring approaches and regulatory compliance typically focus on ambient media although biomonitoring becomes the method of choice when the contaminant is strongly bioaccumulative but present in the surrounding media only near levels of detection. This is the case for mercury where fish monitoring has formed the basis of human health consumption advisories in most of the United States and elsewhere. Zillioux et al. (1993) evaluated existing data on mercury residues and related residue levels with specific effects of ecological significance. Since then, considerable additional work has accumulated on mercury residue-effect relationships using a variety of species. This paper presents a review of this expanded database of environmental exposures to mercury. In addition, it will provide an overview of a wider range of residue-effect relationships that have proven useful in ecological assessment. These include setting of national and international benchmarks for persistent organochlorine contaminants (e.g., PCBs, PAHs, log P >3., etc.) in fresh and marine waters as well as the use of residue-effects relationships in the management of wildlife risks at hazardous waste and superfund sites and others. Residue-effects relationships are particularly important benchmarks for managing top predators, often threatened and/or endangered species whose primary route of exposure is through ingestion of contaminated prey and whose ambient concentrations are often below routine analytical detection limits. Most importantly, the residue-effect relationship integrates exposure and effects over both time and space which, for wide ranging, valued ecological populations, would otherwise be impossible to measure.

Sediment Characterization Data as Indicators for Dredged Material Disposal Suitability

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Evaluations under Section 103 of the Marine Protection, Research, and Sanctuaries Act of 1972 consider potential dredged material proposed for disposal in Ocean Dredged Material Disposal Sites for maintenance dredging projects. The determination of suitability for ocean disposal is based upon physical, chemical, and biological evaluations. Currently, a tiered testing procedure is used for evaluating the potential dredged material. After completion of laboratory analyses and toxicity tests, the concentration of allowable dredged material in the water column can be calculated that will not cause unreasonable toxicity or bioaccumulation. Our study compares available data for sediments from several Florida and Caribbean sites to sediment screening criteria or concentrations that may predict adverse environmental effects. These data are also compared to actual observed toxicity in bulk sediment and elutriate testing for the same samples. Results support the tiered testing procedure that allows for site-specific testing and interpretation. These analyses result in significantly fewer toxic responses than suggested by simple but conservative screening values. These site-specific data provide direct estimates of the potential for environmental impact rather than relying upon potential adverse impacts inferred from other studies. Thus, site-specific data enable ocean disposal of dredged materials with significantly more confidence that adverse impacts will not occur. In addition, due to the conservative nature of screening criteria, more sites can be permitted for ocean disposal with site-specific data in hand.

Biomonitoring Environmental Contaminants Near a Municipal Solid-Waste Combustor: A Decade Later

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During the 1999 nesting season, eggs and nestlings of anhingas (*Anhinga anhinga*) and white ibises (*Eudocimus albus*) were collected from a colony located on the site of a municipal solid-waste (MSW) combustor and analyzed for residues of chemicals potentially released from this facility. Concentrations of most residues, including tetrachlorodibenzo-p-dioxin (TCDD), tetrachlorodibenzofuran (TCDF), arsenic, beryllium, cadmium and lead, were at levels comparable to those found during a similar survey done in 1989, prior to facility start-up. Further, results from a recombinant cell line bioassay system (CALUX^{TM}) found residues of all dioxin-like chemicals to be at background concentrations in birds collected in 1999. Nickel residues were detected only sporadically in anhingas and in eggs from ibises, and decreased significantly in concentration in ibis nestlings in 1999 compared to 1989. While concentrations of mercury in anhinga nestlings and in eggs of both species were comparable to 1989 levels, its concentration was significantly greater in ibis nestlings in 1999. However, levels of mercury in the ibises remained relatively low when compared to birds from other areas of Florida and did not appear to represent a health threat. While lead did not increase in 1999, its concentration in ibis nestlings remained a concern. The most notable temporal trend observed in birds at this site was a general monotonic decrease in levels of selenium residues during the ten-year monitoring period.

Museum Specimens as Historic Biomarkers and their Utility in the Interpretation of Current Site Contamination

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Understanding the historical source of contamination is often necessary in determining the source and cause of biological contamination as well as for evaluating the trends in contamination over time. Archived museum tissues have frequently been used to as a biomarkers to determine source and trends of contamination. For example, hair and feathers have been used as biomarkers for mercury, lead, arsenic and other heavy metals. Although museum tissues can be useful as historical biomarkers care must be taken in interpreting the results. There are a number of factors such as the preservation techniques of tissues, the representativeness of species populations in a museum as well as biological characteristics of the species than can affect the results. This paper examines the use of museum tissues as historical biomarkers of contamination and provides recommendations on their use as biomarkers.

ENVIRONMENTAL FORENSICS II

A Comparison of XRF Data with ICP/AA Data

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Characterization or Identification of Organic Compounds by Ion Compostition Elucidation (ICE) using Gas Chromatography/High Resolution Mass Spectrometry

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Molecular Characterization of Anthropogenic PAHs in Sediments of the Thea Foss/Wheeler Osgood Waterways, Tacoma, Washington

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Molecular Changes During Petroleum Combustion

Stephen Emsbo-Mattingly, Battelle Memorial Institute, Duxbury, MA

Sourcing PAH in Sediments with Innovative Methodologies

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Distribution and Mobility of Lead Contamination in Soils of Florida Shooting Ranges

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A Comparison of XRF Data with ICP/AA Data

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For the past three years MADEP has been using a Niton Corporation XL-700 series multi-element X-ray fluorescence unit (XRF) to collect data on metals concentrations in soil during state funded response actions. The Department has been primarily interested in lead and arsenic concentrations in surface soils at these sites. During the course of these efforts, agency staff have submitted split samples for laboratory analysis for three sites: 13 samples from a former electronic manufacturing site, 59 samples from a major railroad maintenance yard and 13 samples from a former junk yard that has been redeveloped for residential use. The XRF was used as a survey/screening instrument and as a replacement for laboratory analysis in situations where laboratory accuracy was not needed and/or time was a critical factor. The procedure used when screening soil samples was to combine 5 grab samples in a sealed polyethylene bag and shake for at least one minute. The XRF unit was then placed on the bag in three locations to generate three individual contaminant concentrations that were then used to develop an average concentration for the bag/sampling grid. A sub-sample of this bag was subsequently obtained and analyzed at a laboratory using standard Inductively Coupled Plasma (ICP) and/or Atomic Absorption (AA) Spectrometry procedures. A second analysis/preparation technique was used to generate data with better accuracy than that obtained in the screening mode. The preparation of these samples consisted of grinding and sieving the samples to ensure a uniform particle size and to attempt to homogenize the sample prior to its analysis. In addition, these samples were placed in analysis cups developed and obtained from Niton Corp. The accuracy of the unit when used for lead contamination has been excellent. The accuracy when assessing arsenic contamination was found to be variable depending on the lead concentration and the mode in which the unit was used. The best results were achieved when the soil samples were prepared prior to their XRF analysis.

Characterization or Identification of Organic Compounds by Ion Composition Elucidation (ICE) Using Gas Chromatography/High Resolution Mass Spectrometry

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Only a small fraction of the compounds found in contaminated sites and water supplies is found in mass spectral libraries or has known toxicological effects. The EPA lists 2800 high production volume chemicals. These compounds, byproducts, and degradation products might be found in drinking water sources, air, and contaminated sites. Identification of these compounds is necessary to assess risk to humans and aquatic ecosystems. Hence, there is a need for more powerful analytical techniques to identify such compounds. To limit tedious pre-analysis fractionations, compound identification techniques must isolate signals from low-level contaminants in complex mixtures. Excellent component separation is realized by high resolution gas chromatography (separation in time) coupled to high resolution mass spectrometry (selection by exact mass).

Ion Composition Elucidation (ICE) employs a software adaptation for double focusing mass spectrometers to measure the exact masses and relative abundances of the mass peak profiles of monoisotopic ions and the profiles higher in mass by 1 and 2 amu that arise from heavier isotopes such as ^{13}C, ^{15}N, ^{18}O, and ^{34}S. Three measured exact masses and two relative abundances are entered into a Profile Generation Model to provide the composition of the molecular ion or fragment ion. Tables of ion compositions limit the number of possible compounds that could produce the mass spectrum and make feasible library searches of chemical and commercial literature to reach tentative identifications. If a standard can be obtained, the tentative identification can be confirmed. If not, the compound can be tracked to its source using the compound's retention time and ion compositions, which provide greater specificity than a low resolution mass spectrum.

Two applications of ICE will be discussed: identification of isomeric compounds found in a municipal well that served Toms River, NJ, and characterization of two families of compounds found in Superfund sites □ one chemical byproducts and one of microbial origin.

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Molecular Characterization of Anthropogenic PAHs in Sediments of the Thea Foss/Wheeler Osgood Waterways, Tacoma, Washington

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The character of anthropogenic polycyclic aromatic hydrocarbons (PAHs) in surface and near-surface sediments of the Thea Foss and Wheeler-Osgood Waterways in Tacoma, Washington, were investigated with the objective of determining the general source(s). Our investigation differed from previous studies that had focused on the remediation needs of the Waterways. In this study, 42 sediment samples from the Waterways were collected and analyzed for their (1) concentration of 43 individual or groups of PAH, (2) total extractable hydrocarbon "fingerprint" and concentration, (3) grain size and (4) total organic carbon content. Analysis of the sediment data, including comparisons to standard reference materials, indicated that all but two samples contained PAH derived from a *pyrogenic* source(s), i.e., a non-petroleum source(s). The high concentrations and characteristic distributions of PAH in some sediment samples were consistent with the occurrence of coal-derived liquid(s), particularly in some sediments proximal to the historic coal gasification operations near the head of the Thea Foss Waterway. Most sediment samples throughout the Waterways contained PAH distributions attributable to varying degrees of weathering and/or mixing of *pyrogenic* source material(s), e.g., urban run-off, coal-derived liquids, or pitch. Two sediment samples clearly containing PAH derived from *petrogenic* sources, i.e., petroleum-derived sources, were found near the head of the Thea Foss Waterway. It was apparent that the PAH in sediments throughout the Thea Foss and Wheeler-Osgood Waterways were overwhelmingly derived from *pyrogenic* sources, which may be, in part, attributable to historic coal gasification operations. It is reasonable that decades of sediment re-distribution and past dredging activities within the Waterways have contributed to the spreading and mixing of this contamination with other persistent *pyrogenic* sources, e.g., urban run-off.

Molecular Changes During Petroleum Combustion

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This presentation discusses issues that may be significant for environmental forensic investigators, risk assessors, and regulators that practice in the area of petroleum fire incidents. Uncontrolled petroleum fires originating from crude oil releases, vehicular accidents and fire training activities chemically alter the composition of petroleum fuel in several ways. The combusted fuel products pass into the air as gases and PAH enriched soot. Residual fuel frequently retains some of the characteristics of the original petroleum product even when more than 90% of the petroleum is combusted. The data in this presentation can help assess the potential environmental effects of petroleum residuals at fire incident sites

Studies of petroleum distillates with little to no 4 to 6 ring PAH were tested for PAH alteration when ignited and compared to similar levels of evaporative alteration. In this study, kerosene and diesel reference samples were independently weathered to approximately 50% and more than 90% by mass using evaporation and combustion. These reference samples were compared to field samples that contained severely degraded petroleum of unknown origin. The environmental forensic methods used for this study focused on petrogenic volatiles (paraffins, isoparaffins, aromatics, naphthenes, olefins) and semivolatiles (alkylated PAH, alkanes, alkylcyclohexanes, sesquiterpanes, triterpanes, steranes). The interpretive techniques included chemical fingerprinting and principal components analysis (PCA).

Sourcing PAH in Sediments with Innovative Methodologies

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Distinguishing the origin of pyrogenic PAH from multiple sources in sediment presents numerous technical challenges. Generally, the chemical signatures of natural, point and non-point PAH sources are potentially very similar. The effects of environmental weathering and matrix interferences in environmental media often confound the signature of various proximate sources. Consequently, multiple lines of environmental forensic evidence and the creative use of alternative measurement techniques are required to isolate an individual PAH source among others.

Several emerging environmental forensic methodologies have been reviewed and tested for identifying the sources of pyrogenic materials in the environment generated by the manufacture of gas, coke, and tar products in the presence of urban background. The demonstrated effectiveness of these methods in sediment samples offers similar opportunities for source identification projects involving surface and subsurface soils in the future. The analytical methods tested include alkylated PAHs (GC/MS), biomarkers (GC/MS), organic petrology, compound-specific isotope ratio mass spectrometry (GC/IRMS) and Fourier transformed ion cyclotron resonance mass spectroscopy (FTICRMS). The interpretive techniques include chemical fingerprinting, principal components analysis (PCA), diagnostic ratios, organic petrography and fragmentation analysis.

Distribution and Mobility of Lead Contamination in Soils of Florida Shooting Ranges

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Lead is ranked as the No.2 priority hazardous substance on the Agency for Toxic Substances and Disease Registry and the U.S. Environmental Protection Agency (USEPA) priority list of hazardous substances. Lead contamination in soils of several outdoor shooting ranges (rifle, pistol and shotgun) from the use of lead shot/bullets was evaluated by collecting grid soil samples and analyzing total-recoverable (EPA Method 3051a) and Toxicity Characteristics Leaching Procedure (TCLP) Pb in these soils. Preliminary results indicated that high concentrations of Pb were generally present and the soil leached more lead than what is acceptable by the Resource Conservation and Recovery Act (RCRA) and would be characterized as hazardous wastes. The highest Pb contamination (total Pb = 95,388 ppm) was detected in the backstop berm of a 50-yard pistol range that has been in operation for over 30 years. Elevated Pb levels were also determined in plant and surface water samples at those ranges. Sequential fractionation and X-ray diffraction analyses revealed that hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) was the primary crystal Pb mineral existed in lead contaminated soils at most shooting ranges. Lead phosphate was formed in the soil of a shooting range with high concentration of phosphorous. Soil pH and organic matter are two most important factors affecting Pb weathering and transformation. Lead did not migrate downward until being solubilized with organic matter at alkaline conditions. Site-specific distribution and mobility of soil Pb contamination in different shooting ranges indicates a best management practices (BMPs) program needs to be developed, which is critical in assessing potential remedial alternatives.

REMEDIATION - GROUNDWATER

Electrolytic Aeration of Anoxic Groundwater- A Lab Scale Study and Modeling of the Process

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Evaluation of Aerobic Degradation of Pentachlorophenol in Groundwater Using ORC™

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Scott J. MacEwen, CH2M HILL, Herndon, VA
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Eleven Years of Permeable Reactive Barrier (PRB) Technology for the Remediation of VOC Contaminated Groundwater

Stephanie O'Hannesin, EnviroMetal Technologies, Inc., Waterloo, ON, Canada

Containing the Blob: Treatment of Groundwater Contaminated with Coal Tar, Naphthalene, Methyl Naphthalene, Benzene and other Associated Contaminants

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Optimization of Air Sparge/Soil Vapor Extraction Treatment System - Proven Practical Measures

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Evaluating the Success of Groundwater and Soil Cleanup at Sites Impacted by Fuel Oxygenates

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Electrolytic Aeration of Anoxic Groundwater- A Lab Scale Study and Modeling of the Process

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Bioremediation is at the foremost of a larger group of innovative remediation technologies being applied at hazardous waste sites worldwide. During its application, this process may require the addition of nutrients and/or electron acceptors to stimulate appropriate biological activity. For aerobic degradation, oxygen must be available for indigenous microorganisms as a terminal electron acceptor. The most common means of increasing the dissolved oxygen content of groundwater used *in situ* bioremediation are injection of air, liquid air and hydrogen peroxide. The research investigates the electrolytic method of aerating anoxic groundwater to enhance *in situ* bioremediation by indigenous microbes. Experiments were performed in 7.25 ft x 2.75ft wide x 1.75 ft deep horse feeding toughs. The soil used in this study was collected from one of the South Carolina Electric and Gas Company's gas filling stations, which was reported to be contaminated with PAH's and had high amounts of ferrous iron. In lab experiments, tap water was used and sodium sulfite was used to deoxygenate water to create anoxic environment in the tanks. Doses of sodium sulfite used were in excess to those obtained by stochiometry required to react with dissolved oxygen. Experiments were also performed with oxygen releasing compounds (ORC), a commercially available technology for aerating anoxic groundwater. This was done to compare results with electrolytic aeration technique and to check the viability of electrolytic aeration. The results obtained so far show that electrolytic aeration of groundwater with 100 mA electric current is possible and the method is very much competitive with ORC technology. Dissolved oxygen level as high as 2-3 mg/l were obtained in the well located 2-3 feet downstream of oxygen producing well. In on going study, we are in the process of developing a numerical, which will predict oxygen transport under the conditions used during actual lab scale experiments. Based on the experimental setup, a two-dimensional mathematical model will be developed to simulate and evaluate oxygen generation in the tanks. The physical parameters required for the model were measured in situ. The first-order rate constants describing the consumption of sodium sulfite and oxygen generation were obtained by fitting the model to the tank data. With these parameters, the model will be subsequently used to predict the performance of electrolytic cell in contributing to DO levels downstream of electrolytic probe well.

Evaluation of Aerobic Degradation of Pentachlorophenol in Groundwater Using ORC^{TM}

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A pilot study using Oxygen Releasing Compound (ORC^{TM}) has been recently completed to evaluate its effects on pentachlorophenol (PCP) in groundwater at a CERCLA facility in Virginia Beach, Virginia. The site is a former PCP wood treatment dip tank at a military installation where past operations resulted in releases of PCP and diesel fuel to the surrounding soil and water table aquifer. The study was conducted over a period of seventeen months, which included the installation of groundwater monitoring wells, collection of baseline groundwater samples, injection of ORC^{TM} slurry into the surficial aquifer, and post-injection groundwater monitoring. Approximately 1,400 pounds of ORC^{TM} were injected into the groundwater over the 750 square foot area where the dip tank was formerly located. The injection was completed using direct-push (Geoprobe®) methods and included the entire 17 foot interval (6 to 23 feet bgs) within the surficial aquifer. The contaminated soil above the water table had been excavated prior to the pilot test. Groundwater monitoring was performed at up-gradient, injection area, and down-gradient monitoring wells at six periodic intervals for fifteen months after the injection. Monitoring parameters included semivolatile organic compounds, metals, ferrous iron, chloride, carbon dioxide, and alkalinity, in addition to standard field parameters. Results of groundwater monitoring show an average PCP degradation of 92% in the four monitoring wells that demonstrated the highest initial concentrations. Remaining maximum concentrations of PCP are approximately 100 mg/L and minimum concentrations are at or below the laboratory detection limit of approximately 20 mg/L. PCP concentrations in these wells continue to decline with each round, and dissolved oxygen concentrations in these same monitoring wells remain elevated over baseline conditions by an average of 216%, after 15 months of monitoring. Therefore, the ORC^{TM} appears to be further degrading PCP at the completion of the pilot study.

Eleven Years of Permeable Reactive Barrier (PRB) Technology for the Remediation of VOC Contaminated Groundwater

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In the eleven years since the initial research-scale granular iron permeable reactive barrier (PRB) was installed to remediate volatile organic compounds (VOCs) in groundwater, the technology has been applied around the globe, with installations in North America, Europe, Australia and Japan. In varying geologies and geochemical conditions, the technology has proven to be very robust. To date, no site has required rehabilitation, confirming that PRB technologies represent a predictable, long-term-treatment solution in most hydrogeologic environments.

The initial capital costs to install VOC PRB systems are typically equivalent to those costs associated with installing a pump-and-treat (P&T) system, and PRB technology offers significant cost savings due to the very low, long-term operating and maintenance costs. When comparing costs using a net present value analysis for the life cycle of these systems, the cost savings for these PRB systems far surpass those of P&T. Another benefit is that granular iron PRB systems completely destroy VOCs, as opposed to P&T where the contaminants are simply transferred to another medium, such as the atmosphere, or to granular activated carbon which requires further disposal or regeneration.

Over the past decade, the cost to install these PRB systems have decreased dramatically, as the costs of granular iron have been reduced by over 50% and as contractors have become more familiar with PRB installations and have developed cost effective installation methods. The influence of key design parameters such as groundwater velocity variation have been incorporated into the PRB design improving the effectiveness of the technology. PRB systems are remediating sites and bringing closure for many site owners.

Containing the Blob: Treatment of Groundwater Contaminated with Coal Tar, Naphthalene, Methyl Naphthalene, Benzene and other Associated Contaminants

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On a bank of the Thames River in London, Ontario, Canada, an 18th century coal gas generating station disposed of its coal tar in onsite pits. About a decade ago, area residents noted an oily slick (quickly dubbed "The Blob") flowing downstream of the site. It was determined that groundwater was carrying the coal tar into the river. Remedial action consisting of a clay barrier and collection trench succeeded in containing the contamination. The PRP investigated a conventional pump and treat treatment train, involving flocculation, filtration, organo-clay and carbon to capture and remove the contaminants pumped out with the groundwater. Upon further analysis, Purifics®' Photo-Cat® system, based on titanium dioxide photocatalytic technology, was chosen as the most effective and lower cost alternative. This paper will review the decision-making process involved in selecting the Photo-Cat® system, the operating and maintenance costs of the first operational year, the science behind the photocatalytic process and the Photo-Cat®'s success in destroying the contaminants.

Remediation of Perchlorate-Contaminated Groundwater and Soil at Naval Weapons Industrial Reserve Plant (NWIRP) McGregor, Texas

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Beginning in 1999, interim stabilization measures were implemented to abate offsite migration of perchlorate — a chemical that was just surfacing as an environmental pollutant with significant health implications — from NWIRP McGregor. The Navy targeted perchlorate-contaminated groundwater that was exfiltrating to surface water before migrating offsite, source area groundwater, and impacted surface soils. In three years, the Navy mitigated offsite perchlorate migration by rapidly and effectively developing perchlorate treatment technologies from conception through bench and pilot scale testing to full-scale implementation.

- The Navy installed trenches to cutoff and intercept groundwater before it surfaced via springs and seeps. The trenches also effectively served as PRBs that fostered anaerobic zones using in place natural organic media and supplemental soluble carbon sources. Perchlorate concentrations in groundwater were biologically reduced from 20 to <0.004 mg/L using in situ techniques.

- Ex situ treatment systems, including static- and fluidized-bed bioreactors as well as an ion exchange unit, have also been used effectively to address contaminated water pumped from the collection trenches. Effluent concentrations have routinely been below detection limits.

- The Navy developed engineered and in situ anaerobic soil treatment systems, which biologically reduced perchlorate concentrations from 1,800 mg/kg to below detection limits. The in situ soil units also allow amendment-rich water to infiltrate to address source area groundwater and provide polishing for ex situ treatment systems.

- Because of site hydrogeology and seep concerns, the Navy also installed 200 amendment-filled bioborings to *passively* address offsite groundwater contamination in situ. Perchlorate concentrations have been reduced by an order of magnitude in the study area.

- Next generation PRBs were installed in July 2002 to treat perchlorate- and VOC-contaminated groundwater. The PRBs included a variety of organic media as well as a multi-purpose piping system to inject/infiltrate additional soluble amendments over time.

The precedent-setting remediation effort at NWIRP McGregor has received regional and national recognition for its environmental achievement.

Optimization of Air Sparge/Soil Vapor Extraction Treatment System - Proven Practical Measures

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This paper describes the optimization measures that ENSR implemented at an air sparging/soil vapor extraction (AS/SVE) system. In 1998, ENSR designed, installed and operated an AS/SVE system at a former industrial site in Massachusetts to remediate dissolved toluene in groundwater. The original system consisted of 100 driven sparge points and 40 SVE wells over 1.5 acres. Significant mass removal of toluene (> 6,000 lbs.) was achieved within the first year of operation, and a large portion of the site was remediated to below the groundwater standard. However, groundwater in one area of the site was not being remediated, some critical AS points were not working effectively, and field staff experienced difficulties in collecting O&M measurements. ENSR evaluated the original system design, and implemented the following practical measures to optimize system operation:

- Replacement of driven sparge points with augered wells with a sand pack,
- Replacement of the sparge screen placement in the zone of contamination (not below it), establishing horizontal air flow through more permeable layers,
- Refinement of instruments and sampling ports to allow easier, more consistent measurement of system operation by field staff, and
- Down-sizing and reconfiguring the treatment system to target the area still needing remediation.

System improvements were implemented in 2000 and 2001. A significant increase in mass removal was observed following each phase of optimization. Remediation after optimization was achieved with reduced O&M and lower operating costs. Only one well at the site remains above the groundwater standard. The demonstrated improvements that ENSR implemented at this site are now used at other AS/SVE treatment systems.

Evaluating the Success of Groundwater and Soil Cleanup at Sites Impacted by Fuel Oxygenates

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Fuel oxygenates are added to gasoline to increase combustion efficiency and to reduce air pollution in order to meet the requirements of the 1990 Clean Air Act Amendments. The most commonly used oxygenate is methyl *tert*-butyl ether (MTBE). In the United States, the use of MTBE as a gasoline additive started in the late 1970s. Over the past decades, MTBE use has increased significantly. As a result of its widespread usage, reports of environmental contamination by MTBE in the vicinity of Leaking Underground Storage Tanks (LUST) and dispensing equipment have increased as well. Because of its specific physical and chemical properties, MTBE is highly soluble in water, does not strongly sorb to soil particles and strongly partitions into the aqueous phase. As a consequence, MTBE tends to be highly mobile in subsurface environments relative to other gasoline constituents and can potentially migrate at groundwater velocities. Recent reports of MTBE detection in drinking water wells have led environmental managers and regulators to reassess cleanup strategies at MTBE-impacted sites. Concerns have mostly focused on the feasibility of removing MTBE from contaminated groundwater in a cost-effective manner. This work will include a review of the fate and transport of MTBE following accidental releases of MTBE-blended gasoline with an emphasis on the relevance of these fate and transport characteristics on the appropriate strategy to select for cleanup. State of the art information regarding groundwater and soil cleanup at MTBE-impacted sites will be evaluated using recent successful case studies. A short description of the technology used at the site, discussions of the effects of contaminant and site characteristics, evaluation of the technology success and limitations will be presented for each case study. Finally, general cleanup cost estimates will be discussed in an effort to illustrate how the presence of MTBE impacts the costs of remediating gasoline-impacted sites.

ARSENIC

Natural and Anrthropogenic "Background" Levels of Arsenic in Florida's Soils

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Naturally Occurring Arsenic in Overburden in Central Massachusetts

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Bench-scale Evaluation of Sorbents for *In-Situ* Treatment of Groundwater Arsenic

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Elevated Arsenic and Iron in Groundwater at a Gravel Pit Reclamation Project using Manufactured Topsoil

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Arsenic in Landfill Environmentals, Massachusetts, USA

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Arsenic Geochemistry: Ponding, Slime, Iron and Elevated Arsenic in Groundwater

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Natural and Arthropogenic "Background" Levels of Arsenic in Florida's Soils

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Arsenic is a Class A human carcinogen and is a public concern due to its widespread usage in both agriculture and industry. Background concentrations of arsenic in soils are essential for establishing soil cleanup goals. The current Florida Department of Environmental Protection regulatory standards for arsenic contamination in soils, regardless of the taxonomic, geographical differences and land uses, cannot provide an adequate assessment in soil arsenic contamination. This presentation addresses issues related to the determination (sample collection, analyses and data analyses) and interpretation (geometric mean, upper confidence limit of the mean, nth percentile of the data) of natural and arthropogenic sources of arsenic and the definition of arsenic "background" levels in soils. Standardization of soil collection, sample digestion, laboratory and data analytical procedures, and a good quality assurance plan will reduce variability in arsenic determination. Our study indicates concentrations of total Fe and P are two most important soil properties that influence arsenic background levels in near pristine soils. Wet soil suborders in south Florida have naturally high arsenic background concentrations. This was also reflected in the athrogenic background levels of arsenic in urban soils. Arsenic release from bedrock and arsenic bioaccumulation by aquatic organisms are possible explanations for relatively high arsenic in those wet soils. Baseline soil concentration, which is defined as 95% of the expected range of the background arsenic concentrations in different soil categories, is necessary for properly assessing potential arsenic contamination.

Naturally Occurring Arsenic in Overburden in Central Massachusetts

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The Presence of elevated levels of arsenic in a zone that traverses N-S across Central Massachusetts had been periodically noted and reported, however, without a specific reference to neither the origin of arsenic nor the arsenic sources. Suspected sources included past applications of lead arsenate in orchards as a control for coddling moth, industrial applications in metal and leather processing facilities, and/or from natural sources. An accumulated set of data in the archives of state environmental agencies provides a confirmation of the widespread reports of arsenic levels that are well above the regulatory “background” levels (17 ppm) in overburden. We report arsenic data that (1) were compiled from selected sites listed with the Massachusetts Bureau of Hazardous Waste within this region; and (2) data obtained by this study on samples of overburden obtained from drilled profiles at randomly selected sites. The compiled data are for sites within a corridor along the NNE-SSW trending tract that passes through the geographic center of the state. Both data sets have similar arsenic frequency distribution curves (histograms) with identifiable two frequency subsets: 20 to 50 ppm and 50 to 800 ppm. Comparison with distribution curves for lead proves that there is no connection between lead and arsenic therefore suggesting that lead arsenate is not the arsenic source. Microprobe analysis of sulfides from bedrock samples confirms the presence of pyrites (FeS_2) and cobaltites ($CoAsS$) in the underlying bedrock formations. Elevated arsenic occurrences within the overburden of Central Massachusetts is best explained by the derivation of the overburden from local bedrock formations and by the occasional incorporation of sulfides into the overburden which may account for the observed arsenic “hot” spots. The Central Massachusetts “arsenic province” is part of a larger lithotectonic zone as previously reported by Ayotte and others (1999-WRIR 99-4162).

Bench-scale Evaluation of Sorbents for *In-Situ* Treatment of Groundwater Arsenic

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Elevated arsenic concentrations in groundwater, whether the result of natural or anthropogenic influences, represent a human health risk. Over the last decade, with activities ranging from documenting health effects in Bangladesh to revision of international drinking water guidelines, there has been an increased focus on the effects of exposure to high arsenic concentrations in groundwater. In the United States this focus culminated in the recent adoption of a more stringent drinking water standard, lowering the arsenic Maximum Contaminant Level (MCL) from 50 ppb to 10 ppb. Research on innovative treatment technologies to meet the new standards has been conducted in parallel with the health investigations. The Navy has identified arsenic contaminated groundwater In its environmental studies which are conducted prior to the transfer of surplus facilities to local communities. The Navy has a vested interest in identifying treatment technologies that can be shown to operate properly and successfully (OPS) in-situ and in a passive mode. Tetra Tech NUS identified three sorptive media that promised to meet the Navy's requirements. The ability of the three media, an iron-modified zeolite, a surfactant-modified zeolite and activated alumina, to sorb dissolved arsenic from site groundwater was evaluated in batch tests. Two of the sorbents, iron-modified zeolite and activated alumina, were tested further in column tests with synthetic groundwater and influent arsenic concentrations (350 – 450 μg As/L) similar to those observed at the site. Column breakthrough was defined when the effluent arsenic concentration was ≥ 5 μg/L. The results of the tests indicated that activated alumina was capable of extracting dissolved arsenic under simulated in-situ conditions. Based on the column test results, the activated alumina treated >3900 bed volumes prior to breakthrough. The sorption capacity of the activated alumina was >2500 μg arsenic/g of sorbent. Based on these results, the Navy is proceeding with a pilot scale field implementation of activated alumina in a permeable reactive barrier.

Elevated Arsenic and Iron in Groundwater at a Gravel Pit Reclamation Project Using Manufactured Topsoil

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State regulations require gravel pit owners to minimize the area open for aggregate mining. To reclaim gravel pits, soil suitable to establish a vegetative cover is occasionally obtained from nearby agricultural land. Thus, reclamation activities may inadvertently create additional erosion and sediment control problems. In an effort to reduce topsoil mining, some reclamation projects use treated sewage sludge in-lieu of natural topsoil. In this investigation, six acres of an active gravel pit was reclaimed using a mixture of short paper fiber derived from a newsprint pulp and paper mill and commercial fertilizer. To reduce nitrogen leaching to groundwater the manufactured topsoil was blended to achieve a carbon to nitrogen ratio (C:N) equal to 30:1. The established groundwater monitoring well network consists of four monitoring wells: one upgradient and three downgradient of the reclamation area. The database consists of one round collected before reclamation and six rounds post reclamation.

Groundwater data from the downgradient monitoring wells revealed significant impacts from reclamation activities relative to the upgradient well. Organic carbon leached from the manufactured topsoil quickly depleted dissolved oxygen concentrations in groundwater beneath and downgradient of the reclaimed area. There has also been a steady increase in calcium, magnesium, and alkalinity in downgradient wells. Since the rapid depletion of oxygen, two redox sensitive parameters: iron and arsenic, have increased significantly. The reduced forms of iron and arsenic are generally more soluble than the oxidized forms. Therefore, the development of anaerobic conditions will increase the solubility of both iron and arsenic and may have released these parameters from the aquifer matrix. Neither the short paper fiber nor the fertilizer contained much arsenic; therefore, it’s likely the iron and arsenic are released from the aquifer matrix.

Arsenic in Landfill Environments, Massachusetts, USA

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Solid-waste landfills can modify the oxidation-reduction potential (ORP) of underlying groundwater, thereby influencing solubilities of redox-sensitive species. Elevated aqueous concentrations of Fe, Mn, and As have been observed at many landfill sites, but sources are a subject of conjecture. Arsenic may be associated with landfill waste; alternatively, its presence may be from natural sources. Reductive dissolution of hydrous ferric oxide (HFO) coatings on aquifer materials is a common mechanism by which sorbed constituents, particularly arsenic, are released to groundwater.

Overburden, bedrock, and groundwater samples were collected upgradient and downgradient of four landfills in central Massachusetts. The overburden at these sites consists primarily of glaciolacustrine sediments. Bedrock lithology comprises metasedimentary rocks of the mid-Paleozoic Merrimack belt. Groundwater downgradient of the landfills is characterized by low ORP and relatively high levels of arsenic, typically 0.05 to 0.5 mg/L. Elevated arsenic is associated with high Fe and Mn. Fe and As concentrations are broadly correlated, suggesting that both are mobilized by the same process. In contrast, at two landfill sites in southeastern Massachusetts, downgradient groundwater is characterized by low ORP, but concentrations of iron and arsenic are low. Bedrock is distinctly different, consisting of Precambrian granites, and overlying glacial deposits are characteristically lower in iron and arsenic as compared to overburden in the central Massachusetts region.

Landfill leachates high in dissolved arsenic appear to be the unfavorable result of a combination of factors: location within or proximal to bedrock containing arsenic-bearing mineralogies; glacial transport of bedrock minerals; post-glacial chemical alteration and redistribution of iron and arsenic; sorption of arsenic by HFO surfaces; landfill-induced lowering of groundwater ORP; and dissolution of HFO and re-mobilization of arsenic.

Arsenic Geochemistry: Ponding, Slime, Iron, and Elevated Arsenic In Groundwater

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This presentation will use a case study to discuss and illustrate the biological mediation of arsenic concentrations in groundwater.

A company had satisfied its RCRA permitting obligations for a closed Hazardous Waste Management Unit - assessing the unit following cleanup, characterizing the hydrogeology of the site, and monitoring the groundwater for many years. When it came time to end the monitoring, having observed non-detectable levels of chemicals listed on it RCRA permit for three years in succession, the State balked, pointing to elevated arsenic levels in several of the wells. Although arsenic was never a notable or significant constituent in the manufacturing process, was not elevated in wastes associated with the site, nor listed in the permit, the State, approximately 18 years after closure of the unit, sought to re-write the permit to include arsenic and retain the closed unit in its program, thus requiring many more years of monitoring and associated costs.

A coherent, thorough evaluation of site characteristics, including, aerial photography, waste testing, numerous groundwater measurements, field notes, soil metals, background metals, and agriculture activity in surrounding properties was performed. The elevated arsenic concentrations (100-200 μg/L) were shown to be unrelated to the manufacturing facility or its wastes. The high arsenic levels resulted from the biogeochemistry of iron which controlled the arsenic concentrations in the wells. Although many on-site wells exhibited reducing conditions, only wells in areas which periodically endured surface water ponding were noted to foul sampling bailers with slimy bacteria and exhibit high iron concentrations. Only these wells with high iron concentrations exhibited elevated arsenic concentrations.

SITE ASSESSMENT - ENVIRONMENTAL FATE

Innovative Methods to Identify, Map and Plot Historic Areas of Environmental Concern for the Purpose of Developing Accurate Sampling Plans

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Natural Attenuation Rate Clarifications: The Devil's in the Details

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Innovative Methods to Identify, Map and Plot Historic Areas of Environmental Concern for the Purpose of Developing Accurate Sampling Plans

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Various methods have traditionally been used by environmental regulators and consultants to identify and locate historic areas of environmental concern (AOCs). These methods have included reviews of: historic aerial photographs, Sanborn and other fire insurance maps, industrial directories, title and deed records, tax maps, and facility records among other sources. On site geophysical surveys using equipment such as ground penetrating radar (GPR) have also been used. Recent developments in the fields of geographic information systems (GIS) using digital satellite imagery, autocad, and global positioning system (GPS) location mapping using satellite uplinks, when used together and in combination with the traditional methods, have made it possible to identify and located historic AOCs with sub-meter accuracy.

By combining and applying these methods, sampling plans can be developed that allow for the accurate investigation of potential contamination emanating from these AOCs even though there is currently no physical, surface grade evidence of their former locations.

In the project discussed in this paper, historic topographic maps and site plans were available and were analyzed to ascertain the exact location of each AOC with respect to fixed referenced points that were present historically and that currently exist. The AOC locations were identified in the field by a New Jersey licensed land surveyor who, using state of the art GPS equipment, navigated to, and provided coordinates for, each AOC location using the fixed reference points. The AOC coordinates were down loaded into an Autocad system that plotted coordinates and elevations on a current topographic site plan. Accordingly, each sample location proposed in the Site Investigation Work Plan (SIWP) was identified by northing, easting, and elevation coordinates.

Alternatives to NAPL Thickness Measurements for NAPL Characterization

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NAPL thickness measurements in monitoring wells are often used to characterize the extent of NAPL releases. Measured product thickness is frequently used to estimate the thickness of a “floating” NAPL layer. The presence of more than ½-inch of NAPL in a monitoring well triggers a reporting condition in Massachusetts. Additionally, Massachusetts has a minimum cleanup standard (Upper Concentration Limit) of ½-inch of NAPL “in the soil column”. However, the real meaning and value of NAPL thickness measurements is unclear.

Long-term product thickness measurements were available for a release at a fuel storage terminal near Boston, MA. Maximum product thickness measurements in one area of the site exceeded six-inches. However, on many occasions no NAPL was detected in the any of the monitoring wells within the plume; i.e. a “false negative” condition.

In-situ oxidation was chosen as the remedial option for the NAPL. A reliable estimate of the quantity of NAPL in the plume was needed to evaluate the quantity of hydrogen peroxide needed for the remediation. NAPL thickness measurements were deemed insufficient to allow an estimate of the NAPL volume. Additional characterization was performed to determine the vertical and horizontal extent of contamination, and to estimate the mass of NAPL in the plume.

Continuous soil sampling was performed through the NAPL “smear zone”. Field screening was used to select samples for analysis. All samples in the smear zone were analyzed for total petroleum hydrocarbons. A calculation of the total mass per unit area at each soil boring was performed using the TPH data and assumed values of porosity and specific gravity of solids. Total mass within the plume was then calculated by contouring the mass per unit area data. Mass per unit area data was converted to an “equivalent product thickness” for comparison to the measured product thickness data.

Natural Attenuation of a Co-contaminated Solvent-Metal Plume

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A natural attenuation evaluation was performed for two groundwater plumes at the Naval Air Station (NAS) in Pensacola, Florida. The primary constituents of concern (COCs) are tetrachloroethylene (PCE), trichloroethylene (TCE), and heavy metals. Groundwater samples were collected and analyzed for MNA (monitored natural attenuation parameters) and COCs in December 1998, May 1999, and December 2000. Chemical and geochemical data were evaluated to determine the site's MNA potential. Dissolved Oxygen (DO) and redox potential (ORP) indicated anaerobic conditions within the two plumes. Wells upgradient of the two plumes had DO greater than 1.0 mg/L. Methane and sulfide were measured at concentrations well over 1,000 µg/L in several wells. Hydrogen concentrations in these wells also indicated that sulfate-reducing and methanogenic conditions prevailed in the plumes. Chemical data collected since 1994 show that parent compounds such as PCE and TCE have decreased over time. At some locations, the decrease is greater than ninety percent. Data also shows a decrease in groundwater flow direction with wells in downgradient locations being below the MCL for these compounds. Daughter products cis-1,2-DCE and vinyl chloride have been detected in plume wells but are not accumulating in the direction of groundwater flow. Favorable geochemical conditions also appear to be have positively impacted lead and cadmium concentrations in groundwater. Concentrations of these metals have decreased dramatically since sampling first began in 1994 when they were greater than 300 µg/L. In the December 2000 sampling event, most area wells were non-detect for cadmium and lead. It appears that anaerobic conditions, the presence of sulfate, and the formation of sulfide are helping to precipitate these metals as stable sulfides, thereby immobilizing them in the aquifer. Based on the overwhelming evidence for the natural attenuation of chlorinated solvents and metals in the aquifer, MNA was recommended and has been accepted as the site remedy.

Downward Migration of LNAPL at the Hadnot Point Industrial Area, Marine Corps Base, Camp Lejeune, North Carolina

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More than a decade of study at the Hadnot Point former Fuel Farm located on the Marine Corps Base, Camp Lejeune, Jacksonville, NC had yielded what first appeared to be a contaminated project site typical of older fuel farms. Standard investigatory procedures such as installation of approximately one hundred monitoring wells, numerous direct pushes, gauging and sampling were implemented to aid in the delineation of existing free phase and dissolved phase product plumes over a period spanning twenty five years. Resultant data was compiled and used to create an interpreted aerial extent of the plume boundaries that existed at the site. It is estimated that as much as 1,100,000 gallons of gasoline may have been released over a fifty-year time span from 1941 to 1991.

A multi faceted remediation system which included air sparging, soil vapor extraction, biosparging, and free product recovery was designed and installed in 1997 to address the soil and groundwater contaminated plumes and is currently in operation today. These systems constructed at a cost of just over one million dollars, have been successful in removing in excess of 250,000 gallons of fuel in both free and volatile phase.

However, the occurrence of anomalous conditions such as free product presence in a double cased well 153 feet deep, sample results in at least six well pairs exhibiting dissolved benzene levels significantly higher in 50 feet deep double cased wells than their neighboring shallow wells at a depth of between fourteen and twenty five feet deep, and recurrence of unweathered free product in a shallow well after free product absence for ten years, resulted in the necessity of examining the root cause of these contaminant deviations at the project site.

Though it is not normally accepted that an LNAPL could vertically migrate downward below the saturated zone and subsequently reside in the deeper subsurface regions, a combination of multiple hurricanes occurring in a short period of time and aggressive pumping during drought conditions contribute to the complex subsurface conditions necessary for this phenomenon to occur. This presentation details the subsurface and environmental circumstances present at the site along with the advanced geophysical investigations conducted which explain the mechanisms at work allowing for the vertical downward migration of an LNAPL at the Hadnot Point Industrial Area.

Natural Attenuation Rate Clarifications: The Devil's in the Details

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The term "Natural Attenuation" (NA) has been defined as naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media. Monitored natural attenuation (MNA) protocols generally involve the collection of biogeochemical data from groundwater monitoring wells at sites. The data are correlated in time and space with the various chemicals of concern (COC's) to establish predominant biodegradation mechanisms. Modelers using the first-order decay expression typically use the rate coefficient as a calibration parameter and adjust it until the transport model results match field data. With this approach, uncertainties with a number of parameters (e.g., dispersion, sorption, biodegradation, etc.) are lumped together in a single calibration parameter. We examine the problems associated with the lumped parameter approach using two commonly used models, BIOSCREEN and Buscheck/Alcantar Analytical Solution in a variety of practical examples. The natural attenuation decay rate estimated using the lumped parameter approach is distinguished from a biodegradation rate established by isolating processes and examining biodegradation lines of evidence. The half-life determined from empirical data using the lumped parameter approach is often mistakenly interchanged with a biodegradation half-life when it is an all encompassing half-life based on the interaction of numerous processes. We isolate the processes as they are represented in the governing transport equation and provide a rationale approach at parameter estimation to avoid the potential pitfalls of the all-inclusive "attenuation rate". In closing, general guidelines on degradation rates and half-lives are broken into four categories-process clarification, specifics on enumeration, isolation of other processes and biodegradation lines of evidence.

SEDIMENTS III

Characterization and Mapping of Contaminated Sediments, Windermere Arm, Hamilton Harbour, Ontario, Canada

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Estimation of Sediment PCB Concentrations and Masses in a Large Water Body

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Stormwater Impact on Sediment Quality as Determined by Microbial Indicators

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A.J. Englande, Tulane University, New Orleans, LA
Reda Bakeer, Tulane University, New Orleans, LA
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Electroosmotic Dewatering of Dredged Sediments

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Assessing the Effectiveness of Sediment Remediation using Contaminant Transport Models

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Determination of the Environmental Impact of Consolidation Induced Convective Transport of Radiolabeled Contaminants through Capped Sediment Using a Research Centrifuge

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Reverse Layering for *In-Situ* Burial of Nutrient-Rich or Contaminated Sediments

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Characterization and Mapping of Contaminated Sediments, Windermere Arm, Hamilton Harbour, Ontario, Canada

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Windermere Arm is a 50-ha narrow channel located in the southeastern portion of Hamilton Harbour, which is designated by the International Joint Commission (IJC) as one of the primary Areas of Concern in the Canadian waters of the Great Lakes. Sediments within the Arm have historically been contaminated with trace metals, PAHs, and to a lesser extent, PCBs. Sedimentological, geotechnical and geochemical investigations have been undertaken to determine the degree and the spatial extent of contamination. The methodology used in sediment characterization includes acoustic bottom-classification systems, side-scan surveys, in-situ penetration tests, gravity core sampling and vibracoring. Bottom sediment types are identified by an acoustic bottom-classification system called RoxAnn^{TM}, which uses the information on sediment roughness and hardness and is then calibrated against surficial sediment texture. Disturbance of sediment due to dredging, dumping and anchor-dragging is obtained from side-scan and multibeam echosounder records. Physical properties of the sediments are determined by measurements of sediment texture, moisture content and fall-cone shear strength. Contaminant concentrations (PAHs, PCBs, trace metals) are measured at standard intervals in each core. Several contouring methods will be used to produce three-dimensional maps of sediment contamination and to calculate volumes of contaminated sediments. Information on the spatial extent of sediment contamination in the Arm will be used for the selection of the most effective remedial alternative and for identifying sources of certain contaminants. The study is funded by the Great Lakes Sustainability Fund of Environment Canada.

Estimation of Sediment PCB Concentrations and Masses in a Large Water Body

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Decision-making for contaminated sediment sites requires an accurate estimation of the horizontal and vertical extent and the magnitude of the contamination. Accurate estimations of contamination reduce uncertainty in models that simulate the fate and transport of the contaminated sediments and provide a sound basis for choosing among potential remediation and management options. Achieving accurate estimates can be more complex if the region of concern is a large water body, such as a bay. Sediment samples can be widely dispersed and sediment characteristics of large areas need to be estimated from samples that can be several kilometers distant. Results of sediment sampling in Green Bay in Wisconsin and Michigan were collected and organized. Using a geographic information system (GIS), potential interpolation methods and options were evaluated with the intent of reducing uncertainty. Then sediment parameters essential for an estimation of PCB mass were interpolated for the entire bay. Approximately 15,000 kg of PCB were estimated to reside in the sediments, with a wide range of concentrations and masses among various portions of the bay. The assumptions of this estimate are weighed against the assumptions of the authors of other, differing published estimates.

Stormwater Impact on Sediment Quality as Determined by Microbial Indicators

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This study was conducted to examine the fate of microbial indicators from stormwater runoff associated with lake sediments and stormwater suspended particles. Knowledge gained from this study can lead to better understanding of both the impact of stormwater runoff on the lake sediment environment and fate of microbial indicators in lake sediments. Results of the study indicate that a significant increase occurred in the microbial indicator titers for sediments at specific study sites following a given stormwater event. It was found that the sedimentation mechanism is linked to the increase in microbial titers in the lake sediments as stormwater microbial indicators were found to attach onto stormwater suspended particles. Thus, stormwater runoff contributes to microbial contamination and deterioration of sediment quality. At the study sites, the percentages of fecal coliform, *E. coli,* and enterococci attached to stormwater suspended particles were found to be in the range of 9.8 to 27.5 percent, 21.8 to 30.4 percent, and 8.3 to 11.5 percent of the total indicator loading, respectively. Additional sorption may have occurred to non-settleable particles which remained in the water column. Examination of the suspended particle size distribution showed that about 85 percent of the microbial indicators were attached to the suspended particles larger than 5 μm. Based on the collected data, the estimated sedimentation rate constants were calculated to be 0.0370 h^{-1} for fecal coliform, 0.0678 h^{-1} for *E. coli* and 0.0359 h^{-1} for enterococci. The elevated titers of microbial indicators in the sediment were observed to decrease with time. However, a slower rate reduction of microbial indicators in sediment further suggested that bottom sediment may act as a reservoir for prolonging microbial survival and adds concerns of recontamination of overlying waters due to potential sandy solids resuspension.

Electroosmotic Dewatering of Dredged Sediments

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Dredged sediments generally possess very high moisture content and very low hydraulic conductivity. As a result, disposal of these sediments in confined disposal facilities (CDFs) is implemented in stages. A layer of sediment is placed and enough time is then allowed for the dewatering and consolidation of sediments to occur. Innovative methods are sought to accelerate dewatering that allow rapid disposal of sediments in CDFs. Common dewatering techniques such as the use of pumps, drains or chemical additives are often ineffective and/or expensive for the low permeability sediments. Electroosmotic dewatering has great potential to accelerate dewatering in sediments. This study investigated the feasibility of using electroosmosis to dewater dredged sediment obtained from Ispat-Inland site. Bench-scale experiments were conducted using the sediment under the application of a low electric potential as well as under gravity drainage alone. The results showed that an order of magnitude increase in dewatering and consolidation of the sediment occurred under the application of electric potential as compared to the gravity drainage alone. Various factors that require attention during the field implementation of electroosmotic dewatering, such as power consumption, electrode types, outflow quality and management, and quality of dewatered sediment solids, are discussed.

Assessing the Effectiveness of Sediment Remediation using Contaminant Transport Models

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Contaminant fate and transport models are critical components of the decision-making process for large-scale contaminated sediment sites. Models synthesize data on system characteristics with data on system forcing functions to simulate future conditions as a function of key stressors and external perturbations. Fate and transport models can simulate exposure concentrations in the bioavailable zone, including the water column and surface sediment concentrations that drive human health and ecological risks. Exposure concentrations simulated by fate and transport models serve as inputs to bioaccumulation models and human-health risk assessment models. This suite of models provides a quantitative basis to compare sediment management options and evaluate the risk reduction they can achieve over time. Management options include active remediation such as capping and dredging, and also natural attenuation. The reality of long implementation schedules, contaminant releases during dredging, and residual concentrations require consideration in the evaluation of remediation effectiveness relative to natural attenuation. This paper presents modeling methods for simulating active remediation and approaches for assessing the relative effectiveness of remediation given uncertainty in model parameterization. Case study examples from large-scale contaminated sediment sites will be presented that demonstrate the necessity of selecting a basis for comparison of remedial alternatives that is consistent with risk-based remediation goals and realistic implementation conditions. Results of modeling evaluations of the Fox River in Wisconsin will be presented. These results show that an assessment of remediation effectiveness is very sensitive to the representation of remediation schedule, releases during dredging, and residual surface sediment concentrations in the model application. Depending on the assumptions used for releases and residuals, model results show that active remediation by dredging may even increase risks in the short and long-term relative to natural attenuation.

Determination of the Environmental Impact of Consolidation Induced Convective Transport of Radiolabeled Contaminants Through Capped Sediment Using a Research Centrifuge

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The presence of contaminated sediment poses a barrier to essential waterway maintenance and construction in many ports and harbors, which support 95% of U.S. foreign trade. Cost effective solutions to remediate contaminated sediments in waterways need to be applied. Capping is the least expensive remediation alternative available for marine sediments that is unsuitable for open water disposal. Dredged material capping and in situ capping alternatives, however, are not widely used because regulatory agencies are concerned about the potential for contaminant migration through the caps. Numerous studies have been conducted on the effects of diffusion through caps, however, there is a lack of experimental data documenting the effects of consolidation induced transport of contaminants through caps.

This study examines consolidation induced convective contaminant transport in capped sediment utilizing a research centrifuge. Centrifuge modeling simulates the increase the gravitational acceleration (g) of a prototype which is N times larger than the model, where N is gravitational acceleration factor. For contaminant migration, the time of travel in the model is inversely proportional to the square of the acceleration factor in the prototype. In this study, consolidation induced convective transport was modeled for 7 hours at 100-g, which modeled a contaminant migration time of 8 years for a prototype that was 100 times larger than the centrifuge model. In this study, hydrodynamic dispersion was a function of the seepage velocity. Thus, advection and dispersion dominated the migration of contaminants. The centrifuge modeling results were compared to an analytical solution for advection and dispersion.

Reverse Layering for *In-Situ* Burial of Nutrient-Rich or Contaminated Sediments

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The novel process of "reverse layering" involves mining sand deposits beneath nutrient-rich or contaminated lake bottom sediments, allowing the bottom to subside and then placing the clean sands on top to bury the sediments *in-situ*. The process offers an alternative to current dig, haul, and disposal practices when hazardous materials risk factors are judged to be acceptable. The Red Lily Pond Restoration Project, being conducted under a state S319 Watershed Nonpoint Source Pollution Grant to the Town of Barnstable, Cape Cod, Massachusetts, uses "reverse layering" to mine clean, medium glacial sands from beneath the lake bottom, transport the sand on top of anaerobic nutrient-rich organic sediments, creating a barrier which suppresses plant re-growth. To initially deepen the lake, a certain volume of the clean glacial sands (6,000 cy) was diverted to a parking lot for resurfacing. A specially-constructed barge with A-frame supports at both ends allows intermittent removal of deeper sand and application through sand "sprinklers" to complete burial. Over 12 inches (.3m) of clean sand is being applied to bury the obnoxious sediments. Special minicoring procedures were developed to check evenness of sand distribution. The process requires Army Corps, State Wetlands, Chapter 91, and local conservation commission approval. The demonstration project involves the lower basin of a 13-acre pond, containing 2-5 meters' thick sediments, which is underlain by 200 ft. of glacial sands.

RISK ASSESSMENT

Differences in the Dermal Bioavailability of Toluene and Phenol Aged in Soil

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Oral Bioaccessibility of Dioxins/Furans at Low Concentrations (50-350 ppt TEQ) in Soil

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Volatile Air Emissions from Soil or Groundwater - Are They as Significant as Models Say They Are?

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Groundwater to indoor Air - The Exposure Pathway of the Future

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The Assessment of Toxicity and Biodegradability of New Energetic Ingredient Hexanitrohexaazaisowurtzitane (CL-20) in Soil

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Risk Assessment Applications in Atypical Circumstances

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Communicating Risk to Diverse Stakeholders: A European Case Study

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Differences in the Dermal Bioavailability of Toluene and Phenol Aged in Soil

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When organic chemicals age in soil, they become more sequestered with time and less bioavailable. The dermal bioavailabilities of toluene and phenol aged for 3 months in two soils (Atsion and Keyport) were compared to the bioavailabilities of the chemicals without soil (pure chemicals), and freshly spiked in soil. *In vitro* flow-through diffusion cell methodology measured the amount of radioactive chemical which penetrated dermatomed male pig skin into receptor fluid and which became bound to skin following soap and water decontamination, as well as the volatility of the chemicals. Although the majority of pure toluene was volatilized (88% of initial dose), 9% of the remaining dose penetrated skin. Because the volatility of pure phenol (39% of initial dose) was less than toluene, the total penetration of phenol (sum of initial dose in receptor fluid and bound to skin) was 52%. Therefore, the bioavailabilities of the chemicals after volatilization were 77% and 84%, respectively, for toluene and phenol. Adding the chemicals to soil for a brief time (16 h), reduced toluene bioavailability to 4-6% and phenol bioavailability to 26-30%. After aging, the bioavailability of toluene (3-4%) was similar to toluene in soil for a short time. However, aged phenol was decreased to 15-22% bioavailability. As a result of decreased bioavailability, the environmentally acceptable endpoint (EAE) of toluene would increase about 25-fold after aging in soil relative to pure toluene. In contrast, the EAE of phenol would be about 6-fold higher relative to pure phenol. The data indicate that chemical characteristics such as volatilization, not only produce differences in the bioavailabilities of toluene and phenol but also impact the EAEs of the compounds. (Supported through funding from the Hazardous Substance Management Research Center and the New Jersey Commission on Science and Technology).

Oral Bioaccessibility of Dioxins/Furans at Low Concentrations (50-350 ppt TEQ) in Soil

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Animal studies in rodents have indicated that the oral bioavailability of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in environmentally contaminated soils can range from 0.5 to 50%. To estimate the oral bioavailability of TCDD, and the 16 other 2,3,7,8-substituted dioxin/furan congeners, this study used a physiologically based extraction test, designed around the anatomic and physiologic characteristics of the human digestive tract. This test measures the fraction of dioxins/furans in soil that would be solubilized in the gastrointestinal tract (i.e., that would be bioaccessible), and therefore available for absorption. The concentrations of TCDD in the eight soils tested were 1.7 to 139 pg/g (ppt), while the total TEQ concentrations were 6 to 340 ppt. Bioaccessibility of dioxins/furans from these soils ranged from 19 to 34% (averaged across the 17 2,3,7,8-substituted dioxin/furan congeners), with an average of 25%. The total organic carbon (TOC) in these soils was low—less than 4%—particularly for the soil series from which they were collected. Bioaccessibility of individual congeners did not appear to be correlated with degree of chlorination; however, it did appear to be inversely related to TOC. Even though these dioxin/furan concentrations are much less than studied previously, these results are consistent with those from animal studies at other sites, which have generally yielded values of 20–50% relative bioavailability of TCDD in soil.

Volatile Air Emissions from Soil or Groundwater – Are They as Significant as Models Say They Are?

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Human health risk assessments often involve the evaluation of volatile chemicals in either subsurface soils or groundwater. The inhalation of volatile chemicals following volatilisation and diffusion to the soil surface is often found to be the most significant exposure pathway. This is primarily due to the use of models to predict the transport processes and emissions across the soil surface for volatile chemicals present at depth in soil or groundwater. These models are simplistic and often result in conservative and unrealistic results leading to over-estimations of chemical concentrations in breathing zones. The implication of the use of vapour transport models has been investigated by URS at a number of sites in Australia over the last 7 years. Modelled estimates of surface emission rates have been compared with measured emissions data (collected using a surface emissions flux hood and a soil gas probe). The results of these investigations bring into question the validity of these models for use across sites with varying subsurface chemicals and characteristics. Commonly used simplistic models (such as the Johnson and Ettinger Model and others as recommended in RBCA guidance) were found to over estimate the measured surface emission rate to varying degrees at all sites. For some chemicals, such as benzene, the modelled results were inconsistent, ranging from an order of magnitude to several orders of magnitude greater than the measured results (depending on subsurface conditions). However, for other chemicals particularly chlorinated hydrocarbons such as vinyl chloride and 1,2-dichloroethane, the use of models greatly over estimated the measured surface emissions rates. This observation was consistent at a number of sites with varying subsurface conditions resulting in the model predicting unrealistic and inaccurate air concentrations in breathing zones both indoors and outdoors. This paper presents the results of comparisons undertaken at a number of different sites in Australia and discussion on the observations made and potential use of models in predicting emissions from a range of subsurface sources.

Groundwater to Indoor Air - The Exposure Pathway of the Future

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The Federal government and several states are focusing attention on the often neglected exposure pathway associated with groundwater contamination off-gas effects on indoor air quality in buildings. Currently, the state of the science required to assess this exposure pathway is primitive at best. There are only a few models available for the projection of indoor air quality effects associated with groundwater off-gas and soil vapor. To date the Johnson and Ettinger model is the most comprehensive model available, yet it falls short of providing reliable and reasonable results for all but the simplest of sites and the possible input parameter values are seemingly limitless. Other more direct methods such as soil gas sampling and indoor air sampling are also fraught with uncertainty in obtaining reliable results and comparing them to meaningful standards. Since indoor air quality effects associated with site remediation are obviously going to be a major exposure pathway to consider, especially in the new age of natural attenuation, additional, significant research is needed to adequately evaluate this exposure pathway.

The Assessment of Toxicity and Biodegradability of New Energetic Ingredient Hexanitrohexaazaisowurtzitane (CL-20) in Soil

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The energetic compound, hexanitrohexaazaisowurtzitane (2,4,6,8,10,12-hexanitro-2, 4, 6, 8,10,12-hexaazatetracyclo[5.5.0.05,9.03,11] dodecane), also known as CL-20, is a high power low signature explosive that has the potential to replace currently used high explosives due to its higher performance in terms of ballistics, detonation velocity, and safety. In addition, CL-20 containing no halogens is expected to be more environmentally friendly as compared with older propellant formulations. The widespread, high-level interest in CL-20 has resulted in an increase in its industrial production up to several thousands of pounds per year and its eventual environmental fate and transport. The aim of the present study was to assess the potential impact of CL-20 on natural environments such as soils and soil organisms including microbes, animals and plants. Small amounts of CL-20, provided by the US Army, Picatinny Arsenal NJ, was added to forest and meadow soils (New Jersey) at a rates 0, 500, 1000 and 2000 ppm and incubated at 20^{o}C and constant soil moisture 50 % of WHC. In the first series of experiments, the natural input of organic carbon was simulated by soil amendments with glucose, starch, or cellulose at a rate 1,000-4,000 ppm. During one month of incubation, respiration (CO_2 formation) was continuously recorded using an IR gas analyzer (Li-800) and the composition of microbial community followed by direct microscopy (bright field, UV-, AMF, SEM) and isolations. We were able to identify soil fungi, microarthropods, and some bacterial species. No evident changes in the composition of the soil community was established, while soil respiration was slightly stimulated (by 1-5%) after addition of CL-20, the stimulation being proportional to CL-20 amendment rate. In the second series of experiments, soil was mixed with 2000 ppm of CL-20, planted (bean and ryegrass) and incubated under artificial light (300 mmols/m^2/sec of PAR) with 16:8 h light: dark cycle. The plant photosynthesis and soil-plant respiration was recorded continuously with Li-800 during 2 months from the seedling stage to flowering and seed formation. Contrary to our expectation, the effect of CL-20 on plant growth was stimulating rather than toxic: the standing plant crop and photosynthesis rates were 10-20% higher than those of the control, and senescence stage was significantly delayed. In the third series of experiments, we followed the dynamics of residual CL-20 in soil samples incubated at 10-60^{o}C by spectrophotometry of the soil extract. It turned out that decomposition dynamics followed first order kinetics with 50%-decay time varied from 7 days (40 ^{o}C) to several years (10^{o}C). Thus, we can conclude that CL-20 has no toxicity to soil community and has unusual bio-simulative effects needed further clarification.

Risk Assessment Applications in Atypical Circumstances

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Historically, the phrase “Risk Assessment” would bring to mind a three inch thick Superfund-type baseline risk assessment document filled with pages of tables with endless seemingly unrelated algorithms and numbers. Over the past decade, the principles of risk assessment have gained much more wide-reaching acceptance and risk-based solutions may be utilized for many environmental, occupational or other technical problems. The typical objective of the classic risk assessment is to evaluate current risks or future projected risks from exposure to contaminated media within the framework of state or federal waste management and remediation programs. In addition to those still-viable applications, risk-based techniques also are increasingly being used on a voluntary basis (i.e., outside of the standard regulatory arena) to demonstrate the presence, absence, or extent of environmental or health-related concerns in specific exposure circumstances. Likewise, a risk evaluation may be useful in determining the need for, or the legitimacy of, a public health advisory, alone or in conjunction with remedial actions. Finally, risk-based techniques often find their way into the courtroom. Three case studies are presented in which risk-based solutions were employed in a somewhat unconventional manner to assist in the resolution of environmental or health-related issues: reversal of a fish consumption advisory, evaluation of arsenic in soil on and adjacent to a school facility and challenge to a case of alleged methyl bromide exposure in a litigation context.

Communicating Risk to Diverse Stakeholders: A European Case Study

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Many European ports are beginning the lengthy and costly process of clean up. Remediation technologies are being reviewed and considered. Policymakers are considering with the longevity and cost of different technologies. Furthermore, local public groups are just becoming aware of the environmental and public health concerns associated with large scale cleanup projects. Finally, the industrial groups which have been closely associated with ports are concerned about changing legislation and resulting responsibilities and possible negative press.

With the integration of policies and standards around the European Union, many port sites are struggling with changing cleanup standards for various contaminants. For instance, sediment standards are just being set now around the EU. Quite often, the remediation engineering firms chosen to work at particular sites are from different countries, and therefore language and work culture are completely different. All of these variables make clear communication between stakeholders crucial in a port remediation project.

Bilbao, Spain provides an interesting case study of the diversity and scope of stakeholders at a European port site. The primary concerns are to clean the surrounding freshwaters and sediments and to involve industry in the process (to ensure less contamination in the future). The political situation in Bilbao makes for many levels of bureaucracy and oversight from the EU, federal, regional, and local governments. Furthermore, the surrounding population is very concerned about environmental health problems coming from the port's remediation project.

To date, many scientific reports have been issued on the quality of water and soil within Bilbao's port. However, to ensure different stakeholder acceptance, an integrated and proactive communication strategy is necessary, to 'translate' the technical information to non-scientific stakeholders. Additionally, the flow of information must travel in the other direction (from the non-scientific community to the engineering firm and scientists) to address local concerns and changing perspectives.

POSTER SESSION - ANALYSIS

1. A Pilot Study of Passive Diffusion Bag (PDB) Sampling in a Fractured Bedrock Environment

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Barbara A. O'Grady, EA Engineering, Science, and Technology, Inc., Iselin, NJ
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2. Correlation of Field Analytical Detectors in the Analysis of Soil Contaminated with Diesel Fuel

Clayton J. Clark II, University of Florida, Gainsville, FL
Joseph J. Delfino, University of Florida, Gainsville, FL

3. Using Selected Ion Monitoring to Achieve Risk Based Concentration Levels in Ambient Air

Alyson H. Fortune, ENSR Air Toxics Laboratory, Harvard, MA
Richard L. Wellman, ENSR International, Westford, MA

4. EPA Performance Study for Field Measurement of Total Petroleum Hydrocarbons using Ultraviolet Fluorescence Technology

Steve Greason, Sitelab Corporation, Hanover, NH

5. Analysis of Volatile Organics in Produce Using Solid Phase Microextraction and GC/MS

C.K. Tan, Ph.D., Southwest Research Institute, San Antonio, TX
Kevin Shannon, Southwest Research Institute, San Antonio, TX
Robert Acosta, Southwest Research Institute, San Antonio, TX
Jesse Rodriguez, Southwest Research Institute, San Antonio, TX
Ron Porter, Ph.D., MitreTek, San Antonio, TX

6. Laboratory Determination of Diffusion Coefficient of Contaminant Ions using Clay Soil

Xi Yong-hui, Tongji University, Shanghai, PR China
Ren Jie, Tongji University, Shanghai, PR China
Hu Zhong-xiong, Tongji University, Shanghai, PR China

7. Large Volume Sample Stacking for Analysis of EDTA by Capillary Electrophoresis

Lifeng Zhang, Centre for Advanced Water Technology, Singapore
Zhiwei Zhu, Centre for Advanced Water Technology, Singapore
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1. A Pilot Study of Passive Diffusion Bag (PDB) Sampling in a Fractured Bedrock Environment

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In a joint effort between the Navy, United States Geological Survey, and EA Engineering, a pilot study of passive diffusion bag (PDB) sampling was conducted at the former Naval Air Warfare Center in Trenton, New Jersey. The Navy currently operates and maintains a comprehensive ground-water extraction and treatment system for volatile organic compounds (VOCs) and ten metals at the site. The Navy sought to evaluate a New Jersey Department of Environmental Protection (NJDEP)-acceptable ground-water sampling method that minimizes sampling costs and the treatment of purge water, without sacrificing data quality. Research of sampling options led to the implementation of a pilot study on the use of PDB samplers. The use of PDB samplers substantially reduces equipment and labor costs and produces virtually no investigation-derived waste, as compared to conventional purging and sampling techniques. However, unlike typical PDB samplers that are usually constructed of polyethylene-based material and used to monitor for VOCs only, a regenerated cellulose-based material was used in this PDB pilot study in an attempt to also monitor inorganic parameters. Samples from nine bedrock wells, representing a wide range of trichloroethene concentrations, were collected using PDB samplers, the Environmental Protection Agency's low-flow method, and a modified version of the standard 3 to 5 well-volume purge method in March 2000 and March 2001. The majority of the organic data indicate that the PDB samplers yielded similar results to conventional purging and sampling techniques. Even though only minor sporadic concentrations of inorganic parameters were reported above the applicable reporting limits, similar results were observed for several metals including barium and manganese using the three sampling methods. To gain regulatory acceptance by the NJDEP, additional data are being collected to further support the effectiveness of the PDB sampling technique for inorganic constituents. The results of the assessments made to date will be presented for discussion.

2. Correlation of Field Analytical Detectors in the Analysis of Soil Contaminated with Diesel Fuel

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Analysis of soil by field instrumentation is widely used for preliminary soil contamination detection and site delineation. Research was conducted to determine if there is a correlation between the data gathered by field analytical instruments in analyzing soil contaminated with diesel fuel. One instrument was equipped with a flame ionization detector (FID) and the other a photoionization detector (PID). The results showed that the concentration readings of the PID and FID displayed a linear relationship ($R^2 = 0.94$) for soil recently contaminated with diesel fuel. However, for soil containing weathered diesel fuel in the field, a logarithmic relationship between the PID and FID readings was displayed. It was also determined by laboratory experimentation that the PID and FID readings both exhibited log-linear decreases over time for uncovered diesel fuel contaminated soil. Analysis for the composition of diesel fuel, by volume, was also derived for the diesel fuel used in this research and it was found that the targeted volatile and semivolatile compared favorably with estimates found in the literature. It was concluded that the PID and FID can both individually be used to evaluate soil contaminated by diesel fuel and might be interchangeable depending upon the need of the researcher.

3. Using Selected Ion Monitoring to Achieve Risk Based Concentration Levels in Ambient Air

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US EPA Region 3 ambient air Risk Based Concentrations (RBCs) for residential exposure to Manufactured Gas Plant (MGP) contaminants, especially benzene (0.22 ug/m^3), are lower than the customary EPA Method TO-14a reporting limits based on the concentration of the lowest calibration standard used to calibrate instrumentation (1.6 ug/m^3). This leads to uncertainty when reporting these analytes at RBC levels. This paper reports on the successful use of selected ion monitoring techniques to report ambient air concentrations of benzene and other analytes at levels as low as 0.1 ug/m^3. Traditional sampling techniques and instrumentation are used (evacuated stainless steel SUMMA® (or equivalent) canisters analyzed via gas chromatography/mass spectrometry), but the instrumentation parameters are modified such that the detector only scans a few selected ions (those ions associated with the contaminants of concern), rather than a full spectrum of ions. The result is an increase in detector sensitivity, allowing a linear instrument response down to lower levels. This technique proves useful in investigations involving suspected or known carcinogens, sensitive receptors, or any situation where ambient levels of contaminants are compared against risk based concentrations.

4. EPA Performance Study for Field Measurement of Total Petroleum Hydrocarbons using Ultraviolet Fluorescence Technology

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The Sitelab UVF-3100 portable test kit was demonstrated under the U.S. Environmental Protection Agency Superfund Innovative Technology Program from 1999 to 2001. The purpose of the demonstration was to collect reliable performance and cost data for the UVF-3100 and six other field measurement devices for total petroleum hydrocarbons (TPH) in soil. In addition to assessing ease of device operation, the key objectives of the demonstration included determining the (1) method detection limit, (2) accuracy and precision, (3) effect of interferents and soil moisture content on TPH measurement, (4) sample throughput, and (5) TPH measurement costs for each device. The demonstration involved analysis of both performance evaluation samples and environmental samples collected in five areas contaminated with gasoline, diesel, lubricating oil, or other petroleum products. The performance and cost results for a given field measurement device were compared to those for an off-site laboratory reference method, “Test Methods for Evaluating Solid Waste” (SW-846) Method 8015B (modified).

During the demonstration, siteLAB required less than 38 hours for TPH measurement of 212 samples. The TPH measurement costs were as low as $7,090 for Sitelab’s UVF-3100 rental option compared to $42,500 for the reference method. The method detection limits were determined to be 3.4 and 6.32 milligrams per kilogram for the UVF-3100 and reference method, respectively. Sitelab was also the only developer who analyzed the samples for both GRO and DRO hydrocarbons separately (like the laboratory). EPA reported the UVF-3100 exhibited good accuracy and precision, ease of use, and lack of sensitivity to interferents that are not petroleum hydrocarbons. The demonstration findings collectively indicated that the UVF-3100 is a reliable field measurement device for TPH in soil.

A series of ten sub-posters illustrating Sitelab’s successful performance testing the SITE samples will be presented using data and references taken directly from the EPA’s Innovative Technology Verification Report (ITVR).

5. Analysis of Volatile Organics in Produce Using Solid Phase Microextraction and GC/MS

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Public concern has recently focused on the potential impact of a contaminated shallow aquifer on fruit- and nut-bearing trees and plants drawing upon the contaminated aquifer as a source of hydration. Residents who harvest and consumes these fruits and nuts from gardens and indigenous plant species may risk exposure to harmful chemicals. An effort was undertaken by Southwest Research Institute (SwRI) to detect trace levels of volatile organic chemicals in fresh produce using solid phase microextraction (SPE) and gas chromatography and mass spectrometry (GC/MS).

Previous efforts to analyze produce and other foodstuffs for volatile organics have relied upon the use of cryogen to prevent target compound concentration losses during extraction and/or homogenization. However, the effectiveness of the cryogen in retaining the volatile organic compounds, especially those having low molecular weights and low boiling points, was difficult to assess. The challenge was to innovate a technique that overcomes the weaknesses of the cryogen approach.

Instead of submersion of the produce samples in liquid nitrogen then homogenizing in an industrial grinder or piercing the produce samples and submersion in salty water, the whole produce sample is weighed and transferred to a stainless steel bender fitted with an airtight sealed lid. Standards and heated water (to aid in volatilization) are spiked through a septum in the sampling port of the blender lid prior to high-speed homogenization, which drives target volatile organics into the contained headspace. A needle-borne SPME fiber is introduced through the septum and exposed to the headspace, allowing for capture of volatile organics. The needle/SPME fiber assembly is withdrawn from the blender and injected into the GC/MS.

The SPME approach has notable advantages over the other methods. Since the entire produce sample is homogenized in a sealed container, compound concentration loss is minimized. Extraction-to-analysis times are reduced considerably. Detection limits are lower for a wide range of compounds and sample sizes.

6. Laboratory Determination of Diffusion Coefficient of Contaminant Ions using Clay Soil

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This paper describes a special laboratory device to determine diffusion coefficients of contaminant ions using clay soil .The technique is illustrated with a number of laboratory tests involving diffusion migration of contaminants through clay soil from Shanghai, China. The contaminants used in these tests are solutions of inorganic compounds (e.g., NaCl, $CaCl_2$, KCl,$ZnSO_4$,$CuSO_4$ and so on). The device described in this paper is a rectangle box made up of polyethylene plastic plates of 0.3cm thickness, which have quality of good chemical stability. The device is divided into three parts by two polyethylene porous plates. The middle part contains the soil sample, and the other two parts contain source of contaminants and distilled water respectively. The water level of the two parts apart from the soil sample is equal. Contaminant ions migrate from the source solution to the distilled water through soil samples. The contaminant migration in these tests is controlled mainly by diffusion. The results are consistent with the equation developed from the Fick's second law, that is, the logarithm of concentration is linear with the square of diffusive distance. The concentration of contaminant ions at different specified distance of a soil sample is measured after a definite diffusion time .The data are arranged in a semi-logarithm co-ordinate system. The Diffusion coefficient can be calculated from the slope of a line. It is found from the experiment results that the diffusion coefficients of anions (e.g., Cl^-) through the clay are much larger than those of cations (e.g., Ca^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}), and there are obvious relations between diameters and electric conductivities of divalent cations and diffusion coefficients. The results also show that adding of cement to soil reduces the diffusion velocity of contaminant ions greatly.

7. Large Volume Sample Stacking For Analysis Of EDTA By Capillary Electrophoresis

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The widespread use of ethylenediaminetetraacetic acid (EDTA) has requested an urgent monitoring program regarding surface and drinking water. Analysing EDTA at low-level concentrations (such as μg/L in the environmental samples) is quite complex using the conventional GC/MS or HPLC methods. In this study, a simple, quick and sensitive capillary electrophoretic technique -large volume stacking using the EOF pump (LVSEP)- has been developed for determining EDTA in drinking water for the first time. It is based on a precapillary complexation of EDTA with Fe(III) ions, followed by large volume sample stacking and direct UV detection at 258 nm. The curve of peak response versus concentration was linear between 5.0 and 600.0 μg/L, as well as between 0.7 and 30.0 mg/L. The regression coefficients were 0.9988 and 0.9990, respectively. The detection limit of current technique for EDTA analysis was 0.2 μg/L with additional 10-fold preconcentration procedure, based on the signal-to-noise ratio of 3. As opposed to the classical CE method, a 1000-fold concentration factor could be smoothly achieved on this LVSEP method. To the best of our knowledge, it represents the highest sensitivity for EDTA analysis via CE. Several drinking water samples were tested by this novel method with satisfactory results.

POSTER SESSION – ARSENIC

8. Arsenic Everywhere

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8. Arsenic Everywhere

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Initially, the new Arsenic Revolution began with concerns of Arsenic in drinking water. Since that time, the after shocks have shed light on concerns of Arsenic in food, soil, and human biological waste, urine. Many individuals and companies scurried to provide some type of remediation or testing for Arsenic to be able to capitalize on the potential rewards. Because of the haste and desire to produce something, anything first, many of the Arsenic test kits out today are not very accurate or versatile. Industrial Test Systems, Inc. located in Rock Hill, SC has developed an Arsenic Quick Test Kit that can be used to test water, soil and human urine for Arsenic.

The chemistry of the test enables Arsenic levels as low as five parts per billion up to five hundred parts per billion to be detected. The chemistry involves converting Arsenic compounds to Arsine gas. The reaction of an acid, in powder form, enhanced with two metal salts, and Zinc dust generates the Arsine gas that is detected on a test strip. The metal salts play a dual role, speeding up the reaction and verifying no interferences from the particular metals at the levels used. The test was designed to determine the total Arsenic in a sample. The test is not able to speciate the different forms of Arsenic, but the test is specific for inorganic Arsenic.

In other Arsenic test kits, Lead (Pb) is used to eliminate Hydrogen Sulfide. Arsine gas alone can be quite dangerous, especially at high concentrations. The danger becomes increasingly great when Lead (Pb) is added to the chemistry. The Arsenic Quick Test Kit designed by Industrial Test Systems, Inc. can tolerate up to two parts per million of Hydrogen Sulfide without interference. If Hydrogen Sulfide is present in a sample at two parts per million or less, Potassium Peroxymonosulfate, MPS, is involved in the chemistry to oxidize the Hydrogen Sulfide to Sulfate.

The Arsenic Quick Test Kit can be used to test water samples without any special sample preparation or sample pre-treatment. However, it is necessary to pre-treat urine samples and prepare and pre-treat soil samples. Test results, using water or soil samples, can be obtained in ten minutes, and human urine samples currently require twenty minutes to obtain results. Again the versatility of the test kit is displayed with the color chart. One color chart, calibrated at twenty-two degrees Celsius, can be used for the three sample matrices for color comparison. There is some minimal calculation required to obtain the total amount of Arsenic (mg/L) in human urine. But, the Arsenic results for water and soil can be recorded directly from the color chart. Currently, a patent is pending on the unique chemistry of this Arsenic test kit.

POSTER SESSION - BIOREMEDIATION

9. Treatment of OBM Drill Cuttings Soil by Elimination of Biodegradation Limiting Factors using Bio-augmented Landfarming

SM Afifi, United Environmental, Inc. (Middle East Division), Cairo, Egypt
JW Warner, Professor of Civil Engineering, Colorado State University, Ft. Collins, CO

10. Co-Composting of Creosote-Contaminated Soil with Cattle Manure and Vegetable Waste for the Biodegradation of Creosote in Soil

Harrison I. Atagana, Mangosuthu Technikon, Jacobs, Durban, South Africa
RJ Haynes, University of Natal, Pietermaritzburg South Africa
FM Wallis, University of Natal, Pietermaritzburg South Africa

11. Bioremediation of Polyaromatic Hydrocarbons Using a Groundwater Recirculating Treatment System

Peter J. Cagnetta, Science Applications International Corporation, Harrisburg, PA
Daniel B. Lewis, Spotts, Stevens, and McCoy, Inc., Reading, PA

11A. Application of Innovative Product for *In-Situ* Anaerobic Bioremediation of Chlorinated Hydrocarbons in Ground Water.

Eric C. Hince, P.G., Geovation Technologies, Inc., Florida, NY

12. Stimulation of Environment-Polluting Oil Residues Degradation by Microbial Associations

Anca Voicu, Institute of Biology of Romanian Academy, Bucharest, Romania
Smaranda Dobrota, Institute of Biology of Romanian Academy, Bucharest, Romania
Ioana G. Petrisor, University of Southern California, Los Angeles, CA
Mugur Stefanescu, Institute of Biology of Romanian Academy, Bucharest, Romania
Mihaela Lazaroaie, Institute of Biology of Romanian Academy, Bucharest, Romania
Ioan I. Lazar, Institute of Biology of Romanian Academy, Bucharest, Romania

13. Stimulating Simultaneous Anaerobic Oxidation of BTEX and Reductive Dechlorination of Chloroethenes in Groundwater

Pawan K. Sharma, Camp, Dresser, & McKee, Inc., Walnut Creek, CA
Dalia Hildebrand, Camp, Dresser, & McKee, Inc., Walnut Creek, CA

14. Microbial Degradation of Detoxification Products from Chemical Warfare Agents Destruction and Organophosphorus Herbicides

Ivan I. Starovoitov, G.K. Skryabin Institute of Biochemistry and Physiology of Microorganisms RAS, Moscow region, Russia
Inna T. Ermakova, G.K. Skryabin Institute of Biochemistry and Physiology of Microorganisms RAS, Moscow region, Russia
Gennady A. Zharikov, Research Centre for Toxicology and Hygienic Regulations of Biopreparations, Moscow region, Russia

9. Treatment of OBM Drill Cuttings Soil by Elimination of Biodegradation Limiting Factors using Bio-augmented Landfarming

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During the drilling of oil wells at the Egyptian western desert, oil based drill cuttings have been produced. Though the quantity of drill cuttings produced per well is not large, collectively, through out the oil and gas industry, the quantity of these drill cuttings is very significant and represents a major disposal problem for the oil and gas industry worldwide. These drill cuttings are in the range of 40 to 70 percent by volume petroleum hydrocarbons in the diesel range (C12-C18). The drill cuttings have the physical appearance of being pitch black, sticky with a clayey texture. These drill cuttings are completely saturated with petroleum hydrocarbons and liquid oil readily drains from the cuttings.

Bioremediation is commonly accepted as the most efficient, environmentally safe and cost effective method for treatment of the drill cuttings. This paper discusses the conducted project for treating the petroleum hydrocarbons based drill cuttings utilizing landfarming enhanced by bioaugmentation and biostimulation additives. The rate of bioremediation of petroleum hydrocarbons was sensitive to many factors such as the chemical composition of the petroleum hydrocarbons, presence of suitable microbes, soil moisture conditions, water quality, availability of suitable electron acceptors, nutrients (NPK), enzymes, temperature etc.

The soil was analyzed for the presence of indigenous microbes and soil nutrients (NPK). Both were lacking at the western desert site and the bioremediation process has been bioaugmented and biostimulated by the addition of hydrocarbon consuming microbes and with NPK. A proprietary mixture of bio-enhancers has also been used. This paper presents the taken steps to eliminate the biodegradation limiting factors. Charts of TPH concentration with time are presented. Over approximately 1 year of operation the overall degradation rate has been 524 mg/kg/day. In comparison with biodegradation rates reported in the literature for other sites, this is an excellent rate for biodegradation.

10. Co-Composting of Creosote-Contaminated Soil with Cattle Manure and Vegetable Waste for the Biodegradation of Creosote in Soil

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Co-composting of mispah form (FAO: Lithosol) soil contaminated with >380 000mg kg^{-1} was carried out separately with cattle manure and mixed vegetable waste for a period of 19 months. The soil was mixed in a ratio of 1:1 (v/v) with wood chips to improve aeration. The soil-wood chips mixture was then mixed in a ratio of 4 soil-wood chips mixture : 1 compost material (cattle manure or mixed vegetable waste). Duplicate compost heaps were set up on wood palettes overlaid with double layers of nylon straw bags. Moisture, temperature, pH, ash content, C:N ratio of the compost and the creosote concentration of the soil was monitored monthly. The concentration of selected creosote components in the soil was also determined at the end of the incubation period. Temperature was observed to rise to about 40^{O}C in the cattle manure within two months of incubation while temperature in the control and vegetable waste remained below 30^{O}C until the fourth month. Creosote concentration in the control was reduced by 17% at the end of the incubation period while concentration of creosote in the cattle manure and vegetable waste compost was reduced by 98% and 97% respectively. The percentage rate of creosote reduction in the mixed vegetable compost was initially lower than observed in the cattle manure compost. However, the reduction rate became similar in the third month. The difference in the rate of reduction in the subsequent months became smaller until the end of the incubation. The concentrations of selected creosote components were reduced by between 96% and 100% within the same period. There was no significant difference between the level of reduction in creosote concentration in the cattle manure and the vegetable waste compost at p 0.05. Microbial respiration experiments and plate counts of microorganisms show that as microbial population and respiration increased or decreased, percentage reduction in creosote concentration increased or decreased.

11. Bioremediation of Polyaromatic Hydrocarbons Using a Groundwater Recirculating Treatment System

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Releases from a No. 2 fuel oil UST and a motor oil UST resulted in the groundwater being impacted with fluorene, phenanthrene, and pyrene at a site in Reading, Pennsylvania. The groundwater is presently at approximately 11 feet below grade and occurs within the interbedded limestone and dolomite underlying the site.

A remedial options assessment (ROA) identified that natural biodegradation of the hydrocarbons was occurring. In order to maximize the biodegradation rate, a treatment system was designed and constructed which included one extraction well in the former UST area and four injection wells located along the downgradient and side-gradient edges of the plume. Water was extracted from the well at 5 gpm and treated with granular-activated carbon, amended with atmospheric oxygen, and amended with ammonium phosphate fertilizer. The amended water was then injected into 4 injection wells at 1.25 gpm per well. The closed loop recirculation approach ensured the maximum mixing of contaminants, amendments, and indigenous bacteria.

Throughout the first 80 days of operation, the concentrations of fluorene in well MW-3 declined from 466 micrograms per liter (μg/l) to <10 μg/l. During the same time period, the pyrene concentration declined from 78 μg/l to <10 μg/l. The concentration of phenanthrene in well MW-3 declined from 1,232 μg/l to <10 μg/l after 238 days. The decay rates were calculated at 5.69, 1.09, and 0.07 μg/l per day for fluorene, pyrene, and phenanthrene, respectively.

Prior to the start-up of the treatment system, the groundwater at well MW-3 contained a fluorene-degrading microbial population and a pyrene-degrading population of 1,414 MPN/ml and 1,000 MPN/ml respectively. After 78 days of operation, each population increased to over 20,000 MPN/ml and, subsequently after 160 days operation, declined to <500 MPN/ml. The contaminant-degrading populations were stimulated by the addition of the amendments and then subsequently declined as the concentrations of contaminants or growth substrate declined.

The concentration of dissolved oxygen throughout the plume prior to the start-up of the treatment system was <2 mg/l. After start-up and operation of the system, the dissolved oxygen ranged from 6 to 10 mg/l throughout the 12 months of operation.

11A. Application of Innovative Product for *In-Situ* Anaerobic Bioremediation of Chlorinated Hydrocarbons in Ground Water.

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Chlorinated hydrocarbons such as tetrachloroethene (PCE) and its daughter products are extremely recalcitrant contaminants in environmental media. Presently, there are few cost-effective remedial options for these compounds. Geovation has successfully applied an innovative technology for the *in-situ* anaerobic bioremediation of PCE and its daughter products to ground water and the aquifer media at a dry cleaning facility. Geovation's substrate-release composition (SRC™) was successfully demonstrated to create and maintain anaerobic and highly reducing conditions in site ground water. These conditions were created in the SRC™ delivery wells (e.g., eh/ORP went from +206 mV to -315 mV) within two weeks of the initial application. Within six months of the initial application, highly reducing conditions were also measured in monitoring wells more than 100 feet from the delivery wells (e.g., eh/ORP went from +190 mV to -267 mV). Geovation's SRC™ is a solid-chemical composition in granular form which is poured directly into wells or applied in filter socks. SRC™ works by (1) providing a diffusive flux of substrates into aquifer media; (2) creating and maintaining anaerobic and highly reducing conditions; and (3) providing a sustained release of substrates and nutrients which in turn promote the growth of a diverse consortia of anaerobic microorganisms. Information and data will be presented concerning this innovative technology and applications in the field.

12. Stimulation of Environment-Polluting Oil Residues Degradation by Microbial Associations

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Oil production and processing activities have generated complex pollution problems all over the world. Romania, a country with long history of oil industry is faced today with severe hydrocarbon pollution, affecting both surface and underground environments. This paper presents investigations on crude oil degradation efficiency of 23 hydrocarbon-oxidant microorganisms, isolated from terrestrial and aquatic environments contaminated by oil residues, from a Romanian oil field. The hydrocarbon-oxidant microorganisms under study were represented by 3 yeast strains and 20 microbial strains belonging to the genera: *Bacillus, Pseudomonas, Arthrobacter, Corynebacterium, Serratia, Micrococcus*. These microorganisms were used individually, in pure culture, as well as in different associations. It was studied and put in evidence the capacity of the 23 isolated microorganisms to produce biosurfactants and biosolvents, as well as to emulsify monoaromatic hydrocarbons and waxy-paraffinic crude oil. The best results concerning all studied parameters, including crude oil degradation, were obtained for several microbial associations, selected for field bioremediation deployments.

13. Stimulating Simultaneous Anaerobic Oxidation of BTEX and Reductive Dechlorination of Chloroethenes in Groundwater

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This presentation documents the results of a field application in which sodium lactate was injected into a mixed organic groundwater plume. The intent of the sodium lactate injections was to produce dissolved molecular hydrogen in groundwater. The hydrogen would serve as the electron donor in microbially facilitated reduction-oxidation (redox) reactions. The microbes would preferentially reduce the concentrations of nitrate, manganese, iron, sulfate, and other completing electron acceptors, with respect to chloroethenes. With chloroethenes as the favored electron acceptors and the consumption of the injected lactate, the benzene, toluene, ethyl benzene, and xylenes (BTEX) compounds would serve as the electron donor in the redox reactions. Within six weeks after the lactate injections, groundwater nitrate, manganese, iron, sulfate levels were reduced to levels that allowed the chloroethenes to be favored electron acceptors. Eight months after the injections, total BTEX concentrations have decreased from 11,310 to 2,028 ug/L. In the last sampling event all individual BTEX compound concentrations were below State of California Maximum Contaminant Levels (MCLs). During this eight month period, trichloroethene (TCE) concentration has decreased from 6,200 to 2,000 ug/L and cis-1,2-dichloroethene (DCE) concentration increased from 3,700 to 4,200 and as ultimately decreased to 2,300 ug/L. During this same time, trans-1,2-DCE concentration also increased from 1,800 to 2,600 and then decreased to 1,000 ug/L. Vinyl chloride has not been detected. Anaerobic oxidization of DCE is being evaluated as a possible pathway for the DCE concentration decreases. With the consumption of the injected lactate in the groundwater and the continued low competing electron acceptor concentrations, it is expected that microbes will continue to biodegrade the BTEX compounds through anaerobic oxidation with chloroethenes and carbon dioxide serving as the favored electron acceptors.

14. Microbial Degradation of Detoxification Products from Chemical Warfare Agents Destruction and Organophosphorus Herbicides

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In keeping with the 1993 Paris Chemical Weapons Convention, methods are being developed to create technologies for Chemical Warfare (CW) agents destruction. The main problem of CW agents destruction is providing environmental safety. Biotechnological approach for destruction of xenobiotics is considered as the most promissing to provide environmental safety.
In course of joint studies with scientists of Texas A&M University (USA) an integrated chemical/biotechnological method has been developed to create an environmental safe technology for destruction of the detoxification products of mustard-lewisite mixture (MLM). This method includes three sequential steps: (1) detoxification of MLM by alkaline hydrolysis, (2) electrochemical treatment of detoxification products including electrolysis for converting all organic substances to bioutilized compounds and electrocoagulation for removing arsenic salts, and (3) bioutilization of the electrochemical products by microorganisms. Another approach was developed for destruction of thiodiglycol (TDG), the main product of “mustard gas” (HD) detoxification. Microbial cultures Alcaligenes xylosoxydans subsp. denitrificans, possessing the degrading activity against TDG was isolated from the soil samples contaminated by the products of HD detoxification and the most active strain A. xylosoxydans TD2 was selected. The effect of different cultivation conditions on the efficiency of TDG biodegradation was determined. The scheme for TDG metabolism by A. xylosoxydans TD2 was suggested.

For biodegradation of alkylphosphonic acids, the end products of chemical hydrolysis of neurotoxic CW agents, bacterial strains were isolated and selected. These strains are able to biodegrade alkylphosphonates in concentration up to 25 mM during 72 hrs. Dynamics of the growth of these strains in the medium with alkylphosphonates was studied. Some of these strains are able to biodegrade organophosphorus herbicide, glyphosate, in concentration up to 20 mM during 120 hrs. Such strains may be useful for development of technology for bioremediation of soils and water, polluted by organophosphorus compounds.

POSTER SESSION – CHEMICAL OXIDATION

15. Ozone-Peroxide Advanced Oxidation Water Treatment System for Treatment of Chlorinated Solvents and 1,4-Dioxane

Reid H. Bowman, Applied Process Technology, Inc., Pleasant Hill, CA
Philip Miller, England Geosystem, Inc, Irvine, CA
Michael Purchase, Orion Environmental, Inc., Long Beach, CA
Randy Schoellerman, San Gabriel Basin Water Quality Authority, Covina, CA

16. Implementation of an *In Situ* Chemical Oxidation Program for Remediation of Saturated Zone Petroleum Hydrocarbons at the Navy Exchange Service Station Naval Air Station, Brunswick, Maine

Alexander C. Easterday, EA Engineering, Science, and Technology, Bedford, MA
Curtis J. Varner, EA Engineering, Science, and Technology, Newburgh, NY

17. Cost Effective Application of Modified Fenton's Reagent at an Operational Dry Cleaners Site

Prasad K. Kakarla, In Situ Oxidative Technologies, Inc., West Windsor, NJ
Richard S. Greenberg, In Situ Oxidative Technologies, Inc., West Windsor, NJ

18. Thermally Activated Peroxydisulfate Oxidation of Polychlorinated Biphenyls (PCBs)

Paul F. Killian, University of Massachusetts Lowell, Lowell, MA
Clifford J. Bruell, Ph.D., University of Massachusetts Lowell, Lowell, MA

18A. Laboratory Evaluation of Iron Catalyzed Persulfate Oxidation of Trichloroethylene (TCE)

Chenju Liang, University of Massachusetts Lowell, Lowell, MA
Clifford J. Bruell, University of Massachusetts Lowell, Lowell, MA
Michael C. Marley, Xpert Design and Diagnostics, LLC, Stratham, NH
Kenneth L. Sperry, Xpert Design and Diagnostics, LLC, Stratham, NH

18B. Laboratory-scale Study of Iron Catalyzed Persulfate Oxidation of Energetic Compounds in Aqueous Solutions

Nihar Mohanty, MADEP, Wilmington, MA
Clifford J. Bruell, Ph.D, University of Massachusetts Lowell, Lowell, MA
Peter Philbrook, U.S. EPA,North Chelmsford, MA

19. The Thermodynamics of Sodium Permanganate Oxidative Reactions

Brenda K. Veronda, Carus Chemical Company, Peru, IL
Ken Pisarczyk, Carus Chemical Company, Peru, IL
Erik Pedersen, Carus Chemical Company, LaSalle, IL

15. Ozone-Peroxide Advanced Oxidation Water Treatment System for Treatment of Chlorinated Solvents and 1,4-Dioxane

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A suspected carcinogen, 1,4-dioxane is an industrial solvent and an acid scavenger frequently added to chlorinated solvents to neutralize hydrochloric acid. Common analytical methods used in groundwater quality investigations, such as EPA Method 8260, either do not include 1,4-dioxane or achieve relatively high detection levels, on the order of 100 µg/l. Detection of 1,4-dioxane to 3 µg/l requires EPA Method 8270M. The State of California recently adopted a drinking water “action level” of 3 µg/l, prompting more intensive monitoring for 1,4-dioxane in groundwater. As a result of this monitoring, 1,4-dioxane has been discovered in groundwater wells where pump and treat remediation systems are in place to remove chlorinated solvents. Commonly used groundwater treatment technologies, such as air stripping and liquid-phase granular activated carbon (LGAC), have been shown to be ineffective in removing 1,4-dioxane. A line pressure advanced oxidation process (AOP) using ozone and hydrogen peroxide has been shown to effectively remove 1,4-dioxane to below the 3 µg/l. This AOP technology has been integrated into existing remediation systems, both air stripping and LGAC, as a pretreatment for the removal of 1,4-dioxane. In addition to removing 1,4-dioxane to below 3 µg/l, the concentrations of most of the other chlorinated solvents present were significantly reduced. The concentration of 1,4-dioxane treated ranged from 7 to 600 µg/l. The scalability of line pressure advanced oxidation of 1,4-dioxane and chlorinated solvents has been demonstrated from pilot tests of 10 GPM to commercial installations of 1,000 GPM.

16. Implementation of an *In Situ* Chemical Oxidation Program for Remediation of Saturated Zone Petroleum Hydrocarbons at the Navy Exchange Service Station Naval Air Station, Brunswick, Maine

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***Curtis J. Varner**, EA Engineering, Science, and Technology, 3 Washington Center, Newburgh, NY 12550, Tel: 845-565-8100*

A full-scale *in situ* chemical oxidation program utilizing hydrogen peroxide (H_2O_2) to remediate residual dissolved-phase and sorbed-phase petroleum hydrocarbons was applied at the Navy Exchange Service Station, Naval Air Station, Brunswick, Maine. *In situ* chemical oxidation was selected as a final remedial technology to achieve site closure following several years of active soil vapor extraction/air sparging operations, which successfully treated vadose zone contamination and significantly reduced saturated zone petroleum hydrocarbon concentrations. *In situ* chemical oxidation was utilized to mitigate residual saturated zone petroleum hydrocarbons that were found to be recalcitrant to ongoing soil vapor extraction/air sparging operations.

To assess the site-specific effectiveness of *in situ* chemical oxidation and to provide necessary data for design of the full-scale *in situ* chemical oxidation injection program, bench-scale testing was completed using ground-water and saturated zone soil samples collected from the remedial target area. The bench-scale tests evaluated percent oxidation of benzene, toluene, ethylbenzene, and total xylenes; methyl tertiary-butyl ether; and total petroleum hydrocarbons against applied doses of hydrogen peroxide and ferrous-iron chelating agent solutions. Bench-scale testing and *in situ* chemical oxidation injection procedures were completed by ISOTEC Inc., of West Windsor, New Jersey, under subcontract to EA.

The full-scale *in situ* chemical oxidation injection program was designed and implemented using the bench-scale testing results. To evaluate the effectiveness of the full-scale *in situ* chemical oxidation program, ground-water and saturated zone soil samples were collected prior to and following each injection event.

This presentation will detail the results of the bench-scale testing and full-scale *in situ* chemical oxidation program with an emphasis on the correlation of the bench-scale testing to the full-scale *in situ* chemical oxidation effectiveness. The presentation will also discuss the overall effectiveness of the *in situ* chemical oxidation remedial program for reducing dissolved-phase and sorbed-phase petroleum hydrocarbon concentrations as required to achieve conditions necessary for proceeding to site closure.

17. Cost Effective Application of Modified Fenton's Reagent at an Operational Dry Cleaners Site

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Advanced oxidation techniques based on Fenton's chemistry are increasingly surpassing traditional remediation treatments with respect to cost effectiveness, expediency, variety of contaminants mineralized, and the innocuous nature of the end products. Despite its benefits, the field application of Fenton's Reagent in its traditional form has historically been hindered by the instability of oxidizing and catalytic reagents when introduced into the subsurface, and the impracticality of lowering the native pH to acidic conditions. Therefore, a modified Fenton's reagent consisting of chelated iron catalyst and stabilized peroxide capable of functioning in the neutral pH range was developed by In-Situ Oxidative Technologies, Inc. (ISOTEC^{SM}). The modified Fenton's reagent delays formation of reactive hydroxyl radicals, allowing the oxidizing agent to thoroughly disperse in the subsurface first. ISOTEC^{SM} implemented its patented process, which incorporates the modified reagent, to remediate a contaminated groundwater plume caused by an operational dry cleaners located in northeast Florida. The ground water was contaminated with up to 38 µg/l of Trichloroethene (TCE) and 54 µg/l of Tetrachloroethene (PCE) spread over an approximately 8,500-sq. ft area. The low chlorinated solvent concentrations render conventional treatment techniques more costly and less effective, despite the high capital, operation, and maintenance costs involved. Initially, a laboratory bench scale and in-situ field experiments were performed to ascertain the subsurface characteristics, treatment stoichiometry, and process conditions. The results of the laboratory bench scale indicated a 100% reduction in total VOCs found in the ground water sample. A small portion of the groundwater plume was utilized for a field pilot program, which involved a 4-day injection event. The pilot program yielded positive results; the concentrations of all VOC compounds in the treated area measured below Florida Department of Environmental Protection (FDEP) regulatory guidelines. In the full-scale treatment program that followed, the majority of the plume was treated and all contaminant concentrations were reduced to below applicable FDEP groundwater quality criteria (3 µg/l for both TCE and PCE) after three two-week treatments over a six-month timeframe. Closure of the site is expected in the summer of 2002, after 8 quarters of FDEP required post-treatment groundwater monitoring. The entire treatment program was completed for an approximate cost of $18.00 per cubic yard of soil.

18. Thermally Activated Peroxydisulfate Oxidation of Polychlorinated Biphenyls (PCBs)

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Polychlorinated biphenyls (PCBs) are a family of man-made chemicals that were used as coolants and lubricants in transformers, capacitors, and other electrical equipment. Due to harmful effects of PCBs, their manufacturing was banned in 1977; however, their nonreactive properties allow PCBs to persist in the environment. Peroxydisulfate ($S_2O_8^{2-}$) is a strong oxidant that can be thermally activated to form the persulfate free radical ($SO_4 \cdot -$), an even stronger oxidant. Studies were performed to examine the influence of oxidant strength and time on the ability of peroxydisulfate to degrade PCBs (specifically Aroclor 1242). Aqueous and soil slurry samples were spiked with Aroclor 1242, mixed with sodium peroxydisulfate solutions, and placed in a heated water bath set at 60^{o}C. At specific intervals, samples were removed and placed in an ice bath to stop the reaction. The samples were then extracted with hexane, and analyzed on a GC/ECD to determine the concentration of PCBs remaining. In the aqueous samples spiked with 88.5 µg of Aroclor 1242 and oxidized with a 0.125 M solution of sodium peroxydisulfate, there was a steady decrease in PCB concentration, with 19% degraded after 3 hours, 75% degraded after 12 hours, and all of it degraded after 50 hours. In soil samples spiked with 44 µg of Aroclor 1242 and heated for 5 days at 60^{o}C, the samples with the 0.005 M sodium peroxydisulfate solution contain only 49% of the PCBs found in the control sample; the samples with the 0.052 M sodium peroxydisulfate solution contain only 19 % of the PCBs found in the control sample; and the samples with the 0.126 M sodium peroxydisulfate solution contain only 5% of the PCBs found in the control sample.

18A. Laboratory Evaluation of Iron Catalyzed Persulfate Oxidation of Trichloroethylene (TCE)

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The objective of the laboratory study was to examine the conditions under which transition metal ions (e.g., ferrous iron) could catalytically decompose the persulfate anion ($S_2O_8^{2-}$) to produce a powerful oxidant known as the sulfate free radical ($SO_4^{-\cdot}$) with a standard redox potential of 2.6 V. For all $S_2O_8^{2-}/Fe^{2+}$/TCE molar ratios, little further TCE degradation and persulfate decomposition was observed in samples taken subsequent to the first sample (t = 5 minutes for TCE degradation test and t = 30 minutes for persulfate decomposition tests). TCE degradation appeared to occur almost instantaneously and then stall. Increases of iron contents from a Fe^{2+}/TCE molar ratio of 5/1 to 15/1 at a constant $S_2O_8^{2-}$/TCE molar ratio of 20/1 resulted in approximately a 20% increase in TCE degradation. Subsequently, further increases in iron contents resulted in no further improvement in TCE degradation. In contrast, increases of iron contents resulted in proportional increases of persulfate decomposition. In order to ascertain the influence of available ferrous iron, experiments were conducted where ferrous iron was added sequentially in small increments, as opposed to all at once. The final $S_2O_8^{2-}/Fe^{2+}$/TCE molar ratios reached were 20/5/1, 20/10/1, and 20/25/1 and the overall TCE removals were 73%, 84% and 95% after 5 successive additions of iron equivalent to initial Fe^{2+}/TCE molar ratios of 1/1, 2/1 and 5/1, respectively. In comparison to the same final $S_2O_8^{2-}/Fe^{2+}$/TCE molar ratios in the previous experiments (where all the iron was added at once), sequential addition of Fe^{2+} improved the TCE removal by 26%, 27%, and 31% for $S_2O_8^{2-}/Fe^{2+}$/TCE molar ratios of 20/5/1, 20/10/1, and 20/25/1, respectively. In contrast, the persulfate decompositions of these three tests exhibited increases of only 8%, 5%, and 7% consumption, respectively. Sequential addition of ferrous iron resulted in an increased TCE removal efficiency. Therefore, it appears that ferrous iron played an important role in generating sulfate free radicals. Either cannibalization of sulfate free radicals in the presence of ferrous iron or the rapid conversion of all ferrous iron to ferric iron limited the ultimate oxidizing capability of the system. These studies demonstrated that persulfate anions have the ability to degrade TCE under ferrous iron catalyzed conditions.

18B. Laboratory-scale Study of Iron Catalyzed Persulfate Oxidation of Energetic Compounds in Aqueous Solutions

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In situ chemical oxidation (ISCO) technologies are being used for degradation of organic compounds in soil and groundwater. However some commonly used oxidants like the Fenton's reagent and permanganates may have limitations for ISCO applications and therefore cannot be applied universally. For example, persistence of Fenton's reagent in the subsurface has been reported to be insignificant compared to groundwater velocities. Permanganates have been reported to clog aquifers due to the precipitation of manganese dioxide. Chemical oxidation using iron catalyzed persulfate (ICP) potentially represents an innovative technology for the *in situ* treatment of soils and groundwaters contaminated with energetic compounds such as RDX, HMX and TNT. Such contaminants are commonly found at Department of Defense (DoD) sites at concentrations that may inhibit bioremediation. Laboratory-scale batch experiments were conducted to determine capability of persulfate in the presence of iron as a catalyst to oxidize the contaminants. Molar ratios of oxidant: iron: contaminant were changed to study removals. At room temperature, at a ratio of 700: 36:1, up to 39% removal was noted when all of the iron was dosed at one time initially. However, when iron was sequentially dosed, significant increases in removals were noted. The studies show that the form of "available iron" plays an important role in the extent of oxidation. EPA Method 8330 using an HPLC was used to analyze the energetic compounds in water. The experiments are being carried out at the U.S. EPA's Regional laboratory in Chelmsford, MA.

19. The Thermodynamics of Sodium Permanganate Oxidative Reactions

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According to the United States Environmental Protection Agency (USEPA), a significant number of the hazardous waste sites in the United States have contaminated groundwater. Some of the most common contaminants are chlorinated organic solvents such as trichloroethylene (TCE) and perchloroethylene (PCE). In-situ (ISCO) and ex-situ chemical oxidation techniques and technologies have been developed to quickly and effectively oxidize these types of chlorinated contaminants. The key reacting element in these remediation techniques is the oxidant, and knowledge of how the oxidant reacts and the consequences of its reactions are critical factors that can affect the successful completion of a remediation project.

The use of permanganate (MnO_4^-) as the oxidant for in-situ or ex-situ chemical oxidation is characterized by fast reaction rates that result in the complete mineralization of TCE and PCE into carbon dioxide, water and chloride salts. Sodium and potassium permanganate are strong oxidizing reagents, and the reactions need to be thoroughly understood and controlled in order to achieve optimum oxidation results. The kinetics – or rate at which permanganate reactions occur, and the thermodynamics - amount of heat released during a reaction, are important safety factors that depend directly upon the concentration of the oxidant.

Data will be presented illustrating the effects of oxidant concentration on the amount of heat released during these reactions. In addition to the reactions of interest, the presentation will also examine the reactions between the oxidant and other common reducing agents present at remediation sites. How oxidant concentrations radically alter the reaction characteristics and directly affect the hazardous characteristics and conditions that surround the product will be discussed.

POSTER SESSION – CLEANUP STANDARDS

20. Chemical Contamination and Cleanup Standard Setting of Herbicides in Phaiozem of Northeastern China

Qixing Zhou, Chinese Academy of Sciences, Shenyang, P.R. China

20. Chemical Contamination and Cleanup Standard Setting of Herbicides in Phaiozem of Northeastern China

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The phaiozem area is the important base of commercial provisions in China. However, there is a large-scale application of herbicides in the area in order to increase the yield of crops and the productivity of lands in the past decades. It has paid attention to the ecological safety of agricultural soils and the safe quality of crops with the entry of the country into the World Trade Organization. Thus, the current situation of herbicide contamination in phaiozem was systemically investigated. Purification and detoxic function of herbicides in phaiozem was also evaluated on the basis of its eco-toxicological characteristics. It was indicated by the two aspects that contamination of herbicides in phaiozem is now one of the dangerous threats to the quality and health of the soils. The enactment of cleanup standards of herbicides in phaiozem is obviously a matter of great urgency in order to control and remedy contamination of herbicide in the soil. Under the condition of the soil contamination, cleanup standard setting of herbicides in phaiozem was theoretically discussed at four angles: the decision tree of soil-chemical behavior of herbicides, the decision tree of groundwater contamination by hericides, the decision tree of soil enzymes and relevant molecular mechanisms, and the decision tree of ecological effects of herbicides on honeybee, earthworm and sensitive organisms.

POSTER SESSION – ENVIRONMENTAL FATE

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

Michael H. Huesemann, Pacific Northwest National Laboratory, Sequim, WA
Timothy J. Fortman, Pacific Northwest National Laboratory, Sequim, WA
Robert G. Riley, Pacific Northwest National Laboratory, Sequim, WA
Christopher J. Thompson, Pacific Northwest National Laboratory, Sequim, WA
Zheming Wang, Pacific Northwest National Laboratory, Sequim, WA
Michael J. Truex, Pacific Northwest National Laboratory, Sequim, WA
Brent Peyton, Washington State University, Pullman, WA

22. Degradation of Persistent Organochlorine Pesticides in Rhizosphere Soils

XM Zhu, Chinese University of Hong Kong, HK SAR, P.R. China
KC Lam, Chinese University of Hong Kong, HK SAR, P.R. China
S. Tao, Peking University, Beijing, P.R. China

21. 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.

22. Degradation of Persistent Organochlorine Pesticides in Rhizosphere Soils

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Persistent organic environmental contaminants such as HCHs (hexachlorocyclohexanes), DDTs (dichloro-diphenyl-trichloroethanes) and other organochlorine pesticides were widely used before prohibition and distributed globally by transport through air and water. Due to their extensive use in agriculture and industry in the past, environmental contamination with organochlorine pesticides (OPs) has occurred widely.

Evidences for enhanced microbial degradation of xenobiotic chemicals in the rhizosphere have widely reported, suggesting that vegetation may play an important role in facilitating bioremediation of contaminated surface soils. While it is know that these contaminants are more readily degraded or biotransformed by plants or by their attendant rhizosphere microbes in varying degrees, information on the environmental behavior of persistent organic pollutants has been very limited.

This study has been conducted to determine the concentration of r-HCHs and DDTs in the rhizosphere of wheat cultivated in contaminated agricultural soil. The variations of (DDD+DDE)/DDT ratios in rhizosphere and non-rhizosphere soil were significantly different, indicating that the rhizosphere can indeed enhance the DDT degradation in certain degrees. The time trend of (DDD+DDE)/DDT ratios in rhizoshere and non-rhizosphere soil were both evidently increased. The significant differences of concentrations of r-HCHs and DDTs between planted and unplanted soil were not seen, probably due to experimental error or insufficient time for the aging process. Similar trends were also not evident in planted soils as the distance from the plant roots increases. The study only confirmed that the conversion from DDT to DDD and DDE could be enhanced by the presence of plants, however it has not pinpointed which factor plays a more vital role. Observations show that pH was slightly higher in rhizoshere soil than in non-rhizoshere soil. Further studies are needed to elucidate the degradation mechanisms of persistent organochlorine pesticides in the rhizoshere soil environment.

POSTER SESSION – ENVIRONMENTAL FORENSICS

23. Forensic Identification of the Probable Source of PAHs in Sediments at a Suburban Lake

Hector D. Laguette, MA Dept of Environmental Protection, Wilmington, MA
Nicholas P. Corso, Woods Hole Group Environmental Laboratories, Raynham, MA

24. Sourcing Hydrocarbons at Fire Training Areas: A Molecular Characterization of the Combusted and Evaporated Residues of Distillate Fuels

Stephen Emsbo-Mattingly, Battelle Memorial Institute, Duxbury, MA
Scott Stout, Battelle Memorial Institute, Duxbury, MA
Allen Uhler, Battelle Memorial Institute, Duxbury, MA
Kevin McCarthy, Battelle Memorial Institute, Duxbury, MA

25. The Analysis of PCBs in New Bedford Harbor Sediments: Selecting and Optimizing Immunoassay, GC/ECD, and GC/MS Methods Based on Multiple Site-Specific DQOs

Stephen Emsbo-Mattingly, Battelle Memorial Institute, Duxbury, MA
Helen Douglas, Foster Wheeler Environmental Corporation, Boston, MA
Andy Beliveau, U.S. EPA Environmental Services Division, North Chelmsford, MA
Marie Wojtas, U.S. Army Corps of Engineers, Concord, MA
Yixian Zhang, Foster Wheeler Environmental Corporation, Boston, MA
Heather Ferro, Foster Wheeler Environmental Corporation, Boston, MA

26. Fingerprinting Organic Lead Species in Automotive Gasolines and Free Products Using Direct Injection GC/MS

Edward Healey, Battelle Environmental Forensics Investigation Group, Duxbury, MA,
S. Andrew Smith, Battelle Environmental Forensics Investigation Group, Duxbury, MA,
Kevin J. McCarthy, Battelle Environmental Forensics Investigation Group, Duxbury, MA
Scott A. Stout, Battelle Environmental Forensics Investigation Group, Duxbury, MA
Richard M. Uhler, Battelle Environmental Forensics Investigation Group, Duxbury, MA
Allen D. Uhler, Battelle Environmental Forensics Investigation Group, Duxbury, MA
Stephen D. Emsbo-Mattingly, Battelle Environmental Forensics Investigation Group, Duxbury, MA
Gregory S. Douglas Battelle Environmental Forensics Investigation Group, Duxbury, MA

27. Allocation of Commingled Hydrocarbons Derived from Manufactured Gas Plant *versus* Petroleum Handling Operations

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Edward Healey, Battelle Environmental Forensics Investigation Group, Duxbury, MA,
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Stephen D. Emsbo-Mattingly, Battelle Environmental Forensics Investigation Group, Duxbury, MA
Gregory S. Douglas Battelle Environmental Forensics Investigation Group, Duxbury, MA

28. Passive Diffusion Bag Sampler Results from Multiple DoD Installations

John P. Tunks, Parsons, Denver, CO
John Hicks, Parsons, Denver, CO
Javier Santillan, AFCEE/ERT,Brooks AFB, TX
Raphael Vazquez, AFCEE/ERT,Brooks AFB, TX

29. Weight of Evidence Evaluation of Net Sedimentation and Natural Attenuation Rates, Lower Fox River (WI)

Timothy J. Dekker, Limno-Tech, Inc. (LTI), Ann Arbor, MI
Gregory J. Gerstner, Limno-Tech, Inc. (LTI), Ann Arbor, MI
Richard D. McCulloch, Limno-Tech, Inc. (LTI), Ann Arbor, MI
Cynthia P.E. Valente, Limno-Tech, Inc. (LTI), Ann Arbor, MI
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23. Forensic Identification of the Probable Source of PAHs in Sediments at a Suburban Lake

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The presence and distribution of polynuclear aromatic hydrocarbons (PAHs) in the environment are largely a product of the incomplete combustion of petroleum, oil, coal and wood. Anthropogenic sources are the main contributors of PAHs to the environment. Particulates with adsorbed PAHs commonly reach surface water bodies via atmospheric deposition, sewage effluent and surface runoff.

In December 2000, sediment sampling was conducted at Lake Waban, in Wellesley, Massachusetts, as part of an investigation to determine the most likely source of PAHs detected previously in some lake sediment samples. Possible sources of PAHs to Lake Waban were considered to include non-point regional urban deposition and surface runoff, as well as historical releases of petroleum products at a private property that adjoins the lake. In addition to sampling within Lake Waban, sediment samples were also collected at various upstream locations to characterize local upstream conditions regarding the presence of PAHs in sediments. Alkylated PAHs analysis was conducted on all the sediment samples. The review of the analytical results relied on the following lines of evidence to determine the most likely source of the PAHs in the lake sediments: 1) comparison of the analytical results from the upstream and the Lake Waban sediment sampling locations; 2) relative abundances of petrogenic and pyrogenic PAHs in the sediment samples; 3) ratio of fluoranthene:pyrene in the sediment samples; and 4) normalization of analytical results to organic carbon content and to hopane in the sediment samples.

Based on the analytical results for the sediment samples and on the lines of evidence considered in the investigation, most of the PAHs present in the sediment samples from Lake Waban are likely of a pyrogenic nature. However, some varying amounts of petrogenic contamination also appear to be present in the samples. In addition, it is likely that the PAHs detected in the Lake Waban sediment samples are the result of various contributing sources. These sources may include fires, atmospheric deposition and stormwater outfall, biogenic processes, runoff from nearby roads and a railroad bed, and parking lot runoff and historical and recent fuel oil releases from the private property adjoining the lake. PAHs were also detected in the sediment samples collected upstream of Lake Waban, with a predominance of pyrogenic species.

24. Sourcing Hydrocarbons at Fire Training Areas: A Molecular Characterization of the Combusted and Evaporated Residues of Distillate Fuels

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The use of petroleum accelerants at fire training areas was common prior to the 1970's. Typical accelerants included gasoline, kerosene, and diesel. Specialized fire training exercises occasionally employed heavier petroleum products, like residual fuel and crude oils. Consequently, the wide range of potential petroleum and combustion products at fire training areas presents complicated issues for parties interested in fate and transport, risk assessment, and environmental forensics.

Petroleum distillates can retain source signature information after severe environmental weathering. In this study, kerosene and diesel reference samples were independently weathered to approximately 50% and more than 90% by mass using evaporation and combustion. These reference samples were compared to field samples that contained severely degraded petroleum of unknown origin. The environmental forensic methods used for this study focused on petrogenic volatiles (paraffins, isoparaffins, aromatics, naphthenes, olefins) and semivolatiles (alkylated PAH, alkanes, alkylcyclohexanes, sesquiterpanes, triterpanes, steranes). The interpretive techniques included chemical fingerprinting, principal components analysis (PCA), and diagnostic ratios. Collectively, the forensic analyte list and interpretive tools identified the likely origins of multiple weathered petroleum found at the site.

25. The Analysis of PCBs in New Bedford Harbor Sediments: Selecting and Optimizing Immunoassay, GC/ECD, and GC/MS Methods Based on Multiple Site-Specific DQOs

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Electrical capacitor manufacturing plants released polychlorinated biphenyls (PCBs) into New Bedford Harbor (NBH) between the 1940s and 1970s. Past studies characterized the PCBs as mixtures of Aroclors 1242 and 1254 in variable states of degradation. A dredge design plan is under development for the delineation and remediation of PCBs in this 1000-plus acre water body relative to four cleanup goals established to protect a range of environmental receptors pursuant to the EPA the Record of Decision (ROD) of 1998. This large-scale sediment delineation program required the use of multiple analytical methods for the dual purposes of maximizing data usability for site-specific data quality objectives (DQOs) and minimizing analytical costs.

Immunoassay screening methods (EPA 4020) were used to identify samples with concentrations near the ROD cleanup levels and recover costs associated with the analysis of very clean or very contaminated sediment samples that might otherwise have been needlessly analyzed by more expensive methods. Gas chromatographic (GC) methods were used when higher levels of precision and accuracy were required. The majority of these PCB measurements were performed on a gas chromatograph equipped with an electron capture detector (GC/ECD, EPA 8082) calibrated for commonly occurring PCB congeners identified by the National Oceanic Atmospheric Association (NOAA). However, the potential for site-specific PCB compositions necessitated the confirmation of total PCB concentrations using a GC equipped with a low-resolution mass spectrometer (GC/MS, EPA 8270) and calibrated for PCB homologues in order to monitor potential bias.

This study presents the results of more than 4,000 samples analyzed by for NOAA PCB congeners with comparisons to approximately 450 immunoassay and 200 PCB homologue results. These data demonstrated a poor correlation between the immunoassay and NOAA PCB congener methods ($PCB_{Immunoassay} = 1.9 \text{ x } PCB_{\square NOAA} + 0, R^2 = 0.5$). However, the immunoassay data proved very useful when used in conjunction with a decision tree that properly managed the inter-method variability relative the site-specific DQOs. By contrast, a good correlation existed between the NOAA PCB congener and PCB homologue methods ($PCB_{\square Homologue} = 2.6 \text{ x } PCB_{\square NOAA} + 0, R^2 = 0.9$). These relationships helped data users employ field and fixed laboratory methods at frequencies appropriate for the minimization of costly analyses (EPA 8082 and EPA 8270) and maximization the chemical information needed for developing the dredge design plan for NBH in accordance with the ROD.

26. Fingerprinting Organic Lead Species in Automotive Gasolines and Free Products Using Direct Injection GC/MS

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Automotive gasoline has a long and complex history of compositional change. Increasingly sophisticated refining techniques and performance enhancing additives have helped the US gasoline pool keep pace with the needs of the auto industry and the requirements of regulatory agencies. Among the most important additives in the evolution of automotive gasoline was organic lead, specifically tetraethyl lead (TEL). TEL was first introduced into automotive gasolines in 1923 as an antiknock agent. TEL was the lone organic lead compound added to automotive gasoline until 1960, when tetramethyl lead (TML) was formulated, and various lead 'packages' were developed and introduced to the gasoline market. Packages included both physical mixtures (PM) and reacted mixtures (RM) of TEL and TML. Reacted mixtures are the end products of a catalyzed TEL: TML reaction that results in the formation of five organic lead species: tetramethyllead (TML), trimethylethyllead (TMEL), diethyldimethyllead (DEDML), methyltriethyllead (MTEL), and tetraethyllead (TEL). TEL use, followed by RM and PM usage, increased steadily over time as the demand for increased engine performance and fuel economy grew. Ultimately, the average levels of lead in the premium gasoline pool reached a high of approximately 3.0 grams lead per gallon (glpg) around 1970. After 1970, Federally-mandated restrictions (1970 Clean Air Act and 1990 Clean Air Act Amendment) led to a systematic reduction in the maximum allowable lead levels and the introduction of low-lead and unleaded gasolines, culminating with a complete elimination of organic lead additives in automotive gasoline in the U.S. in 1996 (1992 in California).

This poster will describe a specialized analytical method used in the molecular characterization of the five organic lead species found in historic automotive gasolines. The analytical method includes quantitative high-resolution gas chromatography (GC) with mass spectrometry (MS) detection in the selected ion monitoring mode following adaptations of EPA Method 8270. The analysis is performed using a direct injection technique for gasoline and free phase petroleum. Interpretive forensic techniques, utilizing the organic lead results generated with this method will be discussed. Two case studies where organic Pb fingerprinting, used in conjunction with conventional gasoline fingerprinting, was useful in determining liability at historic gasoline contaminated sites will be presented.

27. Allocation of Commingled Hydrocarbons Derived from Manufactured Gas Plant *versus* Petroleum Handling Operations

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Environmental forensic investigations routinely involve characterizing industrial sites that have a complex and multi-use history. In the case of hydrocarbon contamination, many industrial sites' histories often parallel the Nation's energy history, particularly the shift in our reliance from coal to petroleum, including natural gas. As a result, environmental forensic investigations of industrial properties where (or near) historic (~1870's to 1940's) manufactured gas plants (MGPs) that subsequently were used to handle petroleum, are common. Such investigations are often focused on distinguishing hydrocarbons derived from the residues and by-products of MGP versus those derived from petroleum operations. Although hydrocarbons from these two source categories can be readily distinguished by using conventional hydrocarbon fingerprinting techniques (e.g., alkylated PAH and biomarker analysis), the commingled character of MGP wastes and petroleum at many sites can complicate allocation of any liability for clean-up or damages. Unraveling these mixtures based upon the mass, volume, or percent of soil impacted by hydrocarbons from MGP wastes versus those derived from petroleum, can provide a fair basis for successfully resolving liability.

In this study, a novel analytical method and the interpretive techniques used to accurately allocate hydrocarbon sources when faced with commingled materials at a contaminated site is described. The analytical method relies upon quantitative high-resolution gas chromatography (GC) with simultaneous flame ionization detection (FID) and mass spectrometry (MS) detection. Known incremental mixtures of fresh and weathered coal tar and diesel fuel #2 (commonly encountered hydrocarbon mixtures) were prepared and analyzed using this combination of detection techniques. Various integrations and ion extraction techniques were evaluated and the resulting hydrocarbon masses were compared to the known starting percentages. The optimal method(s) for 'unmixing' these known mixtures using the multiple detection techniques was identified and compared to the results that could be obtained from each detection method used alone. The advantages of the simultaneous FID and MS detectors, and shortcomings of their individual use alone, will be presented and discussed. The results of the laboratory 'mixing' study are then applied to a field case study where soils have been impacted with both coal tar and petroleum contamination.

28. Passive Diffusion Bag Sampler Results From Multiple DoD Installations

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Groundwater sample collection using passive diffusion bag samplers (PDBSs) represents a relatively new technology that employs passive sampling methods for monitoring volatile organic compounds (VOCs) in groundwater. The potential benefits and cost savings associated with using PDBS for long-term monitoring are significant, as no purge waters are generated, and labor requirements for sampler installation and retrieval are minimal. Results of a field-scale PDBS demonstration performed at 14 Department of Defense installations between May 2001 and February 2002 will be presented. The primary objective of the PDBS demonstration is to assess the effectiveness of the PDBS method by comparing groundwater analytical results for VOCs obtained using the current (conventional) sampling method with results obtained using the PDBS method. The comparison of the conventional and diffusion sampling results will allow assessment of the appropriateness of implementing diffusion sampling for VOCs at each sampled well. Details will include a general description of the work performed, the common findings for all installations sampled, and an analysis of the effectiveness of the technology. If possible, a list of operational parameters that promote the usability of PDBS, and a list of operational parameters that indicate when poor performance is likely to occur will be presented. A cost and performance analysis also will be developed that includes implementation costs, cost comparison to conventional sampling, sampling cost avoidance generated by PDBS, and a return on investment assessment.

29. Weight of Evidence Evaluation of Net Sedimentation and Natural Attenuation Rates, Lower Fox River (WI)

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Human health and ecological risks from sediment contamination depend on future exposure levels. In order to make accurate long-term predictions of exposures, it is important that models be consistent with long-term trend data, as well as short-term correlations between flows and concentrations. Remedial decisions may also hinge on evaluations of sediment stability. Stability evaluations often employ sediment transport models, but should also be grounded in empirical measurements. A recent sampling program provides both types of information for the Lower Fox River, Wisconsin. (A Preliminary Remedial Action Plan for this site, released by the Wisconsin Department of Natural Resources in 2001, proposes removal of 7.25 million cubic yards of PCB-contaminated sediment.) The sampling program included: regular monitoring of water-column PCBs and solids at 17 stations along the river for one year, with intensive sampling during a spring high-flow event; resampling of surface sediments for PCBs at locations sampled at depth 5 to 6 years previously; and analysis of Cesium 137 profiles from 41 high-resolution sediment cores. The results of sediment and water-column analyses indicate natural attenuation PCB half-times in the range of 7 to 9 years for the water column and 17 to 22 years for sediment. Radioisotope profiles indicate areas with significant inventories of PCBs to be predominantly depositional, with some disturbances found along a former dredged navigation channel. Contemporary Army Corps of Engineers bathymetric data also showed little sediment movement, outside the range of uncertainty inherent in those methods. These results have been used to constrain the performance of FoxSim, a model of PCB fate and transport, in simulating potential future exposures.

POSTER SESSION – HEAVY METALS

30. Heavy Metal Distribution in Sediment Profiles along the Adyar River, Tamil Nadu, India

Hema Achyuthan, V. Dhinakaran, K. Selvaraj Kumar, and S. Srinivasalu
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2. Dept. of Geology, University of Madras, Chennai

31. An Investigation into the Inhibitory of Lead and Nickel on the Mineralization of Hydrocarbons in Soil

Esmaeil S. ALSaleh, Kuwait University, AL-Safat, Kuwait
Ms Hana F. Drobiova, Kuwait University, AL-Safat, Kuwait
Dr Husain A. AL-Awadhi, Kuwait University, AL-Safat, Kuwait
Dr Christian Obekwi, Kuwait University, AL-Safat, Kuwait

32. Integrated Pathway Models to Refine Arsenic and Selenium Concentration Estimates from a Proposed Fly Ash Mono-Fill Re-use

Jeffrey A. Berk, URS Corporation, Cleveland, OH
Joanna Moreno, URS Corporation, Denver, CO

33. Remediation of Lead Shot Contaminated Soils on Residential Properties in Southeastern Massachusetts

Dan Crafton, MA DEP, Lakeville, MA
Mark Begley, MA DEP, Boston, MA
Mike Whiteside, MA DEP, Lakeville, MA

34. Analysis of Heavy Metals and Inorganic Anions from Stormwater Runoff in Two Taunton River Tributaries

Cielito M. DeRamos-King, Bridgewater State College, Bridgewater, MA
Janelle Breton, Bridgewater State College, Bridgewater, MA
Joseph Worrall, Bridgewater State College, Bridgewater, MA

35. Sorption of Heavy Metals on Mineral and Organic Fractions of Contaminated Sludge Lagoon Sediment

Lindy Hartley, University of Toledo, Toledo, OH
Alison L. Spongberg, University of Toledo, Toledo, OH
Deborah A. Neher, University of Toledo, Toledo, OH

36. Addressing Multiple Sources of Lead Exposure with a Community-Based Envrionmental Health Program

Kathy Tegtmeyer, MFG, Inc., Boulder, CO
Amy Morrison, MFG, Inc., Leadville, CO
Bob Litle, Asarco Incorporated, Denver, CO

37. Heavy Metal Uptake by Basil (*Osimum basilicum* L.) Grown on Metal Polluted Soils

Valtcho Zheljazkov, Nova Scotia Agricutural College, Truro, NS, Canada
Andrew Wilcox, Harper Adams College, Newport, Shropshire, UK

38. Mercury in Compost-Soil-Plant System

Valtcho Zheljazkov, Nova Scotia Agricutural College, Truro, NS, Canada
Michael Munroe, Nova Scotia Agricutural College, Truro, NS, Canada

39. Interactions Between Cadmium and Other Heavy Metals (Lead, Copper, Zinc and Arsenic) in Soil-rice Systems of Liaoning Province, China

Qixing Zhou, Chinese Academy of Sciences, Shenyang, P.R. China
Xin Wang, Chinese Academy of Sciences, Shenyang, P.R. China
Yanyu Wu, Chinese Academy of Sciences, Shenyang, P.R. China

30. Heavy metal distribution in sediment profiles along the Adyar River, Tamil Nadu, India

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In recent years, massive economic growth and development has led to excessive release of waste into the environment. The study of sediment profiles can provide much information on the spatial extent and vertical distribution of metal contamination. In this study seven cores of varying lengths were collected from various sites in the Adyar drainage basin. Adyar river is 42 kms long, originating from the Malaipattu tank and draining into the Bay of Bengal. Sediment samples were analyzed for organic matter, CaCO3% and Trace Metal content. The data reveals that there is an increase in the heavy metal concentration in the mouth of the river. The concentration of Ni increases towards the estuary. The amounts of Zn, Pb and Mn fluctuates revealing no particular pattern. Cadmium and cobolt are present in less amounts in the top sediments of the cores samples analyzed but decrease significantly below 60 CMS with depth at the Adyar estuary. To understand the effect of the drainage on the any landscape, geomorphic and morphometric analysis were carried out using the SOI toposheets. The analysis revealed that the river is controlled by the lithology and does not have any major structural control. Wherever the river is flowing over the softer rocks of Gondwana shales and sandstone, it has a narrow channel with a thick column of sediments. The channel width is larger with a thin veneer of sediments when the river flows over the Charnockite rock. The tolerance capacity of the vegetation along the river was studied by testing the stems and leaves of plant species, Mimocea Juliflora. The plant pattern of distribution reveals significant correlation to the trace metal influx of the river. These plants show higher tolerance to the accumulation of Ni at the Adyar estuary and hence their prolific growth at this site. The plants are fewer in number towards the origin of the river probably because of less concentration of Ni and Zn, which get mobilized due to the drainage processes.

31. An Investigation into the Inhibitory Effects of Lead and Nickel on the Mineralization of Hydrocarbons in Soil

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It has been estimated that a total of 50 Km^2 in Kuwait contain high concentrations of crude oil. High levels of lead and nickel were also detected in AL-Douha site. Respirometry assay was used to determine the tolerance of soil bacterial communities to Ni, and Pb. Hydrocarbon contaminated and uncontaminated soils were amended with individual metals at three different concentrations, and the results were compared with the results obtained by using the plate count technique. Respirometry was found to be a simple and rapid method for measuring community metal tolerance. Data obtained by this technique were very reproducible. A direct relationship was found between community metal tolerance levels obtained by respirometry and plate count techniques. An increase in tolerance to the lead nitrate added to soils was observed for the bacterial community obtained from hydrocarbon uncontaminated soil compared with the community obtained from contaminated soil. When nickel sulphate was added to soils; no indication of increased Ni tolerance in hydrocarbon contaminated soil was found. The results indicated higher tolerance to lead nitrate at the community level of both soils compared to nickel sulphate. In addition, lower rates of hydrocarbons (hexadecane, nonadecane, naphthalene, pheneathrene and crude oil) and glucose mineralization were measured in nickel amended soils compared to that in lead amended soils. These results were confirmed by GCMS and HPLC assays. Further respiration and measurements of population growth rates (□) of soil suspensions showed similar results confirming that metal adsorption to soil components was not a limiting factor and indicated that the lower rates of hydrocarbons degradation in nickel amended hydrocarbon contaminated and uncontaminated soils compared to lead nitrate amended soils were probably due to available nickel salts, other inorganic constraints and not to presence of hydrocarbons. In addition, Physical and chemical characterization of both soils revealed similar soil characteristics except for the elevated levels of hydrocarbons and Pb in the contaminated soil. These results are discussed in relation to the potential bioremedial options of the contaminated site.

32. Integrated Pathway Models to Refine Arsenic and Selenium Concentration Estimates from a Proposed Fly Ash Mono-Fill Re-use

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The proposed use of 1.5 million tons of fly ash as structural fill was evaluated on behalf of a confidential client to determine if leachate resulting from the structural fill would adversely impact groundwater at hypothetical downgradient drinking water wells. The approach used in the investigation included the integration of four models (VLEACH, HELP, MT3D, and MODFLOW) to evaluate several inorganic metals (primarily arsenic and selenium) contained within the fly ash. The HELP model was used to establish an infiltration rate from the base of the disposal area to the aquifer. This rate, along with laboratory-measured leachate concentrations and the physical characteristics of the natural soil, were used in VLEACH to evaluate the attenuation of the metals entering the aquifer. MODFLOW was used to construct a two-dimensional groundwater flow model extending to downgradient hypothetical receptors at assumed exposure points. Reduction in contaminant mass by the attenuation capacity of the aquifer was evaluated by using MT3D. The integrated models were used to simulate the mass loading and its cessation after 130 years. At this time, the fly ash would be depleted of leachable metals. The integrated models predicted that a maximum of approximately 2 percent of the arsenic's and 10 percent of the selenium's initial leachate concentrations would reach the exposure points. These results were used to select an appropriate ratio of fly ash to amendments (either cement or lime kiln dust) to ensure that drinking water Maximum Contaminant Levels (MCLs) would not be exceeded at the assumed exposure points.

33. Remediation of Lead Shot Contaminated Soils on Residential Properties in Southeastern Massachusetts

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Field screening and laboratory analysis of surficial soils revealed lead contamination as high as 42,000 parts per million (ppm) on residential properties developed in the drop zone of a former trap range. Initial assessment focused on the area of the estimated drop zone where exposure risk was high, specifically, the transition from woodlands to landscaping, and native soils buried beneath the landscaping. Field screening downgradient and outside of the estimated drop zone revealed migration of lead via storm water runoff. The assessment delineated approximately 3 acres of surficial contamination on 5 residential properties.

In July of 2001, the Massachusetts Department of Environmental Protection began removal of lead contaminated soils from the residential properties. The removal plan included removal of all underbrush and small trees, excavation of the upper 6 to 8 inches of soil, the use of a vactor to remove contaminated soils in around the roots of remaining trees, and very limited excavation of lawn areas. Within the first week of removal activities, the removal plan was modified, due to site specific characteristics, to include removal of the majority of the trees, excavation to depths of 3 feet in some areas due to numerous rocks and boulders, and extensive excavation of lawn areas. A vactor was used to remove lead contaminated soils from the root zones of the few remaining trees. As the removal progressed, field screening with an X-ray Florescence Spectrum Analyzer (XRF) was done to confirm removal. Contaminated soils were reused on the Club_s property to construct a shooting berm in the drop zone of the active trap range.

34. Analysis of Heavy Metals and Inorganic Anions from Stormwater Runoff in Two Taunton River Tributaries

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Stormwater runoff is one of the leading causes of contamination of the nation's rivers, lakes and estuaries. Impaired rivers and streams threaten aquatic life, fish consumption, recreational activities and drinking water supplies. Metals, siltation, bacteria and nutrients (nitrates and phosphates) are among the major pollutants causing water quality problems. Some heavy metals, such as cadmium, lead, mercury, chromium and zinc, are toxic to plants and animals at very low levels. Inorganic anions, such as nutrients and chloride, also contribute to water quality impairment. Excessive levels of nutrients lead to algal blooms and reduce the supply of dissolved oxygen, which results in fish kills. Both nutrients and chloride are potentially harmful to human health at excessive levels. Preliminary studies of heavy metals and inorganic anions from storm water runoff into two Taunton River tributaries were conducted during summer 2001. Our results reveal river sites that have levels of lead and cadmium above what are considered protective for aquatic life. Nutrient levels also increased during rain events at both sites, while chloride levels remained relatively unchanged, except in one storm drain. This drain had chloride levels ten times than that of the adjoining river. Furthermore, the drain discharges in dry weather, indicating a possible point source of pollution. This study will provide information that will help the town of Bridgewater meet Stormwater Phase II regulations.

35. Sorption of Heavy Metals on Mineral and Organic Fractions of Contaminated Sludge Lagoon Sediment

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Phytoremediation has been proposed as an cost-effective technology to alleviate contamination at the many Brownfield sites in metropolitan areas, such as Toledo, Ohio. The goal of the proposed study was to determine the feasibility of using resident plants to remove heavy metals from contaminated soils at an industrial site in Northwest Ohio. A 2-ha field site was characterized for depth profiles (25 cm intervals) of heavy metal concentrations by analyzing 11 cores (1.5 to 3.0 m total depth). The site had previously been used to dump heavy metal contaminated sludge and other industrial waste. Typically, concentrations of zinc, copper, chromium, and nickel decreased, and manganese increased, with increasing depth. Cadmium was absent in most cores, and no trend with depth was observed when present. Representative plant species growing on the site were harvested, divided by organ (fruit, stems, leaves, and roots), and analyzed for heavy metal concentration four times during the 2000 growing season. Concentrations in certain species were elevated compared to those growing on uncontaminated soils. We hypothesize that plants translocate these metals from deep soils during the growing season and deposit them on the soil surface when they die. Sorption characteristics of the lagoon soils demonstrate weak retention capabilities of the mineral fraction. After reaching equilibrium, sediments retained about half the metals than that of local soils. Desorption experiments also indicate a rapid loss of these sorbed metals. Currently being run are similar analyses of the upper sediment fraction, that is relatively rich in root and other plant biomass.

36. Addressing Multiple Sources of Lead Exposure with a Community-Based Environmental Health Program

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An integrated environmental remediation and community health program, known as the Lake County Community Health Program, was selected as the remedial action for residential areas within the California Gulch CERCLA Site (Colorado). The site was the location of extensive mining and smelting operations for more than 100 years. Various site investigations performed during the 1980s and 1990s revealed more than 5,000 ppm lead in some residential soils, and an environmental health study performed in 1991 indicated elevated blood lead levels in some resident children.

The integrated program has been in place in some form since 1994, and to date more than 200 families with young children have participated voluntarily. The program provides blood lead testing and case-management services to young children as well as environmental testing for potential sources of lead exposure, including yard soil, indoor dust, paint and drinking water. Rather than focusing on yard-soil remediation, as is typical for mining communities, this approach allows for case-by-case evaluation of numerous exposure and risk factors to develop appropriate risk-reduction actions for individual residences. The program then completes response actions to address potential sources of lead exposure.

Since 1994, the percentage of young children with elevated blood lead levels (above 10 µg/dL) has dropped by 50 percent, and the community-average blood lead level (geometric mean) has decreased by 15 percent. The remedial actions completed to date are relatively few (<5% of residences) and therefore not likely to be the only factor contributing to lower blood lead levels in the community. The combination of outreach and education programs, availability of blood lead testing and health services, completion of remedial actions in non-residential areas of the site, and the various factors that have produced a steady decline in blood lead levels nationwide are all likely contributors to the observed improvement in blood lead levels.

37. Heavy Metal Uptake by Basil (*Ocimum basilicum* L.) Grown on Metal Polluted Soils

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A container experiment was conducted to study the effect of heavy metal polluted soil on productivity and quality of the basil varieties Trakia and Mesten (*Ocimum basilicum* L.). Soils were sampled from the vicinities of a smelting plant near Plovdiv, Bulgaria at distances of 0.5, 3, 6, and 9 km from the smelter. The two cultivars of basil were grown under standard and controlled conditions on the collected soil samples.

Heavy metal concentration in soils was greatest close to the smelter. Nitric acid extractable Cd, Pb, and Cu in soil at 0.5km distance were higher than their critical concentrations in soil. Heavy metal concentration in plants was correlated to HNO_3 extractable metal concentration in sols. Different plant parts (roots, leaves, inflorescences, stems) contained various amounts of Cd, Pb, Cu, Mn, and Zn. Herbage and essential oil yields of plants grown in soil taken at 0.5 km from the smelter were reduced compared to yields from soils taken at 3, 6, and 9 km from the smelter. Soils taken at 3 and 6 km of the smelter did not influence herbage and essential oil productivity. Despite metal accumulation in aboveground tissue, essential oils from all treatments were not contaminated wtih heavy metals. Plants grown on soils from various distances from the smelter showed some variation in essential oil composition. The tested cultivars of basil could be successfully grown on heavy metal polluted soils without contamination of the essential oil and any major changes in oil quality.

38. Mercury in Compost-Soil-Plant System

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The paper discusses Hg movement in soil-plant-system, maximum permissible Hg concentration in compost in different countries, and the relevance of Canadian guidelines for maximum Hg concentration in composts.

Currently, the Canadian guidelines for maximum trace element concentration allow maximum of 0.8 and 5 mg/kg air-dried mass of mercury in type AA and A compost and B compost, respectively (CCME 1996). These are the lowest concentration of any trace element in composts subject to control by CCME 1996. Before the acceptance of national standards, Ontario and Alberta provincial guidelines for compost A were even more stringent; the values for Hg were 0.15 and 0.2 mg/kg, respectively.

These relatively low maximum permissible concentrations for Hg in compost may restrict the use of compost thus, may encourage incineration and landfilling. Research has been shown that the mean values for Hg in 14 samples of composts from Europe to be 0.9 mg/kg, the range being 0.17 to 3.8 mg/kg. Even source-separated composts in North America have mean concentrations of 1 mg/kg. That means the Canadian guidelines in this respect would be difficult to meet, that is they may be not practically feasible. Introducing of 1 or 2 more classes of composts (such as in Finland) to allow wider range of Hg concentration in the composts may eliminate this problem.

39. Interactions Between Cadmium and Other Heavy Metals (Lead, Copper, Zinc and Arsenic) in Soil-rice Systems of Liaoning Province, China

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Influences of interactions between Cd and other heavy metals (Pb, Cu, Zn and As) on the growth and development of rice plant and the absorption of these heavy metals by rice were studied using the pot-culture method combined with chemical measurement and statistical analysis. The results showed that the growth and development of rice plants were strongly influenced by double-element combined pollution. The decrement in the height of ripe rice plant was up to 4-5 cm, and the yield of rice was decreased by 20-30%, compared with those used for the control condition. The absorption of Cd by rice tissues was promoted due to interaction between Cd and Pb, Cu, Zn or As when added to the tested soil; in particular, when the concentration of Cd added into the tested soil was equal to 1.5 mg kg^{-1}. The increment of Cd in roots, stems/leaves and seeds was up to 31.6-47.7, 16.69-61.5 and 19.6-78.6 %, respectively. The absorption of Pb, Cu and Zn in roots, stems/leaves was inhibited due to the addition of Cd, when concentrations of Pb, Cu and Zn added to the tested soil were equal to 300, 100 and 200 mg kg^{-1}, respectively. The decrement of Pb, Cu and Zn in roots was 42.11, 28.22 and 6.66% and the decrement of Pb, Cu and Zn in stems/leaves was 17.69, 3.75 and 2.54%, respectively. On the other hand, the accumulation of Pb, Cu and Zn in seeds was increased due to the interaction between Cd and the other heavy metals. When the concentration of As added to the tested soil was 30 mg kg, the absorption of As by roots was increased by 9.8% and the absorption of As by stems/leaves was reduced by 3.25% due to the addition of Cd. The upward transporting ability of the heavy metals absorbed by rice plant was increased due to interaction of the heavy metals.

POSTER SESSION - MISCELLANEOUS

40. Electronic Data Management in RCRA Project- A Case Study

Sandeep Ganesh, URS Corporation, Cranford, NJ
Joshua A. Jaffe, Harding ESE, Edison, NJ

41. Application of Saline Wastewater for Production of Agricultural Crops

Esmaiel Malek, Utah State University, Logan, UT
Bradley Giles, Utah State University, Logan, UT

42. Introducing Water Catchment Quality Control into Urban Development Policy in Cameroon (A Case Study of the Municipal Lake in Yaounde)

Francis Ngwa Niba, CEI/CAM, Douala Cameroon

40. Electronic Data Management in a RCRA Project - A Case Study

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The manner in which data is gathered, generated, stored and presented during the course of an Environmental Remediation project has been undergoing a sea change. This is due in no small part to the advances in Information Technology and its manifestations in the Environmental Science and Engineering arena. The present document discusses these Electronic Data Management methodologies as applied in an ongoing RCRA (Resource Conservation and Recovery Act) project. The site is in central New Jersey and is currently an asphalt production plant for a large oil company. The broad objectives of the ongoing environmental effort at the site are – preparing parts of the 360 acre property for sale (Brownfield Re-development) and stabilizing the rest of the property under the USEPA and the state's RCRA guidelines. The field tasks include - soil and groundwater sampling (quarterly), excavation monitoring, stockpile sampling, and Free Product and dissolved phase monitoring. Management standards have been instituted for data collection, storage, sample naming conventions, forms and logs, and sample location names. A database tracking system has been established to account for daily field activities including sample collection and chains of custody. A Relational Database Management System (RDBMS) is being used effectively in conjunction with a Geographic Information System (GIS) to store and analyze the data, and to output information in the form of maps, tables, charts and reports with minimal effort. Customizing and deploying such a system however takes a high level of commitment from the entire project team. Faulty system designs, software problems, and non-adherence to procedures can lead to significant problems. Once in place the Electronic Data Management System has reduced errors, saved time and costs, and most important of all – established data integrity.

41. Application of Saline Wastewater for Production of Agricultural Crops

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Saline wastewater coming from the coal fired power plants owned and operated by PacifiCorp (Utah Power), has applied to the Hunter Research Farm in central Utah, U.S.A., since 1987, or irrigation of various agricultural crops such as alfalfa, wheat, barley, etc. Researchers from Utah State University (USU), Brigham Young University (BYU), and PacifiCorp are involved in this multipurpose project. The primary goals of this research are to maximize crop production and evapotranspiration, while not allowing surface runoff to natural streams or leaching to groundwater. Salinity of the wastewater is about ten times that of the nearby river.

We used the water balance approach, along with the continuous measurements of weather parameters (including precipitation), irrigation (using the sprinkler system), and change in the root zone soil moisture contents (using the neutron probe) to study evapotranspiration (using the Bowen ratio system) throughout the years (1987 - 2001). The results show that the soil moisture contents in the root zone and beyond are slightly lower at the end of the irrigation season (mid November) compared to that measured in the beginning of the season (mid April). This indicates that all saline wastewater applied plus precipitation were consumed by crops. Also, the results indicate that by monitoring the amount of irrigation during the past 15 years, no surface runoff or deep percolation has occurred.

42. Introducing Water Catchment Quality Control into Urban Development Policy in Cameroon (A Case Study of the Municipal Lake in Yaounde)

***Francis Ngwa Niba**, CEI/CAM, via Akem F F, Box 5792, Douala Cameroon*

The contamination of water catchment regions within urban settlement in Africa with particular reference to Cameroon is a problem and takes an epidemic proportion when the same topic is treated in the principal urban zones. In our abstract the Municipal Lake of Yaounde, located in the heart of the administrative capital of the country is taken for a case study.

For a historical review, I have exposed memories of this lake (a natural endowment) more than two decades ago, when it was an economic, social, health and ecological resort. On the other hand, I have examined the lake from about 20 years ago, with out mincing words, from when the general hospital, some Ministerial blocs and a four star hotel (Hotel Des Deputes) dumped all their sewage into the lake. This done by the use of conduit pipes to channel wastewater and solid objects into the lake, thus rendering the site an economic waste, social and health risk. A third part of this abstract start from 1990 when thanks to the introduction of the Liberty Laws amongst which granted individuals or groups of individuals the right to form political parties and other Associations, NGO inclusive, it resulted in some positive changes.

The impact of the creation of NGO for environmental issues as assisted by the coming into force of this general text on Associations goes a long way to prove my reason for a clamour for particular legislation on aspects like Water, soils etc. This I back by the point that due to combine pressure from some NGO, an unusual decision has just been taken by the government. In the decision the government has compelled the said Hotel Des Deputes which is the principal pollutant to pay for remediation cost, and is currently undertaking a sewage disposal project for both the general hospital and the ministerial complex. The lake and its peripheral areas also going to get a face-lift, but until environmental legislation is enacted this effort may not go a long way to assist the general contamination rate of the Country. I think if Cameroon had particular legislation on this, it would go along way to remedy this situation nation-wide.

As conclusion, I have proposals for Non Governmental Associations on the one hand and Government Environmental officers dealing with water and their catchment areas on the other. I attempt what I should call the way forward by opting for some social, economical and ecological reforms that should be carried around this lake. Propose a working ethics for those handling situation of this nature and another code for water quality and quantity control in both urban and rural areas as well as laws on other environmental aspects

Poster Session - MTBE

43. Microbial Bioremediation of Methyl-tertiary-Betyl-Ether (MTBE)

Diana R. Cundell, Philadelphia University, Philadelphia, PA
William H. Brendley, Philadelphia University, Philadelphia, PA

44. Determining the Extent of Gasoline Oxygenate Additive Impacts with in a Rural Bedrock Water Supply Aquifer

A. Lee Gustafson, Harding ESE, Inc., Merrimack, NH
Thomas W. Lazott, Harding ESE, Inc., Merrimack, NH
Jeffrey K. Harshman, Harding ESE, Inc., Merrimack, NH
Mark Ledgard, State of New Hampshire Department of Environmental Services, Concord, NH

45. Risk-Targeted Remediation for MTBE-Impacted Gasoline Stations

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William B. Kerfoot, K-V Associates, Inc., Mashpee, MA
David J. Vossler, Gettler-Ryan, Inc., Petaluma, CA

43. Microbial Bioremediation of Methyl-tertiary-Butyl-Ether (MTBE)

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MTBE is a highly water-soluble, gasoline oxygenate that has been found in over 250,000 contaminated sites, many involving leaking underground storage tanks. The compound is also a suspected carcinogen and adds both odor and taste to water and the challenge therefore has been how to safely clean up MTBE, which has such easy access to a variety of environmental niches.

MTBE bioremediation was attempted using commercially obtained *C. acidophilus* and *E. mutabilis* grown in Chlamydomonas and AlgaGro growth medium, respectively with the species also being co-cultured in AlgaGro. MTBE was added in concentrations of 125 -10,000 ppm (vol/vol). Algal numbers, percentage motility and viability were assessed daily for one week using standard microscopy techniques.

E. mutabilis numbers increased in direct proportion to the levels of MTBE (r = 0.97; 7 days of incubation 169 cells in 10,000 ppm MTBE compared with 61 cells in media alone/ microscope field). Similar effects were seen on *C. acidophilus* with lower MTBE concentrations (<2500 ppm): higher concentrations decreased growth to below control values (after 7 days; 104 cells/ microscope field in media alone and 12 at 10,000 ppm MTBE, respectively). Co-culture of the two algae (1:1 ratio) resulted in a dramatic increase in *C. acidophilus* at concentrations of >1250 ppm with *E. mutabilis* numbers increasing at all MTBE concentrations. This resulted in a total of ~ 500 living protists/ microscope field after 7 days of co-culture in 10,000 ppm of MTBE, compared with 239 in media alone (157% increase).

These studies suggest that levels of MTBE up to 250,000 times those recommended by the EPA, may be naturally removed by at least two species of algae. Further studies are underway to investigate additional combinations of the two algae for bioremediant ability and to identify other organic molecules that may be removed by these organisms.

44. Determining the Extent of Gasoline Oxygenate Additive Impacts within a Rural Bedrock Water Supply Aquifer

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Until recently, rural area water supply wells were not as quickly and widely impacted by gasoline-related releases to the environment as they are today. Undoubtedly, releases of gasoline to the environment potentially occur every day since even the most rural settings involve the use of gasoline storage mechanisms prone to inherent leaks or spills (e.g., regulated underground storage tanks, farm and residential storage tanks, homeowner gasoline-powered machinery, and automobile usage or accidents). Still, the traditional strategies and technologies to characterize and remediate such releases have proven to be efficient and cost-effective while reducing any associated human health or ecological risk below unacceptable levels. However, the investigation methodologies focused largely on characterizing and remediating localized releases of non-aqueous phase liquids (NAPLs) and dissolved-phase benzene, toluene, ethylbenzene or xylene (BTEX) compounds. Other constituents of gasoline fuel, such as the additives utilized to increase oxygen content (oxygenates), are significantly more mobile than NAPLs or BTEX compounds in groundwater and are not as easily, or cheaply, removed from groundwater aquifers. Additionally, an equal release of gasoline with oxygenates (e.g., methyl tertiary-butyl ether) will impact an aquifer quicker, more extensively, and with less of a BTEX-type plume trace than a release of oxygenate-free gasoline. This phenomenon is particularly pronounced within a hard rock (igenous or metamorphic) bedrock aquifer, where oxygenates, almost without limit, pervade fracture and lineament patterns. Compounding this effect is the use of residential water supplies within the bedrock, which are by design situated within bedrock fracture zones of greatest transmissivity and therefore, by default, become individual pumping centers hydraulically connected throughout a residential neighborhood. As a result, innovative or non-traditional approaches such as bedrock fracture trace and lineament studies must be used to augment traditional approaches in order to identifying the source(s) and migration pathway(s) of today's gasoline spills.

45. Risk-Targeted Remediation for MTBE-Impacted Gasoline Stations

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By adjusting concentrations and microbubble type, oxidant systems can be designed for remediation of gasoline components in groundwater, prioritizing attack on the health-risk compounds MTBE, BTEX, naphthalenes, methyl benzenes, TBA, other oxygenates and general alkanes (TPH). Reduction of higher health risk compounds, proportionate to their health risk ranking, allows more efficient targeting of remediation and quicker closure. The oxidation stoichiometry of the systems is discussed for the primary health-risk compounds being targeted. MTBE is a highly mobile compound in vertical transport, having been previously modeled by Vleach (Rong, 1998). By equating removal rate to leaching rate, remediation rate can be set to match transport and dispersivity. Combining the probability of spills, a confidence level can then be set in terms of protecting groundwater quality beneath the service station as an interdiction system following the remediation process. An example installation in Sacramento, California, is discussed with documentation of observed removal rates by compound. The thickness of aquifer, hydraulic conductivity, seepage velocity, and distribution of concentrations are the most critical factors affecting success of interdiction. Secondarily, oxidation concentrations are designed not to exceed levels of injected materials safety, particularly for resins of fiberglass tanks, electrical conduits. The safe ranges and ability to interdict are discussed.

Poster Session - Phytoremediation

46. Accumulation of Heavy Metals by *Azolla spp.*

Anju Arora, Indian Agricultural Research Institute, N. Delhi, India
Anjuli Pabby, Indian Agricultural Research Institute, N. Delhi, India
P.K. Singh, Indian Agricultural Research Institute, N. Delhi, India

47. Phytoremediation's Possibility of Food-Chain Contamination

Sandra Benson, University of South Carolina, Columbia, SC
David Coyle, US Forest Service, Aiken, SC
Lee Newman, University of South Carolina, Columbia, SC, and The Savannah River Ecology Laboratory, Aiken, SC

48. Dewatering, Remediation, and Evaluation of Dredged Sediments

Paul Biery, University of South Carolina, Columbia, SC
Lee Newman, University of South Carolina, Columbia, SC, and The Savannah River Ecology Laboratory, Aiken, SC

49. Soil and Plant Analysis in a Metal Impacted Estuarine System in South Carolina

Jaclin A. DuRant, University of South Carolina, Columbia, SC
Lee Newman, University of South Carolina, Columbia, SC, and The Savannah River Ecology Laboratory, Aiken, SC

50. Toxicity and Bioaccumulation of Lead and Cadmium in Green Macroalgae, *Cladophora fracta*

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Chantana Lamai, Department of Biology, Mahidol University, Bangkok, Thailand
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Suchart Upatham, Burapha University, Chonburi, Thailand

51. Using Sediment Slurry Batch Reactors to Evaluate Mercury Methylation with Regard to Sulfate Concentration

Sarah M. Harmon, University of South Carolina, Columbia, SC
G. Tom Chandler, University of South Carolina, Columbia, SC
Lee Newman, University of South Carolina, Columbia, SC, and The Savannah River Ecology Laboratory, Aiken, SC

52. Estimating Efficiencies of Tritium Phytoremediation at the Savannah River Site

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Chris Barton, USDA Forest Service - Savannah River, New Ellenton, SC
John Seaman, UGA Savannah River Ecology Laboratory, Savannah River Site
Susan J. Riha, Cornell University, Ithaca, NY
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53. Microbiota Involved in Vegetation of Sulphidic Mine Tailings: Greenhouse Experiments

Ioana G. Petrisor, University of Southern California, Los Angeles, CA
Mugur Stefanescu, Institute of Biology of Romanian Academy, Bucharest, Romania
Smaranda Dobrota Institute of Biology of Romanian Academy, Bucharest, Romania
Anca Voicu, Institute of Biology of Romanian Academy, Bucharest, Romania
Chris M. Teaf, Institute for International Cooperative Environmental Research, Florida State University, Tallahassee, FL

54. Removal of Nickel and Lead By Giant Duckweed, *Spirodela polyrrhiza* (L.)

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Maleeya Kruatrachue, Department of Biology, Mahidol University, Bangkok, Thailand
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55. Phytoremediators: Possible Implications in Restoration Ecology and Molecular Medicine

J.Rajiv, University of Delhi, Delhi, India
K.K.Aggarwal, GGS Indraprastha University, Delhi, India
C.R.Babu, University of Delhi, Delhi, India

56. Cultural Approaches to Reduce Nitrate Contamination of Groundwater

Raj K. Shrestha, Nepal Agri. Research Council, Khumaltar, Lalitpur, Nepal
Jagdish K. Ladha,Int. Rice Research Inst., Manila, The Philippines

57. Metabolic Response of Native Southeastern Trees to Trichloroethylene

Sarah Strycharz, University of South Carolina, Columbia, SC
Lee Newman, University of South Carolina, Columbia, SC, and The Savannah River Ecology Laboratory, Aiken, SC

58. Utilization of Apoplasmic Space in Tobacco by Genetic Manipulation for Accumulation of Cadmium

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59. Aromatic Plant Production on Polluted Soils

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46. Accumulation Of Heavy Metals By *Azolla* spp.

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Toxic wastes from various industrial and municipal operations are disposed into soil and water, the two most important compartments of environmentwher these accumulate and enter food chain leading to health hazards. Conventional physicochemical means for treating polluted waters are expensive. On the other hand, bioremediation of wastewaters using various microorganisms and aquatic plants offers eco-friendly and economical ways for in situ treatment of wastewaters. The efficiency of bio-treatment process using aquatic plants for stripping metals from wastewaters depends on the abundance of plant, its ability to grow in water bodies and propensity to accumulate high levels of metals. Free floating aquatic fern *Azolla*, which occurs in symbiotic association with N_2 fixing blue green alga *Anabaena azollae,* is particularly useful because of its high rate of multiplication, worldwide distribution, ability to grow in varied conditions from dilute to polluted water bodies, remarkable capacity to accumulate heavy metals in its biomass. *Azolla* processes may prove superior to other traditional processes especially when environmental and ecological constraints exist and when concentrations of toxic metals in wastewaters are extremely low (1-100 ppm) so that at such concentration no chemical means are effective. *Azolla* processes may be operated in two forms active and passive. The active process can be applied in situ to treat diluted effluents and for concentration or recycling of metals. This study presents ability of three species of *Azolla* namely *A.microphylla, A.pinnata* and *A.filiculoides* to grow in presence of different concentrations of toxic heavy metals like Pb and Cd and accumulate them in their biomass. Cd severely inhibits growth allowing production of only 40-60% of control biomass at 1 ppm concentration and no growth beyond 1 ppm level. At 5 and 10ppm concentration however, fronds of *Azolla* spp. are able to survive and accumulate high amount of metal ions. *A.pinnata* shows highest capacity for concentrating Cd with its concentration reaching 2760 ppm in the biomass of *A.pinnata* after 7 days incubation (275 fold). Cd accumulates more when it is present in high concentration in the medium. But this high amount of uptaken Cd severely affects growth. On the contrary, Pb is less inhibitory to growth of all the three species and even at 80 ppm of lead in the medium the *Azolla spp*. produce 75-91 percent of control biomass. *A filiculoides* and *A.pinnata* are more tolerant than *A.microphlla*. At 40 ppm of Pb, uptake appears to be saturated and concentration of metal in biomass is more at lesser amounts of Pb dissolved in the medium. Thus, *Azolla* species can be employed to design suitable outdoor processes for removal and concentration of heavy metals from metal contaminated effluent.

47. Phytoremediation's Possibility of Food-Chain Contamination

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Phytoremediation is a process where plants absorb pollutants from the surrounding soil or groundwater via their root systems. In the case of organic compounds, plants can take up and degrade the contaminant within the plant tissues. Trichloroethylene (TCE) research has shown that plants will reduce TCE to $CO_{2,}$ water, and organic metabolites, such as trichloroacetic acid (TCA) and dichloroacetic acid (DCA). This research looks at the two different types of insects, *Ostrinia nubilalis* (European corn borers) and *Malacosoma disstria* (forest tent caterpillars) and examines the affects of feeding on TCE exposed plants. *Malacosoma disstria*, which naturally feed on poplars, are defoliants and thus might be affected by the TCE metabolites produced in the leaves. *Ostrinia* nubilalis, though they do not naturally infest poplars, are wood boring insects and consume the cambium of plants, which is where the parent pollutant is being transferred through the plant. Larval size, pupae weight, duration of the pupal stage and emergence to adults, and adult biomass are examined. Analysis is also done to determine the presence of any TCE or metabolites in the insects.

48. Dewatering, Remediation, and Evaluation of Dredged Sediments

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In order to keep U.S. waters navigable large dredging operations may be required. Dredging operations remove large quantities of sediments from many industrial and urbanized harbors and waterways. The presence of contaminated sediments not only contributes to environmental degradation but it also inhibits the efficiency of the US Army Corps of Engineers to dredge, transport, and relocate sediments. Currently, contaminated sediments are stored in confined placement facilities (CPFs), capped, treated, or simply not dredged.

Our research project focuses on the use of plants (primarily grasses and trees) to accelerate the removal of water from the sediments and to promote the degradation/extraction of contaminants. Research plants will be evaluated based on their ability to dewater and degrade/extract contaminants. Monitoring will provide real-time data relevant to the progress of dewatering based on moisture content and dissolved oxygen in the sediments. Ultimately, the success of the project will be based on the final concentrations of the contaminants (compared to regulated concentrations) and residual toxicity (based on seedlings, soil microorganisms, earthworm toxicity test). Remediation of contaminated sediments will allow it to become suitable for beneficial use such as industrial fill, construction, or even reintroduction to open water.

49. Soil and Plant Analysis in a Metal Impacted Estuarine System in South Carolina

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Industrial pollution is a major concern in US rivers, streams, and estuaries. Though recent advances in technology and regulatory mechanisms have helped lessen the amount of pollution discharged, large amounts of industrial waste still effect aquatic environments. This research focuses on determining the concentration of several different metals in soil and plant tissue samples taken from sample sites along the Sampit river near Georgetown, SC. Two major industries are located on and discharge into the Sampit. The metals contained within the effluent from these industries will be the focus of analysis.

Sediment cores as well as root, stem, and leaf tissue samples from the dominant marsh plant, *Spartina alterniflora,* are taken from eight sample sites located upstream, throughout, and downstream from the major industrial section of the Sampit, located in the vicinity of Georgetown harbor. The concentrations of metals found in the sediment and plant tissues should help to assess the possibility of an ecological impact on this estuarine ecosystem due to industrial pollution.

50. Toxicity and Bioaccumulation of Lead and Cadmium in Green Macroalgae, *Cladophora fracta*

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The green macroalgae, *Cladophora fracta* is being used to test toxicity and the accumulation of lead and cadmium in a synthetic solution. *C. fracta* were cultured in modified Chu No. 10 medium which was supplemented with 5, 10, 20, 40 and 80 mg/L of lead and 0.5, 1, 2, 4 and 8 mg/L of cadmium and were separately harvested after 2, 4, 6 and 8 days.

The effects of lead and cadmium on the relative growth, biomass productivity and the chlorophyll content in *C. fracta* indicated that there were significant decreases ($P<0.05$) in the relative growth, biomass productivity and the chlorophyll content when the exposure times and concentration of lead and cadmium were increased. The EC_{50} of cadmium was lower than that of lead during the same duration, suggesting that cadmium was comparatively more toxic than lead. The accumulation of the above heavy metals in the algae showed that there were significant increased ($P<0.05$) metals levels in algal tissue when the exposure times and concentrations were increased. The rates of lead and cadmium accumulation in *C. fracta* decreased rapidly on the first 4 days and then slowly decreased on day 6 and day 8. The bioconcentration factor (BCF) of lead was higher than that of cadmium at the same duration, suggesting that the accumulation potential of lead was higher than that of cadmium in *C. fracta*.

The toxicity symptoms of *C. fracta* exposed to lead and cadmium and cadmium at different concentrations and exposure times showed damage and the reduction of chloroplast, while the controls were green and composed of normal healthy cells. Moreover, loose arrangement and discoloration of chloroplasts and crumbed cell walls were observed. Finally, most filaments were dead at higher concentrations of metals. The symptoms were more pronounced at higher metal concentrations, but they were not specific.

51. Using Sediment Slurry Batch Reactors to Evaluate Mercury Methylation with Regard to Sulfate Concentration

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Mercury is a common environmental contaminant which becomes much more toxic in its methylated form because of methylmercury's ability to easily cross cell membranes, accumulate in biological tissues, then biomagnify through the food chain. From the standpoint of human health risk, it is the accumulation of methylmercury in the edible tissue of fish which has caused recent health advisories and much public apprehension. Inorganic mercury in the environment is converted to methylmercury through bacterial activity and, specifically, through the activity of anaerobic sulfate-reducing bacteria (SRB). It has been shown that wetlands are a major source of mercury methylation in natural systems, presumably due to anaerobic nature of a wetland environment and subsequent elevation of anaerobic bacterial populations. This research addresses the potential risk of mercury methylation in a constructed treatment wetland which has been amended with sulfate to enhance the wetland's capability to sequester metals from the water column. It is generally accepted that the presence of sulfate in sediment will enhance the activity of SRB and thus stimulate methylmercury production. It has also been shown that the accumulation of sulfide (the product of sulfate reduction) will inhibit mercury methylation due to the formation of solid HgS. Therefore, there is believed to be a range of sulfate concentrations which is optimal for the stimulation of methylmercury production. This study attempts to identify this optimal range for a particular wetland system and explore the ways in which bacterial population dynamics affect mercury methylation. A more thorough understanding of these concepts may help future treatment wetland designers to optimize the benefits of bacterial activity while avoiding this dangerous optimal sulfate concentration range. Anaerobic batch reactors were used to simulate natural wetland sediment conditions. Test vessels containing sediment slurries with varying sulfate concentrations were incubated in an anaerobic chamber and periodically spiked with aqueous mercury. Aliquots were regularly removed for measurement of sulfate, sulfide, total mercury, and methylmercury concentrations, in addition to SRB population estimates. Data from this research allows an evaluation of mercury methylation rate with respect to sulfate reduction rate and SRB population growth, as well as a correlation between initial sulfate concentration and final methylmercury production. Through this research, a more detailed understanding of the geochemistry of sulfate and mercury in one particular wetland treatment system has been developed.

52. Estimating Efficiencies of Tritium Phytoremediation at the Savannah River Site

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Current activities at the Savannah River Site (SRS), formerly a Cold War nuclear material production and storage site, include environmental remediation and restoration. Specifically, the U.S. Department of Energy, the Westinghouse Savannah River Corporation, and the USDA Forest Service are working in collaboration to design, operate, maintain, and monitor phytoremediation irrigation systems for the remediation of low-level radioactive and mixed waste at SRS. Current Forest Service projects at SRS include the phytoremediation of groundwater containing the hydrogen isotope tritium. A sprinkler irrigation system has been constructed on an approximately 22-acre plot of pines and hardwoods for the distribution of tritiated groundwater seep discharge that is collected by a pond. The irrigation system has been in operation since April 2001. Daily irrigation scheduling is based on continuous soil water deficit calculations using observed rainfall data and calculated evapotranspiration. Instrument clusters on certain plots consist of time-domain reflectometry (TDR) tubes for measuring soil water content, tensiometers for measuring soil water tension, and piezometer for measuring the depth to the water table. Clusters also contain lysimeters and vapor tubes for collecting water samples for tritium analyses. Tritium mass balances are being calculated and used to estimate remediation efficiency. Future work involves developing relationships between daily irrigation rates, calculated treatment efficiencies, and soil and vegetation characteristics within irrigation plots.

53. Microbiota Involved in Vegetation of Sulphidic Mine Tailings: Greenhouse Experiments

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Intensive mining and ore processing activities from the Black Sea Coastal area have resulted in the production of millions of tons of mine tailings (wastes) directly disposed on land. A large sulphidic tailing dump, located next to flotation stations for metalliferous ore processing at Baia locality - on the Black Sea Coast, is considered a potential source for environmental pollution with heavy metals. This paper presents greenhouse experiments for establishing vegetation on sulphidic tailings from Baia, discussing the interactions between plants and microbiota at the rhizosphere level. These interactions are involved in fertilization of the arid growing support. The paper emphasizes two aspects referring to the dynamics of some microorganisms monitored over 12 months, and the enzymatic studies performed periodically in order to establish global dehydrogenase activity. It was demonstrated the presence, at plant rhizosphere level, of microbial groups involved in carbon, nitrogen, phosphorous and sulfur cycles, inducing good substrate (tailings) fertilization, high enzymatic activity and increased plant growth.

54. Removal of Nickel and Lead By Giant Duckweed, *Spirodela polyrrhiza* (L.)

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The uptake of nickel (II) and lead (II) by giant duckweed (*Spirodela polyrrhiza* (L.) Schleid.) were investigated in synthetic solutions of 1.0, 2.0, 4.0, and 8.0 mg/L of these metals. The metal-enriched solutions were changed every alternate day, i.e. day 2, 4, 6, and 8 over a 10-day experimental period. The percentage removal of nickel and lead at every concentration was highest in the first two days (58-80% and 68.25-91%, respectively). The percentage removal of nickel and lead by *S. polyrrhiza* showed that there was a significant decrease ($P<0.05$) when the exposure times and concentrations were increased. The percentage removal of lead was higher than that of nickel. These results agreed with the metal concentration factor (MCF). The effects of these metals on the fresh weight were also studied. After ten days of exposure, the fresh weight of *S. polyrrhiza* decreased significantly ($P<0.05$) as the concentration of these metals increased. The fresh weight of nickel-treated plants was lower than that of lead-treated plants at the same concentration.

55. Phytoremediators: Possible Implications in Restoration Ecology and Molecular Medicine

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The problem of ecosystem damage is international and probably no country in the world is unaffected. One of the biggest challenges today in achieving sustainability is to reverse the trend of ecosystem damage through restoration and rehabilitation of ecosystems. Phytoremediation is a low input cost effective approach, which preserves the topsoil and reduces the amount of the hazardous materials generated during the cleanup. Legumes have been extensively used as biological inputs in revegetation/reclamation technologies as they are not only a major source of fixed nitrogen in land based systems, but also known to tolerate moderate concentrations of heavy metals. Root exudates - secretions from the plant roots, continuously produced and secreted into the environment are known to have important role in the biological processes and the unexplored chemical diversity of the root exudates is an obvious area to search for novel biologically active compounds including antimicrobials. Recently, we have isolated a chemical compound possessing the properties of a siderophore from the root exudates of a Legume plant, *Tephrosia purpurea*. Potentiality of this compound to serve as a bioremediator in the soils contaminated with toxic metals has been suggested (Aggarwal et al., 1999).

The same purified compound when assessed for its anti-microbial activities was found to inhibit the growth of *M tuberculosis* H_{37} RA under *in vitro* conditions (Rajiv et al., 2001). Therefore a definite search based on phytoremediators may not only lead to the development of soil amendments for site specific restoration technologies but also may lead to the development of new avenues in molecular medicine.

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56. Cultural Approaches to Reduce Nitrate Contamination of Groundwater

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Drinking nitrate contaminated water can cause Methaemoglobinaemia (blue-baby syndrome), which impairs the oxygen carrying capacity of human blood resulting bluish-tinged or oxygen starved baby. The risk of drinking nitrate-contaminated water is likely to be in rural areas in developing countries where nitrate fertilizer applications are increasing without monitoring water quality. Nitrate levels in groundwater have been increasing over recent decades in most countries as a result of excess use of fertilizers to feed increasing population. The input-intensive cropping system has resulted in a problem of a large leakage of N into the environment, thereby polluting the water. Excessive use of N fertilizer in high-value crops grown in DS is economically motivated. Application of 600 kg nitrogen ha^{-1} by farmers in dry season crops has contaminated sixty percent of tube well containing near or above World Health Organization's (WHO) NO_3-N limit for drinking water of 10 ppm. Residual soil mineral N (upper 100 cm) in farmers' field reached up to 694 kg ha^{-1}. Growing catch crops like indigo (Indigofera tinctoria L.) and corn (Zea mays L.) in dry-to-wet transition period reduced residual nitrate level up to 68%. In fallow plots, nitrate was moved down to lower soil profile demonstrating NO_3 leaching in absence of crop. On an average, catch crops were able to reduce nitrate leaching by 40%. As catch crop alone was not able to reduce nitrate leaching substantially, a strategy of increasing N use efficiency of the cropping system by applying N-fertilizer at proper time and amount and judicious management on frequency of irrigation in sandy soils was recommended in addition to including N-catch crops.

57. Metabolic Response of Native Southeastern Trees to Trichloroethylene

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Phytoremediation of trichloroethylene (TCE) from contaminated groundwater has been performed using fast-growing tree species that maintain a high water demand. Tree species with these characteristics make excellent candidates for phytoremediation applications due to their ability to uptake large amounts of groundwater, and therefore contaminant. Several metabolites of TCE have been identified in the tissue of poplars including trichloroethanol, di- and trichloroacetic acids. The presence of these metabolites indicates that TCE degradation is taking place through natural metabolism of exogenous compounds in the plant system. However, it is important to expand the range of plants that can be utilized in varying areas of the country for phytoremediation. In this study, we will be examining native tree and plant species of the Southeast and studying their interaction with TCE. By screening native tree species for the ability to take up and degrade TCE we hope to identify phytoremediation candidates suitable for the Southeast. This study is a greenhouse based project that simulates the effects of groundwater TCE on the plant system**.**

58. Utilization of Apoplasmic Space in Tobacco by Genetic Manipulation for Accumulation of Cadmium

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A concept, called phytoremediation, is one of the solution to reduce the harmful effects of heavy metals without additional energy and large costs. Many natural plants are identified as a “hyper-accumulator” to isolate heavy metals from soil; however, the ability is not enough and there is a need to breed more powerful one. At this point, genetically manipulation techniques are helpful. Two strategies can be recognized to accumulate a metal in living plant cells; firstly, to directly increase the intake flow of the metal; and secondly, to increase the storage capacity of the metal. Our group recently demonstrated the effect of the second strategy on fortifying the iron content in crops (eg. tobacco, lettuce and rice) by over-expressing a gene of the iron storage protein, “ferritin”. However, these strategies may not work well to accumulate non-essential metals, because no specific uptake system for non-essential metals is recognized. Actually, recent reports showed that over-expression of a metal-binding molecule like metallothionein in cell could not enhance the metal intake into cell, while it extinguished the harmful effect of metals. So, we tried to create the third way to accumulate non-essential metals in plant. In our system, it is based on a hypothesis that a metal-binding molecule existed in the apoplasmic space may trap metals independent of the specific uptake system. Alpha-domain of human metallothionein is used for the metal-binding molecule. It is expressed under the regulation of CaMV 35S promoter, and transported to the apoplasmic space of tobacco by the role of transit peptide of tobacco invertase-inhibitor. When the T1 tobaccos were grown in the cadmium containing media, it accumulated about 55% more cadmium than the non-transformant. This is the first experiment to exhibit the possibility that the third way contribute to accumulate non-essential metals in plant.

59. Aromatic Plant Production on Polluted Soils

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A two year field experiment was conducted in the vicinities of Pb-Zn smelter near Plovdiv Bulgaria, at the presence of both soil and aerosol metal pollution to evaluate productivity and phytoremediation potential of coriander, sage, dill, and chamomile. Crops were grown in the vicinities of the smelter at distances of 0.8, 3.0, 6.0 and 9.0 km (the latter was unpolluted and regarded as a control).

The level of pollution at 0.8 km from the smelter reduced yields of fresh herbage and essential oil from all tested crops compared to the control and the yields at 3 km from the smelter. Despite the yield reduction of 12-20 % (relative to the control), coriander, sage, dill and chamomile can be successfully grown and remain profitable crops on heavy metal polluted sites. Heavy metal concentration in the plant tissue reflected the level of soil and aerosol pollution in the area. The highest removal of metals with the yields was as follows: Cd up to 180 g/ha; Pb up to 660 g/ha; Cu up to 180 g/ha, Mn up to 350 g/ha, Zn up to 205 g/ha.

The accumulation of heavy metals in the aboveground herbage of the four crops is tabulated. Overall, there was less variation in Zn content and uptake between plant species than with other elements.

Essential oils from the four crops were free of metals. The concentration of Cd, Pb, Cu, Mn, and Zn in the essential oils was below 0.06, 0.62, 0.25 and 0.3 mg/L respectively, i.e. below the detection limit of AAS.

POSTER SESSION - RADIONUCLIDES

60. Pre- and Post-Mitigation Measurements of Indoor Radon in Homes with Excessive Radon Concentrations

Douglas G. Mose, George Mason University, Fairfax, VA
Fiorella Simoni, George Mason University, Fairfax, VA
George W. Mushrush, George Mason University, Fairfax, VA

61. Indoor Radon Measurements from Homes in Southern Poland

George W. Mushrush, George Mason University, Fairfax, VA
Fiorella Simoni, George Mason University, Fairfax, VA
Douglas G. Mose, George Mason University, Fairfax, VA

62. Radioecological Monitoring and Decomtamination Technology of NORM sludge from Vuctyl Oil and Gas

Vladimir O. Nekoutchaev, Ukhta State University, Ukhta, Russia
Eugenue I. Krapivski, Ukhta State University, Ukhta, Russia
Victor Ryzhakov, Vuctyl Company “Severgasprom, Vuctyl, Russia

60. Pre- and Post-Mitigation Measurements of Indoor Radon in Homes with Excessive Radon Concentrations

Douglas G. Mose, Fiorella Simoni*, and* ***George W. Mushrush****, Chemistry Department, George Mason University, Fairfax, VA 22030, Tel. 703-993-1068, Fax: 703-273-2282*

Using year-long alpha-track radon detectors, indoor radon measurements from about 2000 homes in Virginia and Maryland were mostly found to be between 1 and 30 pCi/L. In approximately 200 of the homes, sub-slab ventilation was installed to reduce the indoor radon concentrations. By random selection, the mitigation by sub-slab ventilation used either 2-inch, 3-inch, or 4-inch diameter exhaust pipe from the basement floor penetration site through to the externally located exhaust fan. Approximately 90 percent of the homes showed successful reductions in radon concentrations to below 4 pCi/L, the US-EPA recommended maximum for the sale of homes. Most of the unsuccessful homes were those in which the sub-slab ventilation system used 2-inch diameter exhaust pipe. The homes in which 3-inch and 4-inch exhaust pipe was used showed approximately the same success rate.

61. Indoor Radon Measurements from Homes in Southern Poland

***George W. Mushrush, Fiorella Simoni**, and **Douglas G. Mose**, Chemistry Department, George Mason University, Fairfax, VA 22030, Tel. 703-993-1068, Fax: 703-273-2282*

In the northern and central parts of Poland, thick layers of glacial deposits contain low uranium concentrations and the homes have low indoor radon concentrations (most less than 1 pCi/L). In southern Poland, in the Sudety Mountains, mountain core crystalline rocks contain numerous sites of uranium mineralization, some of which were extensively mined 50 years ago. Most of the mineralization occurs as small veins of uranium minerals, mineralized fault zones, and zones of hydrothermal enrichment around the perimeter of formerly molten chambers of granite. Soil developed on this terrane has relatively high soil-gas radon concentrations. The measurements of soil radon above the Sudety Mountain granites, gneisses and schists have a geometric mean of about 2000 pCi/L. The highest measurement in the crystalline terrane found to date is about 40,000 pCi/L. Over 50 percent of the homes have indoor radon concentrations in excess of 4 pCi/L, the US-EPA recommended maximum for home sales. In Poland, where a large portion of the population lives in the same area for most of their lives, we anticipate that radon potential based on soil radon and permeability will show a positive correlation with the incidence of lung cancer.

62. Radioecological Monitoring and Decontamination Technology of NORM Sludge from Vuctyl Oil and Gas Field

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Radioactive contamination of oil and gas production and processing facilities is now commonly known to be an important ecological problem throughout the world. The present paper deals with the investigation of naturally occurring radioactive material (NORM) contamination at one of the largest oil and gas-condensate fields in the north of Russia – Vuctyl field.

The geochemistry of radium behavior in produced waters of Vuctyl oil and gas field has been investigated. The main sources of radioactive contamination from this field are radium 226, radium 228 and radon decay products. The main sources of radiation danger from oil and gas production facilities are sludges of produced water, deposits of radioactive salts on the equipment, and previously buried sludges and scale. The natural gas may contain considerable concentration of radon.

The theoretical and methodical bases of the control for the processes of NORM sludge decontamination have been developed. At laboratory and industrial conditions the influence of the processes of leaching, sorption, dissolution, deemanation, thermal, chemical and high temperature processing on the decontamination of the large volumes of sludges with elevated radioactivity have been investigated. The way of transformation of insoluble radium minerals into the soluble forms has been developed.

The industrial installation and technology for NORM sludge decontamination have been created. To the best of the authors knowledge the technology has no Russian analogues. It has been proved, that as a result of decontamination of sludge with a specific activity about 100 kBk/kg the solid insoluble final product may have specific activity no more than 1,5 kBk/kg, and liquid final product – less than 1 Bq/l.

POSTER SESSION - RBCA

63. Does RBCA Work?

Emil Onuschak, Jr., DE Dept of Natural Resources and Environmental Control, New Castle, DE

63. Does RBCA Work?

Emil Onuschak, Jr., PG, *State of Delaware, Department of Natural Resources and Environmental Control, Underground Storage Tank Branch, 391 Lukens Drive, New Castle, DE 19720-2774, Tel: 302-395-2500, Fax: 302-395-2601, E-mail: eonuschak@DNREC.State.de.us*

Since adopting a risk-based site assessment procedure in 1999, both the number and percentage of "old" leaking underground storage tank sites closed in Delaware have increased markedly. Many of these "old" sites previously were undergoing prolonged ground-water monitoring with no clear criteria for their closure.
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POSTER SESSION - REGULATORY

64. Proposed New York State Dredged Material Assessment and In-water or Riparian Dredged Material Management Guidance

Arthur J. Newell, NYSDEC, Albany, NY
Alex Lechich, NYSDEC, Region 2

64. Proposed New York State Dredged Material Assessment and In-water or Riparian Dredged Material Management Guidance

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The proposed guidance was developed jointly by the Divisions of Water and Fish, Wildlife and Marine Resources to provide Department staff with guidance on the statutory and regulatory requirements for dredging activities and to promote uniformity in the management of dredge material throughout the state. The guidance applies only to dredging operations and in-water or riparian management of dredged material. To clarify the sampling, testing and permitting process, the guidance provides an explanation of state law requirements for dredging projects with a general overview of relevant federal requirements. The guidance is offered as a clear approach to environmental review of navigational dredging projects, dredging of channels and berths, dredging of ponds, and other incidental dredging in both marine and fresh waters of the state. The guidance includes environmental objectives for dredging; best management practices for dredging and disposal; sediment quality parameters to measure and sampling requirements; effects based sediment quality threshold values; dredged material management options for three classes of sediment quality; guidance on evaluation of toxicity and bioaccumulation test results; mixing zone analysis; and monitoring requirements. While this guidance contains numerical assessment criteria, it is not law or regulation. Discretion in applying the sediment quality parameters and the associated best management practices is expected and is defensible as long as human health and the environment are effectively protected.

POSTER SESSION - REMEDIATION

65. The Organoclay/Carbon Combination of Efficient PCB Removal

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

66. PCB Contaminated Soil Remediation in a Wetland Buffer Zone using UVF Screening and Weighed Averaging

David Billo, Paragon Environmental Services, Inc., Norwood, MA
Steve Greason, SiteLAB Corporation, Hanover, NH

67. Bioremediation of Polyaromatic Hydrocarbons Using a Groundwater Recirculating Treatment System

Peter J. Cagnetta, Science Applications International Corporation, Harrisburg, PA
Daniel B. Lewis, Spotts, Stevens, and McCoy, Inc., Reading, PA

68. Methane Recovery and Generation Pilot Testing from a Solid Waste Management Unit

Peter J. Cagnetta, Science Applications International Corporation, Harrisburg, PA
Isaac Diggs, Science Applications International Corporation, Oak Ridge, TN
Brooks Abeln, Science Applications International Corporation, Harrisburg, PA
John Keiser, U.S. Army Corps of Engineers, Savannah, GA
Zainul Kidwai, U.S. Army Corps of Engineers, Savannah, GA

69. Rapid Remediation of Jet a Fuel Contamination at the Former Stapleton International Airport in Denver

Dale W. Christensen, Parsons, Denver, CO
Paul Kieler, Department of Aviation, Denver, CO

70. *In Situ* Thermally Enhanced SVE with Bioventing for Treatment of Phenols and BTEX in Soils

M. Talaat Balba, Ph.D., Conestoga-Rovers & Associates (CRA), Inc., Niagara Falls, NY
Darlene Coons, Conestoga-Rovers & Associates (CRA), Inc., Niagara Falls, NY
Cindy Lin, Ph.D., Conestoga-Rovers & Associates (CRA), Inc., Niagara Falls, NY
Susan Scrocchi, Conestoga-Rovers & Associates (CRA), Inc., Niagara Falls, NY
Alan Weston, Ph.D., Conestoga-Rovers & Associates (CRA), Inc., Niagara Falls, NY

71. Evaporate to Remediate Contaminated Soil

Gary N. Dixon, Severn Trent Services, Inc., Goffstown, NH

72. Optimization Strategies for Remediation Systems

David E. Fulton, IT Corporation, Trenton, NJ

73. Lessons Learned from Relying on Data from Improperly Constructed Monitoring Wells

Joseph R. Havasi, URS Corporation, Cleveland, OH

74. A Case Study for Design/Build of a Multi-Phase Extraction System at a Gasoline Station

Thomas W. Porter, EA Engineering, Science and Technology, E. Syracuse, NY
James C. Hayward, EA Engineering, Science and Technology, E. Syracuse, NY
Denise Wallace, Fort Drum Military Installation, Fort Drum, NY

75. Nanoparticle Iron for Source Area Treatment

Richard W. Arnseth, *Tetra Tech NUS, Inc., Oak Ridge, TN*
Keith W. Henn, Tetra Tech NUS, Inc., Pittsburgh, PA
Mark Peterson, Tetra Tech NUS, Inc., Jacksonville, FL
Dan Waddill, Southern Division Naval Facilities Engineering Command, North Charleston, SC
Dana Gaskins, Southern Division Naval Facilities Engineering Command, North Charleston, SC

76. Enhanced Recovery of Light Non-Aqueous Liquids Utilizing Preferential Pathways Induced by Subsurface Utilities

Eric V. Johnson, AMEC Earth & Environmental, Inc., Westford, MA
Samuel P. Farnsworth, AMEC Earth & Environmental, Inc., Westford, MA
Richard Adams,AMEC Earth & Environmental, Inc., Westford, MA
W. Patrick Harrison, CSX Transportation, Inc., Atlanta, GA

77. Contamination Put to Bed: A North Carolina Furniture Manufacturer's Case Study

John T. Burkart, Cooper Environmental, Inc., Charlotte, NC
Dale Lanier, Cooper Environmental, Inc., Charlotte, NC

78. Consolidation of Sanitary Landfills

Alejandro J. Sarubbi, University of Buenos Aires, Buenos Aires, Argentina
G. Sánchez Sarmiento, University of Buenos Aires, Buenos Aires, Argentina

79. The Resolution of Tight Emulsions in Industrial Scale Waste Processing

Robert Scalliet, Dilitec Corporation, Houston, TX

80. A Poor Man's Remediation: Low Tech Chemical Oxidation of VOCs in Soil

Lance S. Traves, Labyrinth Management Group, Medina, OH
Sheldon Taylor, American Weather Seal, Norton, OH

81. The Controling Action of Barrier Wall on Contaminated Migration

Huang Wei, Wenzhou University, China
Ding Wei, Wenzhou University, WZ, Zhejiang, P.R.China

82. Lessons Learned in the Use of Modified Fenton's Reagent for the Treatment of Petroleum Contaminated Soil and Groundwater

Brian V. Moran, Norfolk RAM Group, Holliston, MA
Charles P. Young, Norfolk RAM Group, Holliston, MA
Melissa Parker, Norfolk RAM Group, Holliston, MA

83. Containment of NAPL and Passive Hydraulic Control at a Former manufactured Gas Plant Site

Edward P. Zimmerman, Harding ESE, Inc., Merrimack, NH
Mark Haney, Harding ESE, Inc., Merrimack, NH

65. The Organoclay/Carbon Combination of Efficient PCB Removal

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Organoclays have been used for the removal of small amounts of oil from water very effectively, for some 15 years. What is still less known is the effectiveness of an organoclay/carbon combination, when the filter vessels are placed in series, for the removal of PCB and pesticides. What has been learned is 1. Organoclay is very effective for removal of PCB's by itself. 2. In combination with carbon, nondetectable amounts of PCB are routinely reported. The reason: Organoclay has a large capacity, 50% by weight or more, to remove transformer oil and PCB from water. Activated carbon, on the other hand, is excellent at removing the small quantities of PCB from water, down to 10 ppb or less.

This paper/article will describe the removal mechanisms for PCB removal by the two media, and show actual case histories to prove the point.

66. PCB Contaminated Soil Remediation in a Wetland Buffer Zone using UVF Screening and Weighted Averaging

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In November 2000, *Paragon* collected 37 soil samples from a disposal site in eastern Massachusetts to delineate polychlorinated biphenyl (PCB) concentrations in soil prior to a proposed remediation. *SiteLAB* provided on-Site analysis of these samples for PCBs via ultraviolet fluorescence (UVF). We used the UVF data to delineate approximately 35 cubic yards of shallow (located in a wetland buffer zone) containing PCB contamination exceeding 5 parts per million (ppm). In order to avoid destroying a portion of the wetland and because of the costs involved with PCB disposal, *Paragon* decided to limit soil removal to the identified soil volume exceeding 5 ppm in the wetland buffer zone. *Paragon* notified the local Conservation Commission of our plans via submittal of a Notice of Intent. The Commission granted approval for the project and issued an Order of Conditions allowing us to proceed.

In December 2000, *Paragon*'s contractor cleared and chipped brush from the disposal site and excavated 65.96 tons of PCB-contaminated soil directly into two trailer dump trucks. They transported the soil to an out-of-state hazardous waste landfill under Hazardous Waste Manifests.

Paragon collected 12 post-excavation soil samples from within the excavation and submitted the samples for laboratory PCB analysis by EPA Method 8082. The laboratory analyses determined that PCB concentrations remaining within the excavation ranged from less than 0.086 milligram per kilogram (mg/Kg) to 3.8 mg/Kg. *Paragon* used these results along with concentrations of soil samples previously collected from soil outside of the excavation (the applicable UVF pre-excavation sample results and other laboratory results generated during previous *Paragon* investigations between 1997-2001) to calculate a weighted average PCB concentration for the site of 1.74 mg/Kg. This concentration is less than the Massachusetts Department of Environmental Protection's risk characterization standard of 2 mg/Kg; thus, supporting the submittal of a closure report for the disposal site.

67. Bioremediation of Polyaromatic Hydrocarbons Using a Groundwater Recirculating Treatment System

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Releases from a No. 2 fuel oil UST and a motor oil UST resulted in the groundwater being impacted with fluorene, phenanthrene, and pyrene at a site in Reading, Pennsylvania. The groundwater is presently at approximately 11 feet below grade and occurs within the interbedded limestone and dolomite underlying the site.

A remedial options assessment (ROA) identified that natural biodegradation of the hydrocarbons was occurring. In order to maximize the biodegradation rate, a treatment system was designed and constructed which included one extraction well in the former UST area and four injection wells located along the downgradient and side-gradient edges of the plume. Water was extracted from the well at 5 gpm and treated with granular-activated carbon, amended with atmospheric oxygen, and amended with ammonium phosphate fertilizer. The amended water was then injected into 4 injection wells at 1.25 gpm per well. The closed loop recirculation approach ensured the maximum mixing of contaminants, amendments, and indigenous bacteria.

Throughout the first 80 days of operation, the concentrations of fluorene in well MW-3 declined from 466 micrograms per liter (μg/l) to <10 μg/l. During the same time period, the pyrene concentration declined from 78 μg/l to <10 μg/l. The concentration of phenanthrene in well MW-3 declined from 1,232 μg/l to <10 μg/l after 238 days. The decay rates were calculated at 5.69, 1.09, and 0.07 μg/l per day for fluorene, pyrene, and phenanthrene, respectively.

Prior to the start-up of the treatment system, the groundwater at well MW-3 contained a fluorene-degrading microbial population and a pyrene-degrading population of 1,414 MPN/ml and 1,000 MPN/ml respectively. After 78 days of operation, each population increased to over 20,000 MPN/ml and, subsequently after 160 days operation, declined to <500 MPN/ml. The contaminant-degrading populations were stimulated by the addition of the amendments and then subsequently declined as the concentrations of contaminants or growth substrate declined.

The concentration of dissolved oxygen throughout the plume prior to the start-up of the treatment system was <2 mg/l. After start-up and operation of the system, the dissolved oxygen ranged from 6 to 10 mg/l throughout the 12 months of operation.

68. Methane Recovery and Generation Pilot Testing from a Solid Waste Management Unit

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A methane and recovery generation pilot testing program was conducted within a solid waste management unit at Fort Bragg, North Carolina. The tests were conducted to address soil gas methane concentrations that were potentially in exceedance of North Carolina Department of Environment Natural Resources regulations. The SWMU was historically used to contain construction and demolition debris.

Two in-situ recovery tests were completed. Each test involved the extraction of methane gas through one extraction well and measuring the induced subsurface vacuum at three monitoring points located at distances of 5, 10, and 15 feet from each well. Three vacuum rates were applied to each wellhead. Applied wellhead vacuums ranged from 10 to 30 inches of water column. The corresponding extraction flow rates ranged from 80 to 140 scfm. At one location, the methane concentration in the soil gas at the beginning of the extraction test was 54% and declined to 30% at the conclusion of the 3-hour test. At the second location, the methane concentration was initially 59% and declined to 45% at the end of the test. Initial methane recovery rates for each test area were estimated at 4,355 and 1,058 pounds of methane per day, respectively.

Eight methane generation tests were conducted in the SWMU. At each generation test point prior to the start of the test, the soil gas was evacuated to reduce the methane concentration to generally <5%. The methane concentration in the soil gas at each point was then measured over a 48-hour period. The increase in methane concentrations (and also the declining oxygen concentrations and increasing carbon dioxide concentrations) indicated that methane was being produced in the soil at each test point. At the conclusion of each test, the soil gas methane concentration generally ranged from 30% to 55%, similar to pretest concentrations. The rate of methane generation was calculated using the methane generation rate in percent per day, the air fill soil porosity, the soil bulk density, and the methane gas density. In one area, the methane generation rates ranged from 2.6 to 13.8 mg/kg/day. In the second area, the rates ranged from 19.0 to 26.8 mg/kg/day.

69. Rapid Remedition of Jet a Fuel Contamination at the Former Stapleton International Airport in Denver

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At 4,700 acres, the former Stapleton International Airport (SIA) in Denver Colorado is currently the largest municipal brownfield redevelopment project in the country. Detailed long-range planning, extensive cooperation among all parties, and aggressive remedial actions at the former airport will result in complete remediation of SIA by April 2004, less than 4 years after commencement of the SIA remediation project.

In the years prior to and following closure of SIA in 1995, limited environmental investigations and remedial actions were implemented. However, widespread areas of jet-fuel-contaminated soil and groundwater remained, which prohibited sale of the property for redevelopment. The Jet A fuel was released over many years of airport operation, with numerous sources primarily associated with the airport fuel handling system. In one case, the resulting free product plume extended more than 2,000 feet from the source area. Most of the remaining mass of fuel occurs in the 1- to 6-foot-thick “smear zone” where free product came in contact with and adhered to soil as groundwater levels fluctuated over time.

With a stringent timeframe imposed by the City of Denver and the developer (Forest City), an aggressive remedial approach was necessary. Due to the low volatility of Jet A fuel, the large areal extent of the residual product in the smear zone, and the shallow nature of the smear zone, excavation and offsite disposal was selected as the primary remedy. Significant groundwater contamination was limited because the volatile organic content of the weathered Jet A fuel was relatively low.

Since October 2000 Parsons has remediated 46 of approximately 110 acres directly impacted by contaminated soil. The State has issued No-Further-Action (NFA) determinations for four areas of concern (that directly impacted approximately 3 acres) within the 100-acre Regional Retail Center parcel, which enabled construction of the retail hub to commence less than eight months after the start of remediation. By October 2002, Parsons anticipates that 90 percent of the impacted areas at SIA will be remediated and NFAs will have been issued for an additional 35 acres, which would release more than 600 acres of the former operational area of the airport for redevelopment construction.

This presentation will demonstrate/illustrate the rationale, planning, and execution behind this successful brownfield redevelopment project, which will result in completion of the remediation project and property transfer less than five years after the initial agreement was signed with the developer.

70. *In Situ* Thermally Enhanced SVE with Bioventing for Treatment of Phenols and BTEX in Soils

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Historic activities at a chemical manufacturing facility in New York have resulted in the contamination of the soil and groundwater with a wide range of contaminants, including elevated levels of phenols, benzene, toluene, ethylbenzene, and xylenes (BTEX), polyaromatic hydrocarbons (PAHs), and chlorobenzene. A laboratory treatability study was conducted to assess the feasibility of in situ bioremediation of the vadose zone soils using slurry microcosms supplemented with nutrients and oxygen. The results showed that the current levels of contaminants at the Site are inhibitory to microbial activity and biodegradation. CRA concluded that an alternative treatment technology to quickly reduce contaminant concentrations was required before enhanced biodegradation would be effective. CRA selected thermally enhanced soil vapor extraction (SVE) treatment as the knock-down step followed by bioventing as the polishing step for the treatability testing. Three 20-gallon treatment vessels were filled with representative Site soils and two were fitted with a vapor extraction system, which included an activated carbon trap to remove vaporized chemicals from the air stream. The two treatment vessels were placed in a chamber heated to 35ºC, and the third (without SVE) was used as a control tank, and was maintained at room temperature. The SVE phase of the study ran for three months. Approximately 10 pore volumes of air were removed per day. The extracted air stream and the soils were sampled during this time, and the results showed that the concentrations of BTEX and phenols had been reduced by more than 99 and 75%, respectively. The reduction in phenols and BTEX was accompanied by a significant increase in the microbial population. The two test vessels were converted to bioventing by reducing the airflow to one pore volume per day. One of the vessels was removed from the heated chamber and maintained at room temperature. Bioventing was performed for an additional three months during which biodegradation of contaminants was monitored. The rate of contaminant removal was calculated and the final contaminant concentrations were compared to applicable cleanup standards. The treatment results will be used to design a field pilot test, which will be performed to finalize the full-scale treatment design.

71. Evaporate to Remediate Contaminated Soil

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Contaminated groundwater concerns everyone for obvious reasons. When a factory is situated on a contaminated site there is increased concern: both the factory's own need for clean water, and the neighborhood's concern for remediation of the contamination—even if it was not caused by the present factory operations.

In this presentation, general wastewater disposal alternatives will be reviewed emphasizing evaporation as unique, being a single-step solution; i.e., no secondary operation is required to handle up to 99% of the water.

Consideration will be given to less energy intense methods of disposal (hauling, filtration, and chemical treatment) and comparisons will illustrate how cost may, in fact, favor evaporation—especially where industry requires clean water for production processes.
Regulatory issues will be discussed covering hazardous wastes and air quality issues, as will as technical, economic, and other user concerns (e.g., equipment operator friendliness). The presenter's experience with industrial uses for evaporation will provide a springboard for considerating groundwater contamination by metals, hydrocarbons, detergents, and other materials both organic and inorganic.

72. Optimization Strategies for Remediation Systems

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Over the next decade, the Department of Defense will spend over $1 Billion per year on the operation and maintenance (O&M) of environmental remediation systems. Each of these systems has a life cycle cost that includes the remedial design, construction, and O&M. While the remedial design and construction represents a significant project cost, the O&M phase of the project is where the achievement of the remedial action bjectives are realized. Therefore, a systematic and comprehensive approach is needed for evaluating and improving remediation system performance in order to maximize risk reduction, reduce operating and monitoring costs, accelerate site closure, and ensure protection of human health and the environment. This presentation discusses strategies for optimizing the performance of remediation systems to achieve the remedial action objectives at the lowest cost and within the quickest timeframe. A remedial process optimization (RPO) approach is defined that includes project set-up, project evaluation, data collection, data analysis, and implementation of RPO strategies. Specific approaches include data and cost analysis techniques that focus on system operations, maintenance, and value-added modifications that result in enhanced performance, reduced project costs, and focusing the remediation system towards site closure. Examples of strategies that have been implemented and the resulting cost savings and enhanced performance are presented.

73. Lessons Learned from Relying on Data from Improperly Constructed Monitoring Wells

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A phased Remedial Investigation (RI) was conducted at a government facility from 1995 through 2000. The facility is being converted to an industrial park under an aggressive re-use schedule. Chlorinated solvents (primarily cis-1,2-dichloroethylene and trichloroethylene) were detected in groundwater at one of the sites on base. The solvents were detected in two monitoring wells, D1MW12 and D1MW13, located approximately 10 feet and 75 feet hydraulically downgradient of a former construction and demolition debris (CDD) landfill where solvent wastes were also improperly disposed. The wells were installed by another agency in 1994 and used with wells installed by URS during the RI. This paper will present data utilized from these wells that were used for assessment and preliminary remedial planning purposes, and discuss the perilous fate of these wells and suspicions that were raised during well decommissioning with regard to the adequacy of the well construction. In addition, this paper will present the likely cause of inflated concentrations of contaminants in groundwater at D1MW12 and D1MW13, a summary of remediation activities that were to be conducted to address contaminated groundwater, a revised data set based on replacement wells, the current status of groundwater issues at the site, and some lessons learned from relying on improperly constructed monitoring wells.

74. A Case Study For Design/Build of a Multi-Phase Extraction System at a Gasoline Station

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A case study is presented for a multi-phase extraction (MPE) interim remedial measure (IRM) at an active gasoline station at the Fort Drum Military Installation to address subsurface petroleum hydrocarbon contamination. The subject site is situated on lacustrine deposits consisting of sand and silt. Groundwater is present from 21 to 26 feet below ground surface, with hydraulic conductivity estimated at 2.0 ft/day. Previous investigative activities revealed petroleum-impacted soil, separate-phase product, and a dissolved-phase petroleum hydrocarbon plume were present hydraulically downgradient of the former underground storage tanks. The dissolved-phase plume had also impacted a downgradient wetland area and extends in the direction of a nearby river. A Corrective Measures Study (CMS) was conducted which developed, screened, and evaluated potential corrective measure alternatives to address contaminated soil and ground water. The CMS recommended MPE to remediate subsurface soil and ground water in the upgradient source area, and aquifer air sparging (AAS) with ozone and tiered monitoring to address the downgradient dissolved-phase hydrocarbon plume. MPE combines two remedial technologies: soil vapor extraction (SVE) and liquid recovery. SVE is designed to volatilize low molecular-weight compounds using relatively high volumes of air, while liquid recovery involves the direct extraction of LNAPL and groundwater from the subsurface. With the concurrence of the New York State Department of Environmental Conservation (NYSDEC), EA performed design/build services for both an MPE system and AAS with ozone system at the site. This paper discusses lessons learned during the design, implementation, and operation of the MPE system. Value-added engineering during the design/build process was critical in reducing project costs and facilitating construction. The MPE system consists of 10 recovery wells, extraction piping, and process equipment (vacuum pump, air/liquid separator, oil/water separator, and air stripper). EA is currently operating the MPE system to evaluate the effectiveness of this technology at the subject site and its potential for use at other sites on the Installation.

75. Nanoparticle Iron for Source Area Treatment

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Aquifers contaminated with chlorinated organic solvents present two distinct problems – treating the dissolved plume and addressing the source area. Numerous remedial technologies have been developed to address the dissolved phase contamination in groundwater. A different range of technologies has been developed to treat source areas where a reservoir of contaminant is often stored in a fine-grained matrix. In recent years, the focus of remedial technology development has been on in-situ and passive methods for contaminant destruction. Typically, in-situ and passive technologies have been applied to the dissolved plume and more active remedial technologies have been applied to the source area. Nanoparticle (NP) iron may offer a means to combine the advantages of in-situ and passive treatment with aggressive source treatment. Iron nanoparticles are submicron ($<10^{-6}$ m), bacteria-sized particles of zero valent iron (Fe^0) with (or without) a trace coating of noble metal catalyst (e.g., palladium or platinum). NP iron's large surface area ($>30\ m^2/g$) promotes rapid reactions with dissolved chlorinated organics. Because of their high reactivity and extremely small particle size (typical particle diameters range from 100-200 nanometers), NP iron may be delivered directly into a fine-grained source area where rapid dechlorination of dissolved phase contaminants may speed the dissolution of residual held in the fine-grained matrix. The NP-water slurry can be injected under pressure or by gravity to the source area through existing wells or minimally invasive drive points. There are no depth limitations for the NP treatment technology. The Navy is preparing to test NP iron to treat the source area near Hangar 1000 at Naval Air Station Jacksonville in Florida. Source area delineation is being refined to better target the NP application. NP delivery methods will be tested as will methods for evaluating the distribution and effectiveness of the NP.

76. Enhanced Recovery of Light Non-Aqueous Liquids Utilizing Preferential Pathways Induced by Subsurface Utilities

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At the study site, light non-aqueous phase liquids (LNAPL) are present as a result of historic operations. The recovery of LNAPL poses a remediation challenge in any geologic media. Efforts to recover the LNAPL at the study site have been additionally challenged because the majority of the LNAPL is present beneath a semi-confining peat layer. Remedial investigations have indicated that, to remove the LNAPL, it is necessary to depress the water table below the semi-confining layer.

The semi-confining layer is discontinuous in nature and interrupted by the presence of subsurface utilities. Two 24-inch drainage lines transect the site and provide a boundary for the largest continuous mass of LNAPL. In addition, these 24-inch drainage lines interrupt the peat layer and provide a preferential flow mechanism for the LNAPL through the surrounding bedding material. The 24-inch drainage lines have been slip-lined to prevent LNAPL infiltration into the lines.

Remediation efforts have included groundwater and LNAPL recovery via recovery wells placed in the vicinity of the 24-inch drainage lines. These efforts have resulted in greater than expected LNAPL recovery by taking advantage of the preferential flow induced by the surrounding bedding material around the lines. In addition, the drainage lines likely interrupt other discontinuities and preferential fractures within the peat, therefore providing additional flow mechanism for LNAPL toward the recovery wells.

77. Contamination Put to Bed: A North Carolina Furniture Manufacturer's Case Study

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An assessment involving the property transfer of a North Carolina furniture manufacturing facility detected volatile organic compounds in soil and ground water samples. A comprehensive investigation was performed at the site following the discovery of the contamination. The investigation determined that impacted soil extending from 6 feet below grade level (BGL) to 30 feet BGL (top of ground water) was located near the facility's drum storage area and product pump house. Compounds detected in soil samples included toluene (920,000 µg/kg), ethylbenzene, xylenes, and other regulated compounds. The investigation also determined that a plume of impacted ground water was centered immediately to the west of the product pump house. Compounds detected in ground water samples included toluene (17,000 µg/l), benzene (200 µg/l), ethylbenzene (1,100 µg/l), xylenes (4,780 µg/l), and C5 – C8 aliphatics (6,000 µg/l).

Pilot testing conducted at the site in December 1999 indicted that soil vapor extraction (SVE) and air sparging (AS) technologies could be used to remediate the impacted soil and ground water. An SVE and AS remediation system was constructed at the site in October and November 2000 following state approval. The remediation system was activated in January 2001.

Ground water and air effluent samples have been periodically collected at the site. Total petroleum hydrocarbon concentrations have decreased in the air effluent from 9,463 mg/kg (pilot test) to 160 mg/kg (October 2001). Toluene concentrations have decreased in the ground water samples from 17,000 µg/l (August 1999) to 39 µg/l (October 2001).

The remedial activities have significantly reduced the magnitude and extent of the impacted area. This presentation describes the business management and technical approaches that were utilized during the investigation and remedial phases of this project.

78. Consolidation of Sanitary Landfills

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A Sanitary Landfill (SL) is a structure designed following engineer techniques for mechanical stability and based on sanitary rules for avoiding potential environmental impacts, so that it is friendly with the ecological media and the human beings. Also, it is recognized in Argentina and Latin America as well as in many countries around the world, as the most used technique for final disposal of solid wastes, but at the same time, these landfills are near the cities where the garbage comes from. So that several efforts have been made to recover that land and return to the community. For acquiring this objective is important to understand how and when SL becomes stabilized.

The deformations observed in large SL are due to several factors, i.e. composition of refuse, type of SL, climatic conditions, geology (base layer of soils), hydrogeological (aquifers movements), operative methodology (acquired compaction and differential/total settlements), history of landfilling (sequence of disposal), partial and total heights of refuse, gas & leachate management, inflow of rain water, impermeabilization system, etc.

A SL operated in sequential and correlated steps involves a large-scale consolidation process that can be appropriately modeled as a two-dimensional plane strain model, which exhibits many common features with the one-dimensional Terzaghi consolidation problem. The analysis considers finite-strain effects, the garbage's permeability varying with the void ratio and pore leachate, garbage moisture to flow through it, and vertical expansion with a second layer of garbage creating a new stress framework. The finite element analyses can predict the deformation of the SL final cover as the consolidation process advances, and will enable to design more cost-effectively avoiding unsafe conditions.

79. The Resolution of Tight Emulsions in Industrial Scale Waste Processing

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Waste processing applies scientific principles to the creation of technologies to restore air, water and soils to their status before pollution, transform the pollutants in a manner that they are no threats for the environment anymore and recycle what can be.

As waste such as contaminated soils is a mixture of solids and of one or two liquid phases, recovery and reuse of any of its components require prior separation of the phases. In the laboratory, small scale separations can be done with sophisticated methods but, most often, these methods are too expensive to be applied to large scale operations, especially when the cost of processing is higher than the value of the recovered components. Initiating the processing, then, needs another incentive that overrules this consideration such as damages inflicted on the environment or a threat to public health. The separation methods generally used on an industrial scale: solvent extraction, filtration, centrifugation, thermal processes… are summarily reviewed.

But organic and mineral materials mixed with water are most often a stable emulsion, which has to be economically broken before those means are applied. The innovative process proposed is to submit it to the high shearing forces of a ball mill. The process that incorporates this piece of equipment as well as the equipment configuration, are patented under US Patents #6,056,882(May 2, 2000) and # 6,214,236 (April 10, 2001)and described in this paper.

80. A Poor Man's Remediation: Low Tech Chemical Oxidation of VOCs in Soil

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In situ chemical oxidation of non-chlorinated VOCs in soil using hydrogen peroxide has been used at small but growing number of contaminated sites throughout the United States. Many of the past approaches to this treatment method have relied on proprietary technology and specialized applications. As a result, the use of hydrogen peroxide injection as a cost-effective and environmentally friendly remedial option for contaminated sites may not be as widespread as otherwise possible. This paper presents a case study on the use of a "low tech" approach to the injection of hydrogen peroxide for the successful in-situ remediation of non-chlorinated VOCs in soil and groundwater at an industrial facility in Ohio. The case study includes a discussion of the key aspects of the design and application of a simple and cost-effective injection approach and hydrogen peroxide delivery device. This discussion is followed by an overview of onsite treatment activities and project hurdles that were overcome to obtain a 92% to 99% reduction in the existing soil contamination at the site. After this overview, a summary of the projected cost-savings associated with the use of hydrogen peroxide injection at the site is presented. Finally, the paper ends with a brief overview of the lessons learned during the project that should further assist in the future application of this "low tech" approach to in situ chemical oxidation with hydrogen peroxide at increasing number of contaminated sites.

81. The Controlling Action of Barrier Wall on Contaminated Migration

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The city population has been increasing and city waste has also increased in high speed as economic prosperity and urbanized development is expediting. The rubbish dangers seriously the human's existing environment and threatens people's usual lives. It has become social problem of pollution facing to each country in the world. In the past decades, much research about environment protection is aimed at the pollution of waste water and exhaust gas, but ignorant of the pollution of rubbish and other trash. By investigating information, 80% landfills in Canada has influenced the underwater environment around it in more or less extend. Due to the waste pollution, it has occasionally caused varieties of diseases and has resulted in food poison. In China, the landfill of most regions has not satisfied the demands of sanitary landfill. In fact, most of landfills are in passive states of naturally pilling up, naturally assimilating and incapacity processing. One reason is that the proper field is limited, the other reason is lack of technique condition and finance foundation. With the idea of environment protection enhanced and the knowledge of waste polluting soil, underground water and environment gradually deepen, solving the problem of waste pollution has caused generally attention of academic, engineering fields and all circles. The idea of barrier wall isolating pollution is economic, convenient and easier to construct. Some developed countries have widely used the technique. In China the research starts late in this aspects and more foundation work has been further completed. This paper has discussed the migrating law of contaminant ion and the controlling action of barrier wall. Based on the discussion of the migration model of the pollutant ion in porous media, one dimensional pollutant migration has been studied under ignorance of ion decaying factor in its migration, and assumption that the concentration of the containment contaminant input into barrier wall constant. The function formulas of the concentration of the pollutant ion and its output flow have been deduced. Then, the controlling effects on contaminant polluting of the thick and the material property of a barrier wall have been investigated, and obtained the conclusion that its material property acts more important role on controlling the pollutant concentration.

82. Lessons Learned in the Use of Modified Fenton's Reagent for the Treatment of Petroleum Contaminated Soil and Groundwater

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Norfolk RAM Group (formerly d/b/a Norfolk Environmental) has been successfully using Fenton's Reagent (catalyzed hydrogen peroxide under acidic conditions) since 1996 to replace traditional "excavate and haul" approaches that were not practical or too costly in many situations. With the number of successful projects completed now approaching 100, our experience with Fenton's Reagent in small scale remediation projects has produced a number of practical considerations which have been incorporated into each project undertaken. Of paramount importance is the optimization of the delivery system used to introduce Fenton's Reagent into the contaminated medium (soil and/or groundwater). Key factors to consider during the design of the delivery system include unsaturated zone soils, soil permeability, and the proper use of catalyst. Stoichiometric calculations based on the known release volume or the average contaminant concentrations can be used to provide a quick feasibility evaluation for practicality and cost considerations. Since many of these small scale petroleum remediation projects involve residential fuel oil releases, reaction monitoring is of primary importance where occupants are at home during treatments. Real time air monitoring and effective controls on off-gassing and ventilation are necessary components of each delivery system installation. Although much has been written concerning the controlling of, or lack of control during the reaction of Fenton's Reagent and petroleum, several steps can be taken to maximize the control of each application reaction. Considerations influencing control of the application reaction include the concentration of hydrogen peroxide used, the proper concentration of catalyst applied, the judicious use of off-gas venting controls, the rate of application, the time between each application, the presence or absence of free phase petroleum present and the use of water to cool and dilute.

83. Containment of NAPL and Passive Hydraulic Control at a Former manufactured Gas Plant Site

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Harding ESE was engaged by Northern Indiana Public Service Company to design a containment barrier and a groundwater management system that would prevent the migration of separate phase and dissolved phase hydrocarbons from the site into the neighboring Grand Calumet River while having the structural integrity sufficient to allow for future sediment removal in the river.

In order to maximize containment, reliability, and structural integrity, low permeability sheet piling was selected as the preferred containment option. However, the barrier would create mounding of the groundwater, allowing this groundwater to mingle with the site contaminants and then migrate around or through the sheet pile. To prevent this circumvention of the barrier, it was necessary to provide a form of hydraulic control. Pump and treat, funnel and gate, and passive controls were evaluated for this purpose. The classic pump and treat system was rejected due to long term operating costs. Funnel and gate technology has lesser operating costs, but due to the heterogeneous nature of the site contaminants, location of the gates was problematic and the use of this technology was restricted. Harding ESE determined that the most appropriate remedy is a passive system that relies on the stagnation of site groundwater created by the barrier and a preferential pathway similar to a French drain that diverts the upgradient groundwater around the site, avoiding contact with the site contaminants. A 3-D MODFLOW model was used to design the passive hydraulic control system.

The remedy incorporated a low permeability vegetative cover that restricts rain water infiltration and phreantophte trees that extract groundwater through water-conducting tissues in their root system. This utilization or uptake of groundwater combines with the other mechanisms to avoid mounding and produce acceptable groundwater elevations and flow patterns, thus achieving the remedial objectives. In addition to managing groundwater, the root zone of these trees will be expected to stimulate biological activity capable of degrading the site contaminants as well.

By utilizing passive hydraulic controls rather than the conventional active pump and treat technology, it is estimated that the costs of the remedy have been reduced by as much as $1,000,000. Due to this innovative approach, Harding ESE was given project responsibility from conceptual design through construction, including permitting and Agency coordination, and has been hired as the Design/Build Contractor to construct the remedy of this site.

POSTER SESSION - SEDIMENTS

84. Utilization of The DQO Process in the Application of Sediment Data to the Sediment Quality Triad and its Outcome

Barbara Albrecht, EnSafe Inc., Pensacola, FL
William Hill, Southern Division Naval Facilities Engineering Command, North Charleston, SC
Tom Johnston, Tetra Tech NUS, Inc., Pittsburgh, PA
Allison Harris, EnSafe Inc., Memphis, TN

85. Clean-up Goals for a Coal Tar Deposit in a River Located in the Vicinity of a Former MGP

William Ayling, O'Brien & Gere Engineers, Inc., Syracuse, NY
Tracy Blazicek, New York State Electric & Gas Corporation, Binghamton, NY

86. Human Health Risks Associated with Contaminated Sediment at a Naval Facility in San Francisco Bay

N.L. Bonnevie, Battelle, Duxbury, MA
Donald G. Gunster, Battelle, Duxbury, MA
Virginia Lau, Battelle
Theresa Bernhard, NAVFAC, Washington DC
Michael J. Pound, Southwest Division Naval Facilities Engineering Command, San Diego, CA

87. Use of *In-situ* Dializers for Determination of Sediment Porewater Contaminant Concentrations

A. Lee Gustafson, Harding ESE, Inc., Merrimack, NH

88. Remediation Monitoring at the United Heckathorn Superfund Site

Nancy P. Kohn, Battelle Marine Sciences Laboratory, Sequim, WA
Carmen White, U.S. Environmental Protection Agency, Region IX, San Francisco, CA
Andrew Lincoff, U.S. Environmental Protection Agency, Region IX Laboratory, Richmond, CA

89. Capping Contaminated River Sediments

Joseph Mihm, Camp Dresser & McKee, Massena, NY
Larry McShea, Alcoa Inc., Alcoa Center, PA
Heather VanDewalker, Blasland, Bouck & Lee, Inc., Syracuse, NY
James Quadrini, Quantitative Environmental Analysis, LLC., Montvale, NJ

90. Remediation of a Sediment Contaminated Pond Located on a Sinkhole

Paul Reeser, Parsons, Cincinnati, OH

84. Utilization of the DQO Process in the Application of Sediment Data to the Sediment Quality Triad and its Outcome

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Nearshore sediments near a former waterfront paint stripping, metal refinishing, metal plating shop, and associated hazardous waste storage, were impacted from activities associated with the operations of this military facility from 1935 to 1980's. Sediment analyses in 1993 indicated PCBs, PAHs, pesticides, and metals above screening benchmark values throughout the area. Survival effects were noted in sediment toxicity tests performed with the opossum shrimp, *Mysidopsis bahia,* but not observed in tests with the sheepshead minnow, *Cyprinodon variegatus*. However, sublethal effects were observed in the sheesphead minnow test.

In 1995, two hurricanes, Erin and Opal, were experienced in the Pensacola Bay area. In 1998, a third hurricane, Georges, was experienced. The effect of the hurricanes on the site sediments is uncertain. In addition, past data collection efforts focused on the top six inches of sediment only, and now there is concern about chemical concentrations at greater depth. Dredging could possibly uncover contaminated sediments. Therefore, decision-makers (i.e., EPA, FDEP and Navy) agreed to investigate the area to establish current site conditions.

Using the Data Quality Objective (DQO) process, the investigation was designed to assess whether the sediments create a condition adverse to benthic communities. If adverse conditions do exist, do they warrant remedial action? Before collecting any samples onsite, the inputs, boundaries, and decision-making rules were established. Sampling techniques, chemical analysis, toxicity analysis, detection limits, and order of sample collection were discussed and consensus was reached. A decision-making triad was also developed to direct how the data were to be used. Investigators weighed possible options for the site and explored all potential outcomes prior to entering the field and collecting the first sample. This technique saved valuable time at the end of the study, where decisions were made. In addition, decision-makers were able to fully support the final decision for the site.

85. Clean-up Goals for a Coal Tar Deposit in a River Located in the Vicinity of a Former MGP

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Establishing sediment cleanup goals in river systems can be controversial largely because guidance for developing site-specific goals is limited and understanding of environmental risks is often incomplete. Screening criteria provide a basis for preliminary evaluation of site risks, but clean-up goals require consideration of site-specific risks. Natural attenuation is a component of all sediment sites, as complete removal of contaminants is often not technically possible or practical.

To establish site clean-up goals at a former MGP site, risks associated with PAHs were evaluated using several approaches. A total PAH concentration of 4 mg/kg based on sediment sampling and analysis delineated an area around a pipe where a coal tar deposit was identified. Environmental forensics were used to evaluate the composition of the PAHs in sediment where coal tar was not observed, but elevated total PAH concentrations occurred compared to local background. Evaluating the fate of PAHs included comparing the environmental risks associated with “aged” and “fresh” materials. Urban background concentrations reported for sediment were compared to site levels. Statistical evaluation of sediment concentrations identified median concentrations and statistical outliers. Physical features of the site such as the size of the affected area, public accessibility to the site, sediment type, river bottom substrate, and the potential for downstream contamination were also considered.

Results supported the recommendation to use visual observations for guiding coal tar removal at the site. Sediment concentrations of PAHs surrounding the coal tar impacted area were comparable to urban background levels. The PAH composition of the sediment was “aged” suggesting reduced bioavailability to aquatic organisms compared to “fresh” sources. The affected area was relatively small and the riverbed was comprised of primarily rocks, cobbles, and sand. Silt was limited by the flow patterns in the river. Public accessibility was also limited. These physical features supported the proposed clean-up plan.

86. Human Health Risks Associated with Contaminated Sediment at a Naval Facility in San Francisco Bay

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The focus of this investigation was to more clearly define the extent of sediments at a naval facility in San Francisco Bay that require evaluation in a Feasibility Study based on potential risks to human health. Human health exposures to offshore sediment at the site are limited to the consumption of fish and shellfish, however, due to the prevalence of other chemical sources to the estuary as well as the limited amount of data regarding the bioavailability of sediment associated chemicals, it is difficult to attribute measured tissue concentrations in relatively mobile fish species to any single source. As a result, a two-pronged approach was developed, predicated on the assumption that risk management decisions must be based on exposure pathways providing the most direct link to site-specific sediments. Two objectives were identified: 1) the development of a feasibility footprint based on site-specific exposures via consumption of shellfish; and, 2) to determine whether tissue concentrations in recreational fish species collected from the vicinity of the site are statistically different from those associated with fish from other areas within the Bay. Assuming that all other relevant exposure parameters (e.g., ingestion rate, exposure duration) are equivalent, this approach provides a measure of the relative risks. The results indicated that cumulative risks associated with the consumption of fish shellfish from the site, although greater than 10^{-6}, are comparable to those associated with reference locations. The primary risk drivers are arsenic and chromium, which have been demonstrated to be elevated throughout the Bay. PCBs are elevated in site-specific tissues, however, they represent less than 1% of the total cumulative risk. Based on this information, it was determined that the feasibility footprint should be based on ecological concerns, with confirmation that the areas of highest PCB contamination are addressed.

87. Use of ***In-situ*** Dializers for Determination of Sediment Porewater Contaminant Concentrations

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As part of many site investigations for risk characterization, an understanding of impact to biota which inhabit sediment is usually required. In many cases, contaminant concentrations in sediment are used to estimate the potential impact of constituents on benthic organisms. Estimation of porewater concentrations from sediment data using Henry's law may result in erroneous data being used to calculate the potential risk to biota. In-situ dializers, which operate through osmotic processes, can be placed in sediment to allow collection of samples that are representative of porewater concentrations. Use of in-situ dializers allows laboratory analysis of contaminant concentrations in porewater, which can then be used to accurately estimate potential risk associated with porewater.

This approach has been used at a number of sites, including where specific data were needed to determine constituent concentrations within the upper six inches of sediment, as well as at twelve discreet intervals within the upper 18 inches of sediment. Site-specific in-situ dializer designs have been developed to allow collection of precise depth interval data.

88. Post-Remediation Biomonitoring at The United Heckathorn Superfund Site

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The United Heckathorn Site in Richmond, California, was listed as a federal superfund site in 1990, after California State Mussel Watch monitoring data from the mid-1980s showed that mussels in Richmond Harbor had the highest DDT concentrations in the state. Pesticides had been formulated at Heckathorn between 1947 and 1966. A marine sediment RI/FS was completed in 1994. Between September 1996 and March 1997, 112,660 tons of pesticide-contaminated sediment was dredged from the waterway adjacent to the site. EPA's Record of Decision required post-remediation monitoring for at least five years to assess the effectiveness of sediment cleanup. State Mussel Watch sampling and analysis methods and four State Mussel Watch stations in Richmond Harbor were adopted for the post-remediation biomonitoring program to allow comparison of pre- and post-remediation DDT bioavailability. Mussel tissue and water samples were collected annually, starting six months after sediment remediation. All samples were analyzed for chlorinated pesticides, and lipid concentrations determined in all tissue samples. For the first three years, total pesticides in water were analyzed, but in 2001 and 2002, dissolved pesticides and total suspended solids were added to address pesticides associated with suspended particles. In fall/winter 1997, mussel tissue concentrations were slightly higher than pre-remediation levels. The next two years of monitoring showed a decrease in tissue concentrations to below pre-remediation levels, but not a dramatic decrease that would indicate significantly reduced bioavailability. This triggered a sediment investigation that showed that surface sediment DDT concentrations exceeded the cleanup goal, and some concentrations were higher than those originally found during the RI/FS. The sediment investigation and the most recent years of tissue and water concentrations suggest continued bioavailability of pesticides near the Heckathorn Site.

89. Capping Contaminated River Sediments

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An in-river capping pilot study was conducted by Alcoa in the Grasse River in 2001. A subaqueous cap was constructed over PCB-containing sediments in a seven acre portion of the river (750' long, 400' wide, 16' deep) using various combinations of capping materials and placement techniques. The objectives of the study were to evaluate: placement techniques; coverage effectiveness; potential entrainment of underlying sediment into cap material; particle size fractionation; water column impacts; costs; and recolonization by benthic organisms.

The cap placement techniques included surface and subsurface clamshell placement and a tremie pumping method. The cap materials tested included a 1:1 sand/topsoil mixture, a granular bentonite clay layer and AquaBlok (a manufactured composite aggregate core coated with bentonite clay). The cap materials were installed in thickness' ranging from 2-to 24-inches thick.

The study was conducted with a test cell and a pilot cell phase. Extensive monitoring was performed. Cap materials were tested for grain size distribution, total organic carbon (TOC), lift thickness and PCBs. Water column samples were analyzed for field parameters, suspended solids and PCBs. Benthic samples were collected prior to and after capping. The test cell monitoring results were evaluated to select the placement techniques and cap materials for use in the pilot cells.

Results of the pilot study indicate that capping of PCB-containing sediments can be successfully implemented in the Grasse River. Optimal results were achieved with a 12 inch lift of 1:1 sand/topsoil material applied at the water surface or subsurface via a clamshell. Monitoring data collected during the study demonstrated acceptable cap uniformity and thickness, no significant PCB entrainment from the in-place sediments, and no significant fractionation of the cap material during placement. A WINOPS clamshell positioning system and crane operator experience were important to the success. Water quality impacts during capping were negligible.

90. Remediation of a Sediment Contaminated Pond Located on a Sinkhole

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Sediment in a mid-western pond was contaminated by sludge from a package sanitary treatment system. The pond water is considered a Water of the State because it discharges to a sinkhole, and remediation restrictions were made by the state regulators because of this.

Two options to clean the pond were considered. The first was to dredge the pond. Costs for dredging a ¼ acre pond, however, were relatively high. Also, without being able to see the bottom of the pond, verification would be difficult.

The other option was to drain the pond, thicken the sediment in the pond bed, and haul it off-site. The state, however, had several concerns about this method. The first was that the water being discharged was considered contaminated. NPDES concentrations limits would have to be met. The second concern was that the state did not want thickening agents brought into the pond bed. Further study of the pond geology demonstrated that most of the pond bed is located within a silty clay layer with a water table higher than the pond bed. Thus water contacted by the thickening agent could be kept in the pond. This arrangement allowed the project to proceed in a cost-effective manner, while maintaining the highest protection to the environment.

Remediation of the pond began with dewatering. Ammonia was reduced by enhanced aeration, while solids were treated using a particulate filter. 800 tons of sludge, as well as 95 tons of cement kiln dust, was disposed. A compacted layer of sludge existed underneath a loose layer. While the amount of sludge was nearly ten times the amount originally estimated, the final cost was only slightly higher than original estimate. The site has been completely restored without damage to the underlying cave system or adjacent watershed.

POSTER SESSION – SITE ASSESSMENT

91. Environmental Screening of an Entire City
Daniel J. Adomaitis, Illinois State Geological Survey, Champaign, IL

92. Interim Offshore Monitoring Program at Portsmouth Naval Shipyard
Aaron Bernhardt, Tetra Tech NUS, Inc, Pittsburgh, PA
Jo Ellen Hinck, Tetra Tech NUS, Inc, Pittsburgh, PA
Debbie Cohen, Tetra Tech NUS, Inc, Pittsburgh, PA
Fred Evans, Engineering Field Activity Northeast, Lester, PA
Jason Speicher, Engineering Field Activity Northeast, Lester, PA
Marty Raymond, Portsmouth Naval Shipyard, Portsmouth, NH

93. An Environmental Assessment of the Historic McKinley Bridge and Approach Structures
Mark R. Collier, Illinois State Geological Survey, Chicago, IL

94. Defining TCE Plume Source Areas Using the Membrane Interface Probe (MIP)
Beth McAndrews, Earth Tech, Inc., Englewood, CO
Bill DiGuiseppi, Earth Tech, Inc., Englewood, CO
Kim Heinze, University of Waterloo, Waterloo, Ontario, Canada

95. Site-to-Background Comparisons for Trace Elements in Soil
Jonathan Myers, IT Corporation, Albuquerque, NM
Karen Thorbjornsen, IT Corporation, Knoxville, TN

97. Computer-Assisted Radar Tomography as a Means to Document Subsurface Features in Support of Site Remediation
Michael Warminsky, AMEC Earth & Environmental, Somerset, NJ
Stephen E. Posten, AMEC Earth & Environmental, Somerset, NJ
Anthony DeRubeis, Witten Technologies, Inc., Boston, MA

91. Environmental Screening of an Entire City

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Recent population growth in Pinckneyville, Illinois, a city of 5,600 people located approximately 60 miles southeast of St. Louis, has resulted in increased traffic that overwhelms the existing two-lane State Route system. The Illinois Department of Transportation (IDOT) has proposed widening Illinois Route 13/127 to four lanes. Since the current route of this highway runs through the major commercial corridor of Pinckneyville, with little room for expansion along this route, IDOT is looking at eight possible solutions to re-route traffic using either existing local streets or by bypassing the city altogether, which taken together encompass essentially the entire city of Pinckneyville.

The ISGS conducts preliminary environmental site assessments (PESAs) for IDOT road construction projects. PESAs assess potential environmental threats while construction projects are still in the planning stage. Implementing PESA findings improves worker safety, and reduces liability and overall costs. Most environmental site assessments involve one or a few parcels. However, the PESA for this project included over 30 current, former, or possible UST sites, five LUST sites, and a CERCLIS site. Further complicating this project were potential subsidence hazards from abandoned and inactive coal mines surrounding the city. A study of this magnitude presented unique problems, including getting access to closed and abandoned mine facilities, determining land ownership for several sites, sorting through site histories where local recollection was the only source of information that could be found, and being sensitive to politics that revolved around local merchants= fear of losing their prime locations along the major highway through Pinckneyville if a bypass were chosen around their city instead of using existing roads through it.

92. Interim Offshore Monitoring Program at Portsmouth Naval Shipyard

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Portsmouth Naval Shipyard (PNS), Kittery, Maine is located on an island in the Piscataqua River, referred to as Seavey Island. The Piscataqua River is a tidal estuary that forms the southern boundary between Maine and New Hampshire. The Navy determined that interim monitoring was warranted for the offshore area around the shipyard (Operable Unit 4) to provide current data on the offshore areas to determine whether onshore remedial actions, natural process, and/or other sources have affected the chemical concentrations in OU4. Therefore, an Interim Record of Decision for OU4 was signed in May 1999 that requires the Navy to conduct interim offshore monitoring for OU4. Sampling is being conducted at 14 monitoring stations located around PNS and at four reference stations in the Great Bay Estuary. The sampling program consists of collecting sediment, mussel, and juvenile lobsters at the monitoring and reference stations, which are analyzed for a variety of parameters. To date, five rounds of samples have been collected. The results of the data collected from the second round were used to develop preliminary remediation goals (PRGs) for the offshore areas. The data collected from the first four rounds also identified areas around the shipyard that require further evaluation to determine extent of contamination, based on exceedences of the PRGs. The first four rounds were evaluated in a Baseline Report (currently draft), which recommends the time of year that future samples should be collected, discontinuing lobster sampling, and discontinuing the collection of acid volatile sulfide samples from the 0 to 2 cm interval. Future recommendations may include the deletion of monitoring stations from the sampling program or the deletion of parameters from the analyte list.

93. An Environmental Assessment of the Historic McKinley Bridge and Approach Structures

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To extend its tracks over the Mississippi River, the Illinois Terminal Railroad constructed the McKinley Bridge in 1910, linking Venice, Illinois with St. Louis, Missouri. The camelback bridge was initially designed to carry freight cars and interurban trains along two inside lines into downtown St. Louis; two outside lanes were added to accommodate increasing automotive traffic in the 1930s. Safety concerns surrounding severely deteriorated segments of the bridge prompted the Illinois Department of Transportation (IDOT) to close the 91-year-old McKinley Bridge in October 2001 until a massive rehabilitation effort could be undertaken.

Because the McKinley Bridge extends over commercial and highly industrial areas of Venice and St. Louis, the Illinois State Geological Survey (ISGS) conducted a Preliminary Environmental Site Assessment (PESA) of the bridge ROW in order to provide IDOT with information regarding the presence of hazardous materials potentially affecting the project. Previous USEPA investigations revealed that several parcels along the ROW contained a mixture of contaminants including dioxin, PCBs, heavy metals, and industrial solvents. The complexity of the PESA was amplified due to an ongoing cleanup and investigation of parcels along the bridge ROW that were identified by the US Army Corps of Engineers to have radioactive residues from a uranium refinery.

The historical use of the area since the 1940s proved to be the key to the contamination impacting the bridge ROW. The non-homogeneous fill material and the alluvial deposits underlying the bridge provided an excellent medium for the migration of surficial hazards. Decaying radioactive debris lingering in the ROW from the dismantling of the uranium refinery in the 1980s is responsible for the previously undocumented levels of radioactive contamination beneath the McKinley Bridge.

94. Defining TCE Plume Source Areas Using the Membrane Interface Probe (MIP)

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A variety of traditional characterization methods, such as soil gas surveys, soil and groundwater sampling, and fixed laboratory analysis are commonly used to define the extent and magnitude of soil and groundwater contamination in volatile organic compound source areas. One significant limitation of these methods is that they require multi-media sample collection to define the full unsaturated and saturated vertical profile in any given location. Additionally, attaining higher resolution by increasing sample frequency increases costs substantially. A relatively new technology, the Membrane Interface Probe (MIP), was used to define TCE plume source areas at F.E. Warren AFB in Cheyenne, Wyoming and at a confidential security products manufacturer in Tennessee. The MIP proved to offer significant advantages over traditional drilling and direct-push methods and yielded data critical to a full understanding of subsurface conditions. The near-continuous MIP analysis minimized the number of soil and groundwater samples required to fully delineate the extent of the plume-head source areas. Additionally, the MIP is able to collect data in the vadose and saturated zones, providing detailed vertical contaminant profiling information, and geologic conditions based on soil conductivity, that aided in the development of the site conceptual model. The MIP was not without its disadvantages, principal among these the relatively high detection limit (approximately 100 ppbv in soil gas, 100 ppm in soil and 100 ppb in groundwater) making the method useful for source characterization but limited for delineating lower levels of contamination. Additionally, the data obtained from the MIP is considered screening level data and needs to be supplemented with analytical soil or groundwater data to fully support risk or remedial decisions. In summary, the vertical profiling obtained using the MIP aided in the interpretation of the complex relationship between the presence of gross contamination in soil and groundwater and the geologic conditions controlling contaminant distribution.

95. Site-to-Background Comparisons for Trace Elements in Soil

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An integrated statistical and geochemical evaluation of naturally occurring elements in soil has been successfully applied at several facilities undergoing investigation and cleanup. Element concentrations demonstrated to be naturally occurring have been eliminated from consideration during risk assessment and remediation. Multiple statistical procedures are first performed to test for different modes of contamination (i.e., hot spots versus slight but pervasive contamination) and to graphically display site and background data sets for visual comparison. Elements shown to have elevated concentrations in the site data set relative to background are then subjected to geochemical evaluation, which is based on the natural associations of trace elements with specific minerals in the soil matrix. Correlation plots of trace elements versus major elements are constructed to explore these mineralogical associations. Geochemical evaluation provides mechanistic explanations for apparently high, yet naturally occurring, element concentrations. Anomalous samples that may contain a component of contamination can also be readily distinguished from uncontaminated samples. This site-to-background comparison technique utilizes existing analytical data obtained during typical site investigations, although site and background data sets of adequate size and quality are required for proper comparison. Examples from investigations across the United States illustrate the technique's utility in a variety of geological regimes and project sites. Because site-to-background comparisons based solely on statistics are prone to high decision error rates, the integrated statistical and geochemical evaluation is superior for establishing the provenance of elevated trace element concentrations to support site characterization, risk assessment, and remediation. Significant cost savings have been realized at sites where this comparison technique was applied.

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97. Computer-Assisted Radar Tomography as a Means to Document Subsurface Features in Support of Site Remediation

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Site remediation activities at a solvent contaminated site in New York State require the installation of an injection grid throughout the area of a mapped contaminant plume. Within this area, a French drain network had previously been installed, and several transite (asbestos/cement) water distribution mains had been approximately located by the local water utility. No as-built drawings were available for the French drain network, the location of which is essential to avoid “short-circuiting” of amendments proposed to be injected into the subsurface under the remedial action. In addition, accurate maps of the water distribution mains were not available, and the materials of their construction precluded accurate location using conventional technologies. The Witten Technologies, Inc. CART Imaging system was used on the project site to provide a comprehensive three-dimensional image of subsurface features within the area of interest (approximately ½ acre). This system combines existing ground-penetrating radar technology in a multi-channel array, precision positioning control, and three-dimensional synthetic-aperture radar (SAR) imaging. Image data derived from the field application clearly depicted the presence of the shallow French drain network, and the deeper water distribution mains. Relative to the latter, the technology identified an additional (discontinued) main that was no longer depicted on local water utility distribution schematics. Image data was accurate to within several inches both horizontally and vertically, and achieved a maximum penetration depth of 12 feet. Features identified from image interpretation were subsequently plotted as an overlay to a standard project site CAD map, and are currently being used to guide the final design of the remedial action injector array.