

Program One
Tuesday, May 25, 1999
Risk-Based Decision Making
Jefferson A



**TARGET CLEAN UP
LEVELS AND
REMEDICATION**

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Chemical desorption from soil and sediment is of central importance to most environmental concerns including remediation. Desorption affects chemical fate, toxicity, and associated risk to human and aquatic life as well as the efficiency of most remediation technologies. Desorption is commonly modeled as a reversible partitioning process in fate, risk, and remediation models. However, the reversible model has failed to predict the long-term persistent release of contaminants to the environment. Even with the most advanced remediation technologies (physically, chemically and/or biologically enhanced), it is often observed that a fraction of the sorbed contaminant remains in the soil or sediment. The existence of this remaining fraction has hindered the closure of many clean up operations. Knowledge and prediction of desorption is necessary for designing more effective remediation schemes. If it could be shown that pollutants would not be released from sediments in any significant concentrations, either abiotically or via biological means, they would be of little practical concern and could be safely left in place. In this case, the impact on remediation costs could be enormous.

The overall objective of this research is to develop a predictive correlation to model contaminant release for both laboratory and field observations. A semi-empirical irrevers-

ible sorption isotherm model, based on the laboratory-observed parameters, has been developed and used to correlate most field observations reported in the literature. Chemicals used in this study include an aromatic compound (toluene), halogenated aromatic compounds (1,2 dichlorobenzene), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and a chlorinated pesticide (DDT). Several types of sediments containing various organic carbon contents have been tested. This new isotherm has also been incorporated into a transport model to examine the impact on remediation. It has been shown that this two-step desorption often extends remediation time by up to two orders of magnitude and that clean up time is inordinately sensitive to the selection of the target aqueous concentration level; both results are commonly observed in the field.

Key words: sediment, criteria, adsorption, desorption, availability



**SITE CHARACTERIZATION /
RISK ASSESSMENT OF
TETRACHLOROETHENE
(PCE)-CONTAMINATED SITE**

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A confidential healthcare client purchased property in eastern Iowa in order to expand its facilities. A Phase I Environmental Site Assessment (ESA) revealed the property purchased was the site of a former dry cleaning operation. A combination of innovative (i.e., direct-push sampling with mobile laboratory) and traditional Phase II sampling, and testing, performed by Howard R. Green Company, confirmed that site soil and groundwater were contaminated with tetrachloroethene (PCE) and trichloroethene (TCE). Maximum concentrations of PCE and TCE in groundwater were 538 and 209 mg/L, respectively, and 108 and 1.51 mg/kg in soil. Additional sampling and

testing was performed to characterize the vertical and horizontal extent of contamination in the soil.

The concentrations of the chlorinated solvents in both the soil and groundwater were low enough that the IDNR was not concerned and did not require corrective action. However, being a healthcare provider and concerned that the high statewide standard for PCE in soil (780 mg/kg) may not provide ample protection for several exposure pathways, the client retained Howard R. Green Company to assess the risk to the public from the contamination at the site.

Howard R. Green Company performed a receptor survey and subsequently developed site-specific target levels (SSTLs) for contamination based on the receptors identified, which included eight non-drinking water wells, a protected groundwater source, and two building basements. Calculations were performed using accepted risk factors, models, and chemical-specific toxicity values. Howard R. Green Company then recommended remedial activities to the client in order to minimize risk.

Key words: chlorinated, solvents, risk, tetrachloroethene, assessment



WILDLIFE APPLICATIONS TO REMEDIATION DECISION MAKING

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Decision making associated with chemically contaminated waste sites is generally based on 1) contaminant bioavailability to potentially exposed populations and 2) the toxicity and biological persistence, and therefore, the pertinence of the contaminants present. Though human populations are

generally of primary concern, wildlife inhabiting contaminated sites can be front-line indicators of chemical exposure and effects due to their intimate association with the site. This association provides a sensitive means of detecting potential for exposure and effects-associated adverse responses, the magnitude of which can provide a means for determining the prioritization of remediation processes.

Wildlife exposure and health effects assessments are now being used in the remediation decision-making process. Specifically, the development of geographic distributions of chemical exposure and effects in wildlife can be used to 1) test the validity and accuracy of assumptions drawn from modeling exercises, 2) investigate the dose-related effects of exposures to chemical mixtures where pertinent toxicity data are unavailable, and 3) evaluate adverse health effects in wildlife species residing on the site. Further, once remedial actions have been taken, wildlife health can then be used to demonstrate the extent of reduction of waste site-related risk to wildlife by comparing post-remediation wildlife health to that found on the site prior to remediation. These approaches have been recently applied to the 27-square-mile Rocky Mountain Arsenal (near Denver, Colorado) in its conversion from a US Army nerve gas / munitions / pesticide production facility to a US Fish and Wildlife Service National Wildlife Refuge.

This presentation will first introduce material condensed from a meeting held in May 1999 to build consensus among federal agencies on the role for wildlife in remediation decision making. It will then provide relevant examples on successful use of the approach, emphasizing both strengths and pitfalls pertinent to remediation decision makers and risk managers. Examples of evaluations that have used this approach will include studies at Rocky Mountain Arsenal investigating local rodent community demographics, breeding population assessments of European starlings (employing nest box-enhanced use of the site),

deer mice placed in on-site enclosures, and species-specific health effects evaluation of American badgers. Sponsored by NIEHS ES04696.

Key words: wildlife, decision making, efficacy testing, remediation prioritization

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Environmental Management
Jefferson A



**THE ROLE OF HYBRID
POPLAR TREES IN
BROWNFIELD AND INDUS-
TRIAL SITE MANAGEMENT**

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The industrial age, with its emphasis on centralization and manufacturing, has impacted the environment by creating 'brownfields' and other industrial contaminated sites. With sufficient time, 'nature' will detoxify and revegetate these impacted sites. However, when society cannot wait for natural attenuation, more focused remediation strategies must be employed. The use of phytoremediation, and in particular hybrid poplar trees, offers numerous benefits as a site cleanup alternative.

Ecolotree® Inc. has designed and installed hybrid poplar systems at 13 brownfield and industrial contaminated sites. These applications have helped to demonstrate the following capabilities of hybrid poplars:

1. Finding the 'hot spots' where contamination is toxic to plants. Phyto-toxicity can often be used to characterize site contamination more economically than traditional soil sampling. Other remediation techniques can then be employed in phyto-toxic zones to reduce the contaminants to non-toxic levels.

2. Making the site more aesthetically pleasing and acceptable to the neighboring community. Hybrid poplar and grass systems

can be used to provide visual buffers and wildlife habitat for stark, blighted industrialized areas.

3. Managing water. Hybrid poplars exhibit high water uptake rates, which minimizes the amount of precipitation available to infiltrate contaminated soil, and can potentially prevent or greatly reduce contaminated groundwater flow off site.

4. Stabilizing soil. Plant roots help stabilize soil and prevent erosion. In doing so, phytoremediation can minimize human exposure to blown soil by inhalation or contact.

Laboratory and greenhouse studies have shown that hybrid poplars are also capable of taking up and degrading numerous contaminants, such as TCE, TNT, atrazine, and the BTEX compounds. There is little data, however, regarding the effectiveness and speed of phytoremediation in cleaning up actual field sites. Therefore, it has become essential to infer what should happen in the field based on good science.

Ecolotree® installations have been used for PAH-contaminated soil in Tennessee, boron- and arsenic-contaminated fly ash in Missouri, ammonium-contaminated soil and groundwater in Iowa, and PCP- and PCB-contaminated soil at a sawmill demolition site in Oregon. Significant financial savings have been reported, as exemplified by \$2,000,000 in savings over more traditional technologies at a casting sand landfill in Michigan.

Key words: brownfields, phytoremediation, phyto-toxicity, aesthetics, stabilization



MONITORED ENHANCED NATURAL ATTENUATION (MENA)

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Monitored Enhanced Natural Attenuation (MENA) is a remedial approach being developed in Iowa for application at former manufactured gas plant (FMGP) sites. This approach involves enhancing the natural processes so that remedial objectives can be more readily and effectively achieved in a reasonable time frame than with the natural processes alone. Examples of the application of MENA are monitoring with free product removal, monitoring with hydraulic or physical containment, or monitoring with enhancement of biological activities. This approach emphasizes treating the contaminated site as a continuous, integrated system rather than breaking it down into subsections that are treated separately. This paper provides an overview of the components of MENA and their relationships. Included are the role of site characterization and an optimized groundwater monitoring program; potential enhancements of source control and the natural attenuation processes, both above and below the groundwater table; and an overview of issues and challenges in assessing natural attenuation processes at FMGP sites.

Key words: natural attenuation, source control, monitoring programs



EFFECTIVE MANAGEMENT OF LAGOONS TO REDUCE THE FATE AND TRANSPORT OF CONTAMINANTS INTO THE SUBSURFACE

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Animal waste, usually in liquid form with significant amounts of suspended solids content, is stored in earthen lagoons. These lagoons are often lined with clay to reduce the seepage of contaminants into the subsurface. Animal waste is rich in nitrogen and ninety five percent of the nitrogen is in the form of ammonium NH₄-N. Ammonium, being a cation, is absorbed by the lagoon liner and remains immobile as long as anaerobic conditions exist. In the present study, contaminant transport simulations were carried on a lagoon liner of one-, two-, and three- foot thicknesses using the SWMS-2D program. It was found that the breakthrough times of ammonia are 2.5 times higher for a three-foot liner than using a one-foot liner. But constructing a lagoon with three-foot liner increases the cost of the construction. As an alternative to constructing a lagoon using thicker liner, simulations are made on a one-foot liner with the top few centimeters of the liner being replaced with new liner material. Comparison of breakthrough times of contaminants will be presented to aid in the frequency of the replacement time interval. In addition to reducing the costs of the liner construction, the scraped-liner material can be used as organic fertilizer, which is very rich in ammonium.

Key words: animal waste, lagoon, liner, contaminant transport, effective management

Program One
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Wetlands
Jefferson A



**LEAD AND ZINC REMOVAL
BY LAB-SCALE CON-
STRUCTED WETLANDS**

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Constructed wetlands have the potential to trap and remove metals in mine wastewater. In order to determine the effectiveness of constructed wetlands for treating selected heavy metals in neutral mine effluent, seven lab-scale constructed wetlands were set up to treat a synthetic, slightly basic mine water containing 34.2 mg/L SO_4^{2-} , 0.05 mg/L Pb and 0.30 mg/L Zn. Another lab-scale-constructed wetland was set up to treat synthetic smelter effluent with a shock load of SO_4^{2-} , Na^+ , and Pb. Temperature, hydraulic loading, and substrate composition generally did not affect treatment efficiency. The pH of the effluent was reduced to near neutrality. An average removal of 90% of lead and 72% of zinc was observed in all eight wetlands. In wetlands operating on synthetic mine water, sulfate was completely removed, likely by conversion to sulfide by sulfate-reducing bacteria. The effluents had little or no toxicity in whole effluent toxicity assays. In the wetland operating on synthetic smelter effluent, only about 25% of influent sulfate was removed and a breakthrough period of four days for sodium was observed which showed that the wetland was not effective for removing sodium. Whole effluent toxicity assays on undiluted wetland effluent had 100% survival of fathead minnows and *Daphnia magna*. Survival of *C. dubia* was zero in undiluted effluent, but 75-100%

survival was observed when the effluent was diluted to half strength.

Key words: metal removal, lead, zinc, mine wastewater, constructed wetland



**NATURAL ATTENUATION
OF CHLOROPHENOLS IN
ANAEROBIC WETLAND
SEDIMENTS**

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Freshwater wetlands are among the most important and complex ecosystems on earth. They serve as a sink for complex organics, consisting of cellulose, lignin, and chitin. These organics undergo slow degradation to labile carbon, which is available for utilization by bacteria in complex wetland environments. With their high density of microbial populations, as compared to terrestrial environments, wetland sediments are highly effective at consuming and processing labile, detritus litter. Such utilization of background organic matter and elevated microbial populations has encouraged close evaluations of wetland systems for bioremediation. In this study, we will focus on a wetland system contaminated by numerous solvents and hydrocarbons.

The abundant supply of low-molecular-weight organic substrates in wetland sediments, generated from decomposition of organic matter, has the potential to enhance dehalogenation of chloro-organics. In this study, kinetic rates of dechlorination of chlorophenols in anaerobic, organic-rich wetland sediments and biotransformation pathways of chlorophenols through dehalogenation in wetland sediment are examined in detail. Determination of low-molecular-weight (LMW) organic acids in wetland sediment is crucial in predicting metabolic activities of microorganisms. This is evidenced by LMW organic acids being impor-

tant intermediate breakdown products between large biomolecules and ultimate mineralization products, i.e., methane and carbon dioxide. Additionally, the LMW organic acids levels produced from wetland sediments confirm the availability of reducing power for reductive dechlorination in wetland sediments. Material balances for the transformation and degradation of tetrachlorophenols (TeCP) will be presented in the context of the relative potential for their remediation in wetland sediments systems through natural remediation processes.

Key words: wetland sediments, methanogens, dehalogenation, chlorophenols



CHLORINATED VOC TREATMENT IN CONSTRUCTED WETLANDS

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Natural attenuation, specifically via reductive dechlorination of chlorinated solvents, is gaining increasing acceptance as the method of choice for *in situ* remediation of chlorinated VOCs such as trichloroethene (TCE). At many sites, however, conditions do not lend themselves to natural attenuation processes that are significant or robust enough to protect potential receptors; either the processes are not observed at all or the travel time of the contaminants in the subsurface is insufficient for the processes to completely degrade the contaminants. An option is the construction of a treatment wetland on site to passively intercept shallow groundwater or to serve as an upwelling treatment system for pumped groundwater from greater depth. The treatment "concept" is that TCE and other chlorinated VOCs would be reductively

dechlorinated to lower chlorinated daughter products or biodegraded via methanotrophic processes to CO₂ as the compounds passed through the highly organic sediment of the wetland. The organic sediments would retard the movement of contaminants relative to groundwater flow, resulting in a longer detention time of the contaminants in the wetland sediments. Plant uptake and metabolism of the compounds in the rhizosphere would provide further treatment. This paper will present the current state of the science of treatment wetland design for chlorinated VOCs. Three facets of design will be emphasized: a) plant uptake and metabolism of chlorinated VOCs by wetland plants, b) bioavailability/biodegradation relationships in organic soils, and c) methanotrophic and methanogenic microbial relationships in wetland rhizospheres. Ongoing studies will be presented and a design for an application of wetland treatment.

Key words: phytoremediation, natural attenuation, TCE

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Sediment Assessment and
Remediation
Jefferson A



**INTEGRATED SEDIMENT
CHARACTERIZATION:
CASE STUDIES**

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Knowing the geographic extent of sediment contamination within a bay or estuary does not provide sufficient information for a site manager or stakeholder to make optimal decisions on how to manage sediments deemed an ecological risk or regulatory violation. Interactions between contaminants and sediment components, the mode of introduction of contaminants into the sediments, post-depositional weathering, and diverse mobility characteristics control behavior of contaminants in marine sediments, their bioavailability, risk, and the best approach to their management.

There are many different reasons to address contaminant levels and potential behaviors in sediment, and the depth of detail required for each is different. When sediments are examined for regulatory compliance, the primary goal is to be sufficiently protective that no sediment which may have the potential to negatively impact the environment slips through a site assessment. To this purpose, relatively crude tools are sufficient, as long as they are designed to err in the direction of protectiveness. On the other hand, once sediments have been designated as either of

potential concern or uncontaminated, a less blunt instrument is required to allow for more focused, cost-effective and environmentally-protective management of the sediments in question, as well as better delineating the extent of impacted sediments. The potential consequences are enormous - a sufficient understanding of intrinsic recovery processes may prevent the unnecessary outlay of millions of dollars, or signal those sites on which limited resources should be focused for ecological risk reduction.

Improved decision-making processes can be developed if contaminant distributions and behaviors at the micro- and macro-scales are understood. In such an approach, either sample collection for a site assessment can be guided, or gaps between standard data points can be interpolated with on-site field screening tools such as field-portable X-ray fluorescence (FPXRF) for metals, fluorescence for PAHs, and the use of bioluminescent phytoplankton for toxicity assessment. Sediments are then divided up into sediment management units (SMUs). A characterization of these SMUs may include an assessment of contaminant/sediment biogeochemistry, including *in situ* contaminant fluxes, contaminant concentration, mass, organic content, and surface area distribution as a function of grain size, intrinsic microbial health and activity, sediment toxicity, and other sediment characteristics which will impact bioavailability, risk, and management choices. With such information in hand, a site manager can make a streamlined and informed decision about what remedial options are available, based upon the site-specific sediment characteristics, allowing for rapid progress toward a decision and completion. Thus, advanced characterization of SMUs of concern can bridge the gap between raw concentration and toxicity data obtained from chemical and biological analysis of the sediments (site assessment) and intelligent sediment management plans (feasibility studies and site manage-

ment) by offering a guide to meaningful interpretation of the data.

Methods developed and results from contaminated sediment sites under assessment will be presented.

Key words: marine sediment, screening, assessment, management



CHARACTERIZATION OF THE ROLE OF MACROPHYTES AND MICROBIAL POPULATIONS IN GOVERNING THE FATE/TRANSPORT OF METHYL MERCURY IN HIGHLY CONTAMINATED ESTUARINE SEDIMENTS

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This multidisciplinary project seeks to quantitatively elucidate the role of master chemical variables, microbial diversity, and *Spartina* plants in limiting Hg methylation and bioavailability in contaminated saltmarsh sediments. We are studying a highly contaminated Superfund site (LCP Chemicals site) located in southeastern Georgia (Brunswick). For over seventy-five years, several industrial ventures, including a chloralkali plant, which operated until 1994, occupied this site and disposed chemical wastes on site and into the adjacent saltmarsh. The site is situated on a few hundred acres and borders a brackish tidal marsh dominated by emergent grasses (*Spartina alterniflora*). As a result of industrial activities, the saltmarsh sediment is highly contaminated with mercury levels ranging in the parts per thousand near the site to low parts per million in the vicinity of Purvis Creek.

In order to more rapidly constrain variables affecting Hg speciation and cycling, we have placed contaminated sediments from the

LCP site inside a specially designed Bioremediation and Environmental Research Mesocosm (BERM) facility, consisting of several greenhouses, secured laboratories, and mesocosms, which are working scale models of a contaminated site. The BERM is unique in that contaminated sediment can be placed into a controlled, contained mesocosm environment for study of various remediation strategies under a simulated tidal cycle. During phase I, we have constructed three sediment cells, two of Hg-contaminated sediment (-10 ppm total Hg) which are vegetated and unvegetated with *Spartina*, and one pristine sediment reference cell which is also vegetated. Each cell has a surface area of 2 x 4 m, contains approximately 8.5 cubic yards of sediment, and is flooded twice daily to 30 cm above the sediment surface. Currently, we are quantitatively determining whether the sedimentary environment of the saltmarsh mesocosms mimics that of the native marsh and the rate at which the equilibration occurs. During equilibration, monitoring includes process rate measurements (i.e., sulfate reduction rates), pore water chemistry, and microbial community analysis (16S tRNA probing for SRBs and total bacteria).

In phase II of the project, we will elucidate the microbial and chemical controls of methyl Hg formation over a seasonal growth cycle of *Spartina* in these tidal concentrations (methyl Hg and total Hg) in the solid phase and pore water of each mesocosm. We will also monitor Hg methylation rates in sediment incubations. The ultimate goal of these studies is the development, selection, and design of passive and active remediation technologies for Hg-contaminated sediments.

Key words: mercury, marine, sediment, plants, microorganisms



ASSESSMENT OF THE EFFECTS OF BIOTURBATION ON PAH CONTAMINATION IN SEDIMENTS

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Freshwater oligochaetes such as tubificid worms are generally the dominant in-dwelling fauna at freshwater contaminated sediment sites. These organisms are conveyor belt feeders and have a tremendous impact on the reworking of the surficial sediments and the migration and fate of contaminants in those sediments. In this paper the influence of tubificid worms on the fate of polycyclic aromatic hydrocarbons (PAHs) is explored. PAHs are common sediment contaminants that are persistent.

Past and ongoing experiments explore the effect that oligochaete bioturbation has on PAH-contaminated sediments. Worms are introduced into small laboratory microcosms containing beds of contaminated sediment with a continuous laminar flow of overlying water. The effect of worm bioturbation on sediment characteristics and contaminant redistribution and fate in these experiments are highlighted. The worms have been observed to physically change the porosity of the sediment and redistribute the organic carbon profile of the bed through their burrowing and feeding activities. The organisms are also observed to influence the fate of PAHs by several processes. The amount of PAHs released into the overlying water is significantly greater in the bioturbated than in unpopulated control. Burrowing also aerates the sediment bed and enhances the potential mineralization of PAHs by aerobic bacteria. In addition, oligochaete worms have demonstrated the ability to di-

rectly biotransform PAHs, a process which is explored in more detail in a companion paper. Ultimately, these experimental results can be used to evaluate the feasibility of enhanced natural attenuation by native oligochaetes present in contaminated field sediments.

Key words: PAH, sediment, aging, bioturbation, oligochaete



IN SITU CAPPING OF CONTAMINATED SEDIMENTS: COMPARING THE FUNCTIONAL EFFECTIVENESS OF GRANULAR VERSUS CLAY MINERAL-BASED SEDIMENT CAPS

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Ecological problems caused by sediment contamination occurring in deep water or wetland environments may be remediated through dredging and removal or in some cases by *in situ* capping - defined as the placement of a subaqueous covering or cap of clean isolating material over an in-place deposit of contaminated sediment. Dredging and removal of contaminated sediments may be the most practical remedial method in many situations and sometimes necessary for navigational purposes. However, in some circumstances, dredging and removal may not be the most environmentally protective and/or cost-effective approach. *In situ* capping approaches are often considered to be more protective of faunal and floral communities inhabiting impacted ecosystems than dredging alternatives, or converting the impacted area to a closed cell. According to current regulatory philosophy and recommendations, the three primary functions of an *in situ* sediment cap include: (1) physical isolation of the contaminated sediment from the benthic environment; (2) stabilization of contaminated sediments,

preventing resuspension and transport to other sites; and (3) reduction of the flux of dissolved contaminants into the overlying water column. To date, most *in situ* capping projects appear to involve the use of primarily granular (e.g. sandy) capping materials. Although such capping materials may adequately serve to meet stated cap functions at many sites, their relatively high permeability and low clay and organic matter content may limit their ability to reduce contaminant flux into the overlying water column. Furthermore, non-cohesive, granular materials can also be prone to erosional losses and redistribution, thus minimizing their effectiveness in isolating and stabilizing contaminated sediments. Finally, the thickness required to meet performance goals, many times on the order of three feet, can have a deleterious effect on channel hydraulics. As an alternative to granular sediment caps, a new *in situ* capping technology, AquaBlok™, has been developed for use in either deep water or wetland ecosystems. AquaBlok™ is a clay mineral-based capping material that offers numerous functional advantages over granular capping materials including: lower permeability, higher resistance to erosive forces, and considerably higher attenuation capacity for many types of contaminants. The likely need for thinner AquaBlok™ caps at many sites would also minimize navigational constraints. In this paper, we compare the potential functional effectiveness of a typical granular sediment cap to that of a typical AquaBlok™ sediment cap, as each would be installed within “typical” impacted deep water or wetland ecosystems.

Key words: sediment, contamination, sub-aqueous, cap, AquaBlok™



EFFECTIVENESS OF ENVIRONMENTAL DREDGING

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Dredging is a remedial process operation for contaminated bed sediments in ports and waterways. By the use of hydraulic or mechanical dredges, bed material is extracted from the bottom of aquatic systems. Although environmental dredging has been employed at a selected number of sites, its overall effectiveness is still problematic. A study is ongoing and findings to date indicate that although the operation may be efficient in removing bulk quantities of the contaminated mass, leftover residues, and resuspended and other quantities are ongoing sources that impact effective cleanup at some sites. Dredging effectiveness measures are defined and quantified. These include before-and-after concentrations of the impacted media, mass balances that account for the various fractions, etc. Information and effectiveness data will be presented on detail studies at three sites.

Key words: dredging, remedial processes, sediments



AIR EMISSIONS FROM EXPOSED, CONTAMINATED SEDIMENTS AND DREDGED MATERIAL

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The sediment-to-air fluxes of two polycyclic aromatic hydrocarbons (phenanthrene and pyrene) and a heterocyclic aromatic hydrocarbon (dibenzofuran) from a laboratory-contaminated sediment, and those of three polycyclic aromatic hydrocarbons (naphthalene, phenanthrene and pyrene) from three bed-sediment field sites were investigated in experimental microcosms. The flux was dependent on the sediment moisture content, air-filled porosity, and the relative humidity of the air flowing over the sediment surface. The mathematical model predictions of flux from the laboratory-spiked sediment were in excellent agreement with observed values. The fluxes of compounds with higher hydrophobicity were more airside-resistance controlled. Conspicuous differences were observed between the fluxes from the laboratory-spiked and two of the three field sediments. Two field sediments showed dramatic increases in mass transfer resistances with increasing exposure time, and had significant fractions of oil and grease. The proposed mathematical model was inadequate at predicting the flux from the latter field sediments. Sediment re-working enhanced the fluxes from the field sediments due to exposure of fresh solids to the air. Variations in flux from the lab-spiked sediment as a result of change in air relative humidity

were due to differences in retardation of chemicals on a dry or wet surface sediment. High moisture in the air over the dry sediment increased the competition for sorption sites between water and contaminant, and increased the contaminant flux.

Key words: contaminated sediment, CDF, air emissions

Program One

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Bioavailability of Contaminants Jefferson A



BIOAVAILABILITY OF SOIL LEAD, CADMIUM, AND ZINC AS INFLUENCED BY PHOSPHORUS AND OTHER SOIL

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Five contaminated soils/mine waste materials (TCR, AR, USDA, Chat, Dearing) collected from a tri-state mining area were used to evaluate the effect of P rate, P source, preacidification, and time on soil Pb, Cd, and Zn bioavailability. Total metal concentrations of materials (4M HNO₃ digestion) ranged from 1200 to 9100 mg Pb/kg, 30 to 190 mg Cd/kg, and 4500 to 42600 mg Zn/kg. Seven treatments used in this study were as follows: zero P (control); 2500 mg P/kg as triple super phosphate (TSP2500), phosphate rock (PR2500), acetic acid followed by TSP (acetic), and phosphoric acid (H₃PO₄); 5000 mg P/kg as TSP (TSP5000); and PR (PR5000). Predetermined amounts of CaO were added for all except for the control and PR-treated samples 24 hrs after P treatment to neutralize the soil pH. Triplicate samples were incubated for five different sampling times (3 days and 1, 4, 12, and 24 weeks) at 20% gravimetric moisture content and 25°C. Air-dried samples were analyzed for soil pH, bioavailable Pb by the *in vitro* bioaccessibility test (Physiologically Based Extraction Test- PBET). X-ray

diffraction data was collected for the <10 μ m size fraction separated by using an ATM sonic sifter. Addition of acetic, H₃PO₄, and TSP5000 reduced soil pH approximately down to 5.0 in all five materials used, while PR had no effect on soil pH. Calcium oxide was able to increase soil pH to 7.0. Phosphorus treatments reduced the bioavailable Pb in both stomach and intestinal phases significantly in all five materials used. Phosphoric acid was the most effective treatment for Dearing with PR being the least effective. For all other materials used, PR was equally or more effective than both TSP and H₃PO₄ in reducing bioavailable Pb by PBET. Phosphate rock was most effective in reducing Cd and Zn levels in PBET extractions in most of the materials used. X-ray diffraction results of H₃PO₄-treated Dearing materials showed the most intense pyromorphite peak, which is in agreement with PBET results.

Key words: lead, cadmium, zinc, phosphorus, bioavailability



BIOAVAILABILITY OF DESORPTION-RESISTANT PAHS

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Slow release or recalcitrant desorption processes have the potential to control both the long-term fate of contaminants in sediment systems and the ability to remediate sediments to required levels. Experiments will be presented that attempt to determine the extent to which desorption-resistant PAHs are bioavailable to a bacterial consortium. The PAHs naphthalene, phenanthrene, and fluoranthene were chosen as an example of the range of PAHs commonly found in contaminated sediments. Sediment obtained from Dickinson Bayou, Texas, was spiked with a radiolabeled PAH of interest and subjected to

sequential desorption over a minimum of two months. The extent to which the PAHs on these sediments could be degraded was studied using small slurry reactors. The factors that influence the biologically mediated desorption and transformation of these compounds will also be addressed.

Preliminary studies with naphthalene indicate that desorption-resistant naphthalene is available to a naphthalene-degrading mixed culture. The presence of naphthalene vapor as an additional naphthalene source increased the rate and extent of mineralization of the desorption-resistant naphthalene. Continuing studies with other PAHs (phenanthrene and fluoranthene) will allow comparison of the activity between different PAHs and provide more insight into the factors influencing the bioavailability of desorption-resistant PAHs.

Key words: PAHs, sediment, desorption-resistant contaminants



BIOACCUMULATION AND BIOTRANSFORMATION OF PYRENE BY THE FRESHWATER OLIGOCHAETE *LIMNODRILUS* *HOFFMEISTERI*

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Oligochaetes are often found in very high densities in organically enriched aquatic sediments. Many species bioturbate these habitats by bulk ingestion, which are then defecated at the surface. During this process the common oligochaete *Limnodrilus hoffmeisteri* significantly reduces the sediment concentration of pyrene in spiked sediments as a result of burrowing as well as metabolism. Results indicating the influence of the organisms on upper sediment properties, contaminant flux, and fate will be reported. These results suggest that oligochaetes may play a significant role in the transport and biodegradation of PAH-contaminated sediments in the field, and might show some potential in passive

bioremediation measures. Further experiments with a concentration series of ^{14}C -labelled pyrene were designed to evaluate the fate of pyrene during this feeding process, calculating the biota-sediment accumulation factor (BSAF) to establish bioaccumulation rates and analyzing the produced fecal matter to estimate the net reduction in pyrene content after passage through the gut. Groups of *L. hoffmeisteri* were placed into tubes containing 0, 25, 100, 250, 690 or 2000 mol/gdw of radiolabelled and nonradiolabelled pyrene, and allowed to burrow. Feces and animals were collected from tubes after 2, 5 and 10 days; feces were analyzed for pyrene and organic C content, and animals for pyrene, lipid content, and wet weight. Results indicate rapid bioaccumulation of pyrene, particularly at high-sediment pyrene contents. The fecal pyrene content in the two highest treatments peaked after 5 days before showing a marked decrease by day 10. This decrease in fecal pyrene content might be a result of increased metabolism with time, or indicate bacterial breakdown of ^{14}C -labelled pyrene into more water-soluble breakdown products. Additional experiments with radiolabelled pyrene are planned to study the biotransformation of the congener into metabolic breakdown products.

Key words: oligochaetes, pyrene, bioaccumulation rates, bioremediation

Program One

Wednesday, May 26, 1999

Sediment Remediation--

Grasse River, New York

Jefferson A



HISTORICAL OVERVIEW OF GRASSE RIVER INVESTIGATIONS

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The Grasse River, located in Massena, New York, has been the subject of numerous remedial investigations by ALCOA, Inc. (ALCOA) since 1989. These investigations have been completed as a result of the United States Environmental Protection Agency's Administrative Order issued to ALCOA on September 28, 1989, and amended on May 24, 1995. The portion of the Grasse River to be discussed is located along the northern boundary of New York State in the town and village of Massena, and encompasses approximately 8.5 miles. This stretch of river extends from Massena (just downstream of the Route 37 bridge) to the confluence with the St. Lawrence River.

The first comprehensive study conducted within the lower Grasse River, referred to as the River and Sediment Investigation (RSI) Program, was conducted (in two phases) between 1991 and 1994. As part of RSI Phase I activities, 140 sediment, 62 water-column and 248 biota samples were collected at various locations throughout the river to quantify the concentrations of polychlorinated biphenyl (PCBs) and other constituents. The highest detected PCB concentrations in various media were collected at the following locations: sediment adjacent to Outfall 001

[2,200 parts per million (ppm)]; water column—just downstream of the Unnamed Tributary [0.5 parts per billion (ppb)]; and biota—near the mouth of the Unnamed Tributary (brown bullhead fillets, 9.1 ppm). Additionally (although not part of the RSI Program), an extensive sediment-probing program was implemented within the Grasse River during 1992.

To further characterize the river's physical and environmental setting, the RSI Phase II was conducted. RSI Phase II sampling events included the collection of 51 sediment (from four specified areas—not including Outfall 001), 172 water-column, and 142 biota samples throughout the lower river. A benthic community assessment was also conducted. The highest detected sediment PCB concentration (216 ppm) was detected near the confluence with the Unnamed Tributary. Results of the water-column sampling efforts indicated an extremely low PCB detection frequency throughout the river, while statistical analyses of the fish data determined that PCB concentration in resident fish reflected no statistically significant change since completion of the RSI Phase I (with the exception of spottail shiner results from the mouth of the river). Additionally, benthic community assessment results indicated a community dominated by diptera (midge larvae), oligochaetes (aquatic worms), Ephemeroptera (mayflies), Trichoptera (caddisflies), and snails.

To address the PCB-containing sediments located adjacent to Outfall 001, ALCOA initiated a Non-Time-Critical Removal Action (NTCRA) during the summer of 1995. NTCRA operations accomplished the removal/dewatering/disposal of approximately 2,600 cubic yards of sediments (along with 400 cubic yards of boulders/debris). Based upon the estimated sediment volume remaining, approximately 84 percent of the targeted sediment was removed. However, although the triple-tiered silt containment system utilized was able to mitigate the escape of total suspended solids (from the removal area), some

PCBs did escape. Higher post-removal (versus (pre-removal) PCB concentrations were detected in the surface sediments (of some areas), water column, and caged/resident fish within the vicinity of the NTCRA area.

The Supplemental Remedial Studies (SRS) Program was initiated in 1995 to provide a better understanding of the origin, fate, transport, and bioaccumulation of PCBs within the lower Grasse River. Since the program began, more than 1,500 fish tissue, water-column, semi-permeable membrane devices (SPMDs) and sediment samples have been collected and analyzed for PCBs and an array of conventional water and sediment quality parameters. The principle conclusions drawn from these data collection and analysis efforts indicate that future reductions in fish PCB body burdens will be proportional to the surface area of the river remediated.

Based upon results and conclusions of the SRS Program, and given the characteristics of the Grasse River, ALCOA is preparing to implement a Particle Broadcasting Treatability Study within the lower Grasse River. Currently, ALCOA envisions this treatability study will consist of placing approximately 6 inches (minimum) of clean material throughout a substantial upstream portion of the Grasse River. Prior to implementation, ALCOA will undertake a series of pre-design and baseline characterization studies to facilitate the most efficient design for the study. Information gleaned from during- and post-investigations shall be used to identify and evaluate potentially appropriate remedies for the lower Grasse River, which will ultimately be used in development of a final Analysis of Alternatives Report for the Site.

Key words: PCBs, Grasse River, sediment, particle broadcasting



GRASSE RIVER NON-TIME- CRITICAL REMOVAL ACTION (NTCRA) SUMMARY

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Assessment of the River and Sediment Investigation (RSI) Program data collected from the Grasse River identified elevated PCB levels in an area of sediment located adjacent to ALCOA, Inc.'s (ALCOA) Outfall 001. As a result, ALCOA conducted a NTCRA during the summer of 1995 to address the polychlorinated biphenyl (PCB)-containing sediment within this area. From July 1995 through September 1995, ALCOA accomplished the removal/dewatering/disposal of approximately 2,600 *in situ* cubic yards (cy) of sediments (along with 400 cy of boulders/debris) from the vicinity of Outfall 001.

Removal of boulders/debris first was accomplished utilizing mechanical excavation equipment. Sediment was removed using hydraulic dredging techniques (specifically, a horizontal auger dredge). During sediment removal activities, the area was isolated using a triple-tiered silt containment system. Dredged slurry was dewatered on site via screening and filter presses with the filtrate sent to an on-site water treatment system consisting of two treatment trains. Each train contained a sand filter, four sets of dual-bag filters, and dual cells of liquid-phase granular activated carbon. The treated water was discharged back to the Grasse River. All dewatered sediments [with *in situ* PCB concentrations as high as 11,000 parts per million (ppm)] and boulders were disposed in ALCOA's on-site secure landfill.

Based upon the estimated sediment volume remaining (i.e., 550 cy), approximately 84 percent of the targeted sediment was removed during the NTCRA. The operations also achieved approximately 27 percent removal (based on maximum concentration isopleths and data collected immediately

following dredging) of the total PCB mass estimated to be present in the Grasse River. As dredging operations progressed throughout the NTCRA area, the project experienced some operation/technological limitations. Even after all practicable efforts were taken, an average of approximately 4 inches (and a maximum of 14 inches) of sediment remained. This likely was due to several issues, including the presence of "hardpan" which limited the dredge's ability to overcut the general uneven/rocky nature of the river bottom.

Along with the removal and disposal operations described above, NTCRA Environmental Monitoring Plan was implemented to document the operations and assist in the evaluation of the various aspects of the dredging and dewatering operations. The NTCRA Environmental Monitoring Plan provided the collection of water column, sediment, air, and biota samples (along with operational data) at various times and locations before, during, and after the NTCRA. Post-NTCRA sampling data indicated that the average PCB concentration in the top foot of sediment was reduced from 518 ppm to 75 ppm (approximately 86 percent). If only sample cores with 0-3 inch data in the NTCRA area are considered, the average PCB concentration was reduced from 176 ppm to 75 ppm (approximately 57 percent). Thirty percent of the locations sampled exhibited an increase in sediment PCB concentration within the top foot from pre- to post-conditions.

A total of 11,667,211 gallons of filtrate were processed throughout removal operations, and 93 percent of the effluent samples did not contain total PCBs greater than the Method Detection Limit of 0.065 micrograms per liter (mg/l). However, water-column sampling conducted both during and after the removal operations indicated that PCBs did escape the silt-containment system. The data also indicate that the PCBs escaping from the removal area migrated downstream. On several occasion, PCBs were detected above the acute Federal Ambient Water Quality

Criteria of 2 parts per billion (ppm) (up to 13.3 ppb) at locations immediately adjacent to the silt-containment system, and once at a downstream location. Results of the biota monitoring activities (both caged fish and resident fish sampling) provide further evidence of the release of PCBs from the containment system surrounding the NTCRA area. Specifically, post-NTCRA analytical results for certain resident fish collected in the vicinity of the NTCRA area indicate that PCB concentrations were as much as six times higher than PCB concentrations from previous years.

Key words: NTCRA, PCBs, sediment, monitoring, dredging



GRASSE RIVER SUPPLEMENTAL REMEDIAL STUDIES PROGRAM: IMPLEMENTATION TECHNIQUES

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In 1995, ALCOA initiated a Supplemental Remedial Studies (SRS) program of the polychlorinated biphenyl (PCB) contamination in the Grasse River, (Massena, NY) that had previously been documented by a conventional river and sediment investigation. The SRS involved an in-depth study of the sources of PCBs (to the water column and fish) and the PCB fate and transport in the river system. The resulting information has provided a valuable database for the objective, scientific evaluation of the potential benefits (and impacts) of various remedial alternatives Alcoa will consider. The SRS program also included the collection of data before, during, and after dredging of the most upstream sediment source area in the river; this limited remedial action was done as a Non-Time Critical Removal Action (NTCRA).

Key aspects of the SRS program included:

- A highly interactive technical team comprised of representatives of ALCOA (both

the Massena facility and ALCOA's Technical Center in Pittsburgh), scientists and engineers from three consulting and engineering firms, and select academic research institutions for special studies.

- A technical approach that involved clear problem definition (i.e., question statements) and hypothesis generation, and the design of studies designed to provide the needed answers.

- A strong focus on field studies including routine and diverse studies of PCBs in the water column, sediments, and biota in the River. A strong focus was also placed on the solids balance in the river (i.e., sediment transport, scour, and deposition).

- A major reliance on analysis of PCBs by congener rather than by Aroclor because of the former's lower detection limits, higher reliability, and utility in fate and transport analyses. Congener data were especially valuable in documenting the nature and extent of biodegradation that the sediment-bound PCBs had been subjected to.

- A significant laboratory program which focused on measurements of PCB diffusion out of sediments, PCB biodegradation (in sediment microcosms), sediment resuspension, and the influence of capping on PCB flux out of the sediments.

- Modeling studies, including PCB fate and transport in the water column, aquatic food chain uptake, and sediment transport. Comparison of model predictions and field data were especially helpful in assessing the validity of PCB fate and transport assumptions in the models.

- Frequent review, including peer review by extra-mural scientists, of the collected data and associated conclusions. This review would then lead, if necessary, to the modification of ongoing studies or to the implementation of new studies.

Key words: PCBs, sediments, rivers, fate, transport



CHARACTERIZATION OF PCB SOURCES AND FATE IN THE LOWER GRASSE RIVER

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The lower Grasse River, a tributary to the St. Lawrence River at Massena, New York, has been the focus of numerous investigations and remedial efforts by ALCOA. In 1995, ALCOA initiated a Supplemental Remedial Studies (SRS) program designed to develop an understanding of the mechanisms controlling the origin, fate, transport and bioaccumulation of PCBs within the lower Grasse River. As a part of this study, more than 1500 fish tissue, water column, semi-permeable membrane device, and sediment samples have been collected and analyzed for PCBs to the water column and resident fish via a water column-based food web. Because surface sediment PCB levels throughout the river are highly variable with an absence of dominant “hot spots,” reductions in water-column and biota PCBs would occur in rough proportion to the surface area of the sediments remediated.

Key words: PCBs, sediments, diffusion

Program One

Thursday, May 27, 1999

Nonaqueous-Phase Liquids

Jefferson A



ENTRAPMENT CHARCATERIZATION OF NAPLS IN THE SUBSURFACE USING PARTITIONING TRACERS: A LABORATORY EVALUATION

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Scientific enthusiasm for tracer techniques that involve multiple partitioning and nonreactive tracers has lead to the development of quantitative field methods for estimating the amount of NAPL in subsurface zones based on the assumption that partitioning occurs at equilibrium. However, few controlled laboratory studies have been performed to verify the applicability and accuracy of existing theoretical constructs and computational methods of previous multiple-tracer studies. With few controlled studies, there also exists major gaps in our understanding of the processes and parameters that influence the behavior of partitioning and nonreactive tracers during field characterization events, particularly in spatially heterogeneous subsurface systems varying in the degree of saturation of NAPL contamination. In this study, controlled laboratory experiments at the column and intermediate scale were performed to fundamentally evaluate parameters that influence the behavior of reactive and nonreactive tracers in settings where NAPL is heterogeneously distributed. In particular, column- and intermediate-scale studies have been performed with medium-grain sand to determine the influence of aqueous-phase velocity on partitioning and nonreactive tracer responses through zones of heterogeneously distributed NAPL at residual saturation and

adjacent to zones of pooled NAPL at continuous, free-phase saturation. Study results show that the retardation of alcohol partitioning tracers dramatically decreased with increasing aqueous-phase velocity, a clear indication of the dominance of kinetic, rather than equilibrium, controls at higher velocities. These results indicate that the use of existing assumptions, in particular equilibrium partitioning behavior and homogeneously distributed NAPL at residual saturation, are not appropriate for heterogeneously complex NAPL zones and, if used with such mass transfer limited systems, may lead to gross underestimation of NAPL amounts in extending tracer techniques from laboratory to the field.

Key words: multiple tracers, NAPL detection, equilibrium partitioning



MODELING OF NET INTER-PHASE MASS EXCHANGE IN NAPL WATER SYSTEMS UNDERGOING BIODEGRADATION AT THE SPILL-SITE SCALE

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Spills of waste chemicals that are in the form of nonaqueous-phase liquids produce complex configurations of entrapment distributions in naturally heterogeneous aquifers. Entrapment can occur either in residual form or in the form of pools at stratification interfaces. Slow dissolution of the entrapped NAPLs into the flowing aqueous phase contributes toward groundwater contamination. The effective mass addition to the flowing groundwater within the entrapment zone may be reduced under conditions of natural or

enhanced biodegradation, thus reducing the aqueous-phase concentrations at downstream receptor locations. A numerical model that simulates subsurface transport for systems where NAPL-degrading microbes are present and that accounts for effective multi-component NAPL dissolution from pools and degradation kinetics at the discretization scale is presented. This model can be used to evaluate and design biostabilization and bioisolation schemes for remediation. The model is a finite-element scheme that couples flow, single-species transport, rate-limited dissolution, oxygen availability, biomass transport, and degradation at the spill-site scale. The dissolution component of the model is experimentally validated in one-dimensional, bench-scale column experiments and two-dimensional intermediate-scale tank experiments consisting of a homogeneous matrix and coal tar pools of various lengths. The model is also validated using data from microbe-enriched batch experiments. This paper presents the coal tar dissolution and intermediate-scale transport results, data from the microbe batch experiments and the coupled finite-element model formulation.

Key words: NAPL, biostabilization, dissolution, remediation, modeling



LONG-TERM COMPOSITION DYNAMICS OF PAH-CONTAINING NAPLS AND IMPLICATIONS FOR RISK ASSESSMENT

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Nonaqueous-phase liquid (NAPL) contaminants containing polycyclic aromatic hydrocarbons (PAHs) are common subsurface contaminants. Examples include coal tar, creosote, diesel fuel, and other petroleum-derived materials. Management of

sites contaminated with PAHs is complicated by the fact that these contaminants typically exist as very complex mixtures. A risk assessment approach can be applied for complex mixtures if the waste can be characterized using a single-risk metric that represents the composition-dependent toxicity profile of the mixture. This paper examines the factors governing human health risk assessment for PAH-containing NAPLs, through numerical simulation of composition dynamics in groundwater for thirty-year time periods. The model describes the interdependence of the dissolution rates of individual compounds, and the shifts in the NAPL composition that occur due to the large differences in aqueous solubilities. The model also accounts for the possibility that selective dissolution causes precipitation of the less soluble constituents. Simulations describe natural environmental processes as well as three remediation processes: pump-and-treat, bioremediation, and solvent extraction. Risk is estimated and its dependence on contaminant removal and NAPL composition shifts is described. A compound like benzo[a]pyrene has significant potential to contribute to risk because of its carcinogenicity, and despite continuous NAPL depletion, the concentration of benzo[a]pyrene increases over several decades due to the increase in its relative abundance in the NAPL phase. Naphthalene, which is much less carcinogenic than benzo[a]pyrene, can significantly contribute to risk because it may persist at high concentrations in groundwater. Because PAHs can contribute to risk for different reasons and because of the interdependence of their behaviors, compositional approaches to risk assessment lead to better risk predictions for PAHs than simple lumped metrics such as total petroleum hydrocarbon (TPH).

Key words: NAPL, PAH, risk assessment, groundwater, remediation

Program One
Thursday, May 27, 1999
Surfactant-Based Remediation
Jefferson A



**ENHANCING
BIOREMEDIATION WITH
IN SITU BIOSURFACTANT
PRODUCTION**

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Polycyclic aromatic hydrocarbons (PAHs, e.g. phenanthrene) may occur in the environment as a result of fossil fuel combustion or as by-products from industrial processes. PAHs include mutagenic and carcinogenic compounds, emphasizing the need for efficiently controlling their fate and transport. Because PAHs are hydrophobic, they tend to sorb strongly to soil particles. PAH bioremediation in soil is often limited by the rate at which PAHs can desorb from the soil.

Previous research has shown that surfactant addition increases the rate and extent of desorption and biodegradation of phenanthrene in soil. However, few studies have examined how *in situ* biosurfactant production affects desorption and biodegradation. The goal of the research described herein is to examine the effects of *in situ* biosurfactant production on the bioremediation of phenanthrene from model soils.

This presentation will address the following three research questions: (1) does *in situ* biosurfactant production increase the rate and extent of phenanthrene desorption; (2) are biosurfactant producing bacteria more effective at phenanthrene degradation than non-biosurfactant-producing bacteria; (3) does phenanthrene location (intraparticle pore versus surface) affect the availability of sorbed phenanthrene to the bacteria?

Two types of bacteria were used for comparison in this project, a biosurfactant-producing-bacteria, *Pseudomonas aeruginosa* 19SJ, and a non-biosurfactant producing bacteria, *Pseudomonas saccharophila* P15. Teflon particles having an average diameter of 0.5mm were used as model soils. To investigate the effects of intraparticle porosity, both non-porous (NP) and porous (P) particles were used. Type P particles were used to simulate nanopore channels in soils that bacteria cannot physically access. All studies were performed in up-flow soil columns (1/2-inch diameter, and 2-inch length).

Studies showing comparisons of phenanthrene desorption and degradation from porous and non-porous particles in the presence of 19SJ and P15 and under abiotic conditions will be used to provide insight into the proposed research questions. The results of this work will be used to assess if in-situ biosurfactant production should be investigated at pilot or field scales.

Key words: biosurfactant, surfactant, bioremediation, desorption



MICRO-VISUALIZATION OF COLLOIDAL GAS APHRONS INTERACTION WITH OIL

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Flushing nonaqueous-phase liquids (NAPL)-contaminated sediments with Colloidal Gas Aphrons (CGAs) is a promising remediation technology. CGAs are defined as micron-sized air bubbles stabilized by surfactant molecules. But it is a well-known fact that CGAs undergo coalescence in the presence of NAPLs. Models of bubble coalescence, particularly in the presence of nonaqueous-phase liquids, are very important to develop the constitutive relationships, which

are essential to scaleup of laboratory results and for the design and optimization of field CGA remediation systems.

In this study, an etched-glass porous micromodel, along with a fiber-optic microscopic system, is used to evaluate the behavior of CGAs in the presence of oil. The Glass micromodel allows detailed and consistent exploration of interfacial phenomena in the porous media and the results are expected to be invaluable in developing an understanding of the coalescence process.

Experiments are conducted by first wetting the glass micromodel with water. Then an oily phase is introduced to partially displace water. Finally water is reintroduced in the micromodel to drive out the oily phase until a certain saturation has been reached. Pictures of the micromodel are then captured using the fiber-optic microscopic camera to quantify the initial oily phase distribution. CGAs are then pumped into the micromodel. The rate of coalescence is observed and quantified via image-processing tools. The experiments were conducted at various oily phase saturations. A model has been developed which takes into account the behavior of CGAs in the presence of oil.

Finally, the results of the experimental work are evaluated by incorporation of the developed constitutive relationships within a STARS(CMG, Inc.)-based CGA model of Cheah (1998). The results are compared with the experimental work.

Key words: CGAs, micromodel, coalescence, STARS, image processing



SURFACTANT-ENHANCED DISSOLUTION OF NON-AQUEOUS-PHASE WASTE CHEMICALS: EFFECT OF FLOW DIMENSIONALITY

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Organic chemical wastes, in the form separate-phase nonaqueous-phase liquids when entrapped in heterogeneous soil formations, act as long-term sources of groundwater contamination. Because of their very low solubility, only a small fraction of the NAPL gets depleted through natural dissolution. Addition of surfactants to the flowing groundwater increases the rates of dissolution drastically, making it feasible to remove the NAPL from the soil. This paper presents a fundamental investigation of the mechanism of the dissolution of entrapped NAPLs. A two-dimensional apparatus and experimental methods were designed to measure mass transfer from entrapped LNAPL zones to a flowing surfactant solution. Enhanced dissolution experiments were performed in which contaminated source zones of different lengths were placed in a bench-scale tank. Continuous measurement of entrapped LNAPL saturations using a dual-gamma attenuation system provided valuable information on the relation between dissolution fronts propagation and dimensionality of groundwater flow. Dissolved LNAPL breakthrough curves, together with saturation measurements, enabled us to overcome deficiencies identified in prior research such as assumption of one-dimensional flow, assumption of local equilibrium during mass transfer, idealization of transient mass transfer, and the negligence of mass transfer coefficient scaling factors between different contaminated soil block sizes. Transient numerical modeling

of the performed experiments helped in the identification of the parameters that mostly affect mass transfer. Phenomenological models that describe the mass transfer rate coefficient under enhanced conditions are proposed. It is expected that the types of models that are developed in this research can be used to design field-remediation schemes under more realistic conditions of multi-dimensional flow.

Key words: mass transfer, surfactant, enhanced dissolution, nonaqueous-phase liquids, flow

Program Two
Tuesday, May 25, 1999
Brownfields
Jefferson B



HYDRAULIC CONDUCTIVITY INFLUENCE ON UTILIZATION OF ILLINOIS' TIERED APPROACH TO CORRECTIVE ACTION OBJECTIVES (TACO)

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Improper design and analysis of hydrogeologic tests can introduce errors in hydraulic conductivity estimation by an order of magnitude or more. Introduction of erroneous hydraulic conductivity values into Illinois' TACO calculations leads to errors in contamination concentration calculations. Manipulation of Illinois' TACO parameters indicates hydraulic conductivity is the most sensitive, variable input parameter. Variation of hydraulic conductivity by one (1) order of magnitude causes contaminant concentration calculations to differ by several orders of magnitude. Thus, improper hydrogeologic evaluation may lead to gross miscalculation of the potential impact of contamination to human health and the environment.

Key words: hydraulic conductivity, risk-based analysis



TRIBAL APPROACHES TO BROWNFIELD REDEVELOP- MENT ISSUES

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Like blighted urban areas, Indigenous Nations in the U.S. often have abandoned or underutilized commercial or industrial properties with potential environmental contamination within the confines of their reservations. Like urban brownfields, often contamination problems are discovered long after the responsible parties have disappeared. Financial incentives, tools, and risk-management techniques have been created in urban settings to help facilitate the redevelopment of brownfield sites. The element of tribal sovereignty and self-determination alone makes reservation settings unique. Coupled with cultural differences and historical relationships, it is clear that reservation environments need to develop approaches to brownfield redevelopment issues different than urban settings. This presentation will explore differences in tribal and urban redevelopment philosophies and suggest possible elements of a tribal brownfield redevelopment process.

Key words: Native/Alaskan American, brownfields, minority colleges, minority lands



ENVIRONMENTAL SOLU- TIONS THROUGH EFFEC- TIVE PLANNING

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The U.S. Army Corps of Engineers (USAGE) has developed and is using an innovative and extremely effective planning process to achieve environmental solutions at more and more hazardous waste sites every month. Since 1995, application of the Technical Project Planning (TPP) Process has typically accelerated site-characterization schedules and reduced related costs by more than 10 and 15 percent, respectively.

The TPP Process is...

- A comprehensive and systematic planning process that satisfies all the planning requirements of U. S. Environmental Protection Agency's (EPA's) mandatory agency-wide quality system (EPA Order 5360.1);
- A critical component of USAGE's quality management system that conforms to the American National Standard for planning the collection and evaluation of environmental data (ANSI/ASQC E4);
- USAGE's institutionalized process for ensuring cost-effective environmental solutions are achieved for compliance and remediation problems at all hazardous waste sites; and
- An effective planning process for achieving environmental solutions because it brings together technical personnel, regulators, and stakeholders from the community throughout the planning and decision-making activities.

This presentation will describe the TPP Process, introduce key planning techniques, and share case history information and anecdotes. The description of the TPP Process will enable attendees to begin using the TPP Process. The introduction of key planning

techniques will offer insight to those responsible for determining the technical, regulatory, and management aspects of environmental solutions for hazardous waste sites. Lessons learned, information, and data will be presented for projects ranging from a \$50,000 phase at a brownfields site to a fast-tracked \$20M site involving no less than 25 engineers, scientists, managers, regulators, consultants, responsible parties, and stakeholders from the community.

The TPP Process has been credited for “providing a method through the madness of hazardous waste site planning.” The TPP Process is unique and well suited for accelerating progress and reducing costs at many of today’s and tomorrow’s hazardous waste sites. Use of the TPP Process involves critical planning considerations that help design data collection programs which leverage the most appropriate, existing or emerging site characterization and remediation methods, to achieve the environmental solution needed at each hazardous waste site.

Key words: planning, process, management, quality, data



MICHIGAN BROWNFIELD REGULATORY REVIEW

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In 1995 and 1996, the State of Michigan enacted landmark legislation which dramatically changed the legal philosophy created at the Federal level through the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980. CERCLA had created the fearsome concepts of joint and several liability and retroactive liability, which were a radical departure from traditional Anglo-Saxon-based law. The 1995 amendments to the Michigan Environmental Response Act (MERA), codified in part 201 of Public Act 451 of 1994, the Natural Resources

and Environmental Protection Act, are referred to as “Part 201”. Part 201 provided critical liability reform and a new strategy for clean-ups based upon actual risk and realistic probable exposure. The 1996 legislation provided new financial incentives in an overall system designed to ensure brownfield redevelopment on a massive scale. Under these laws, new buyers can acquire contaminated property without liability, provided they comply with certain provisions, including the performance of a Baseline Environmental Assessment (BEA) prior to or within 45 days of acquiring the property. Michigan communities can now offer tax increment brownfield financing, tax credits against the Michigan Single Business Tax, and loans and grants for development-related activities. An internal report of the MDEQ in 1996 indicated that over 400 Baseline Environmental Assessments were filed in the first year of operation, more than 10 times the number of cumbersome covenants-not-to-sue issued in the previous four years under the old legislation. The 1996 financial package created a state board to oversee redevelopment and authorized municipalities to create their own local boards, which are beginning to happen. This paper will describe the results of Michigan’s strategy.

Key words: brownfields, Michigan, regulations, business strategy



TURNING INNER CITY INDUSTRIAL LAND INTO A NEW CIVIC PARK FOR SPRINGFIELD, MISSOURI

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This paper will examine the processes and problems involved in acquiring land in the inner city, former industrial heart of Springfield, Missouri, for creation of a new Civic Park. An increase in the hotel/motel tax was passed in February 1998 to create the funding for a new tourist attraction in the center of

Springfield. When complete, the Civic Park will include 250 acres of land in the Jordan Creek valley through the center of Springfield and include a new convention center, recreational ice arena, an amphitheater, landscaped open space, and a water feature. Along this valley was the original location of Springfield, associated industries, and railroad yards. Many industries, commercial businesses, and a railroad are still in operation within the proposed park footprint today. The processes involved with evaluating potential environmental impacts of the properties, including the results of both site history research and site investigations, will be described. Anticipated cleanup costs were developed in order for the City to negotiate a purchase price from present landowners. The types of historical industries involved, environmental issues noted on the properties, negotiations with landowners, and cleanup responsibilities will be discussed.

Key words: environmental impact, site investigations, cleanup responsibilities



MANAGING SENSITIVE MGP REMEDIATION PROJECTS: A CHURCH AND A SCHOOL

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In the late nineteenth and early twentieth centuries, gas was produced at manufactured gas plants (MGP) from coal and distributed to residential, commercial, and industrial customers throughout northern Illinois. Nicor Gas evaluated the recent use of historical MGP sites in its northern Illinois service territory and determined that the Morning Star Baptist Church site in Kankakee, Illinois, and the Ottawa School Site in Ottawa, Illinois, warranted priority consideration. Based on initial site inspections, neither site appeared to

present significant or immediate health risks. However, because of their use by potentially sensitive populations, Nicor Gas enrolled both sites in the Illinois Site Remediation Program. Site investigations, source removal actions, and the construction of engineered barriers were completed with the cooperative partnership of all stakeholders with minimal disruption. Potential liability to the utility is now being properly managed and the current site owners have benefited from desirable site improvements. This paper tells the story of two site remediation projects that were successful because of the utility's aggressive efforts to identify, involve, and communicate with all stakeholders.

Key Words: MGP, coal tar, remediation, benzene

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ROLE OF HYDROGEN IN CORRELATING MICRO- COSM AND FIELD- DERIVED RATE CONSTANTS FOR TCE

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Natural attenuation is being evaluated for a groundwater plume underlying a wetland at the Petro Processors, Inc., Superfund site near Baton Rouge, La. Petro Processors Inc. operated an unengineered disposal facility for industrial wastes from 1962 to 1981. The facility consisted of several unlined pits in two separate disposal sites, "Scenic" and "Brooklawn", named for the adjacent surface roads. The material deposited included a wide range of

industrial solid waste and free-phase organic chemicals. The proposed talk will address a groundwater plume at the Brooklawn site that gives strong indications of reductive dechlorination of chlorinated ethenes and ethane. Field measurements of chlorinated ethenes, ethanes, and redox indicators (including hydrogen) and a LiBr tracer test have been conducted in a groundwater well array within the plume. Microcosm-derived rate constants have also been determined in aquifer materials from wells within the array. Laboratory microcosm results indicate a very large TCE-dechlorination rate constant ($>60 \text{ yr}^{-1}$) with significant conversion to ethene. Hydrogen was monitored over time within the batch microcosms and *in situ* within the array. Hydrogen data shed light on the relationship between microcosm-derived rate constants and *in situ* dechlorination. The effectiveness of using hydrogen to diagnose redox conditions within plumes will also be discussed. Results will be presented in light of recent studies of hydrogen preferences for chloroethene-degrading bacteria and consortia.

Key words: natural attenuation, TCE, groundwater



IMPACT OF MIXED-CULTURE SUPPLEMENTATION ON DEVELOPMENT OF A HIGH-RATE, PCE-DECHLORINATING CULTURE

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The viability of bioremediation of perchloroethene (PCE) has received increased attention with the recent discovery of a variety of microorganisms capable of rapidly dechlorinating the compound in respiratory processes generally labeled halorespiration. These organisms have been isolated from acclimated enrichment cultures using various inoculum sources. However, the continued viability of many of these halorespirers appears to depend on satisfying complex nutritional requirements

that were not exerted in original mixed-culture conditions. This research focuses on the successful development of a mixed-enrichment culture capable of rapid transformation of PCE, and the enhancement of this activity when this acclimated culture was supplemented with supernatant or biomass from other mixed cultures. Enrichment cultures were developed from a sample obtained from a municipal wastewater treatment plant digester. A PCE-acclimated culture was developed via enrichment on lactate and increasing doses of PCE. Within 1 year, seeded batch reactors demonstrated the ability to rapidly transform 248 mM of PCE ($< 100 \text{ mg/g VSS-d}$) to ethene within 10 days. Vinyl chloride was the only major transient product, and dechlorination was accompanied by significant methane production. However, despite little change in the acclimation protocol, dechlorination and methane production rates gradually began to decrease in the stock-culture reactor. The concurrent persistence of acetate suggested that the change was influenced by a loss of acetoclastic methanogenic activity due to inhibition by PCE. Previous researchers have indicated that methanogens are not capable of directly catalyzing dechlorination reactions. Their likely role is to provide some type of extracellular nutrient or protein that is needed by other organisms in the culture. This hypothesis was tested through a series of experiments in which aliquots of the PCE-acclimated culture were diluted by 20% with aliquots of three different actively methanogenic cultures or the supernatant from spun cultures. Coculturing resulted in increased PCE removal (30-50%) and methane production (39-77%) rates. The rates were enhanced most significantly by adding an unacclimated acetate-enrichment culture, despite the fact that controls showed that this culture was unable to dechlorinate by itself. Similar patterns were seen when the PCE-acclimated lactate-enrichment culture was supplemented with the supernatant from these three methanogenic cultures. Because no dechlorination was

observed in supernatant controls, the benefit gained from the addition of supernatant appeared to be the result of the some type of extracellular component of the coculture. The aided dechlorination reinforces the assumption that losses in dechlorination during extended acclimation may be the result of the negative impact of PCE on non-dechlorinating organisms. These findings reflect the importance of ecological interactions between microorganisms in ensuring conditions suitable for rapid dechlorination of PCE *in situ*.

Key words: anaerobic, bioremediation, PCE, acclimation



THE USE OF HYDROGEN-RELEASE COMPOUND (HRC™) FOR CAH BIOREMEDIATION

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Hydrogen-Release Compound (HRC) is a simple, passive, low-cost and long-term option for the anaerobic bioremediation of chlorinated aliphatic hydrocarbons (CAHs) via a reductive dehalogenation pathway. Applications to other classes of chlorinated compounds that are anaerobically degradable by this mechanism are under investigation. HRC should be viewed as a tool for the enhancement of natural attenuation at sites that would typically require high levels of capital investment and operating expense.

HRC is a proprietary, food-grade, polylactate ester that, upon being deposited into the subsurface, slowly degrades to lactic acid. Lactic acid is then metabolized to hydrogen, which in turn drives the reductive dechlorination of CAHs. This has been demonstrated effectively in the laboratory and in the field. HRC is a moderately flowable, injectable material, that facilitates passive barrier designs for the remediation of dissolved-phase plumes and the associated contaminant that is hydrophobically sorbed. The use of HRC is contraindicated for free-phase DNAPL unless the total mass to be

remediated is within the scope of economic feasibility, i.e., smaller impacted areas.

Evidence suggests there is competition between reductive dehalogenators and methanogens in which the methanogens compete for the use of hydrogen in the conversion of carbon dioxide to methane. It is believed that a low concentration of hydrogen favors the reductive dehalogenators and starves out the methanogens. The objective, therefore, is to keep hydrogen concentrations low. The time-release feature of HRC, which is based on the hydrolysis rate of lactic acid from the ester and the subsequent lag time to hydrogen conversion, facilitates this objective. HRC, therefore, becomes a passive form of enhanced natural attenuation in contrast to the more capital- and management-intensive alternatives now available. Laboratory and field results will be presented that will expand on the first uses of HRC by various members of the engineering and consulting firm community.

Key words: hydrogen release compound, anaerobic bioremediation, reductive dehalogenators, methanogens



MICROBIAL POPULATION SHIFTS IN SOIL AS A FUNCTION OF SURFACTANT APPLICATION

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Surfactants that increase the solubility of nonpolar organic contaminants (NOC) in soils often do not effectively increase microbial degradation rates. In fact, for most surfactants, solubility enhancement is achieved only at concentrations greater than the critical micelle concentration (CMC), which often corresponds to significant decreases in degradation rates of NOCs. In a previous study, we showed marked inhibition of phenanthrene and hexadecane degradation by indigenous soil microorganisms at concentrations of Witconol SN 70 (nonionic, alcohol ethoxylate) above the CMC, but slight

enhancement in degradation at sub-CMC surfactant concentrations. Inhibition of phenanthrene and hexadecane degradation occurred despite a significant increase in NOC solubility above the CMC, and was apparently not caused by gross toxicity of this surfactant to all microbial populations. Other potential mechanisms of inhibition include reduction in NOC bioavailability when bound in surfactant micelles and inhibition of microbial attachment at mineral and organic surfaces. However, to our knowledge, very little work has been completed to evaluate changes in microbial community structure across a range of surfactant applications. Consequently, the goal of this study was to reexamine hexadecane and phenanthrene degradation in light of potential surfactant-driven shifts in microbial populations. We hypothesized that surfactant applications spanning sub- and supra-CMC conditions would result in significant changes in the soil microbial population that may correlate with changes in NOC degradation rates. Experiments were conducted to evaluate microbial degradation rates of ^{14}C -phenanthrene and ^{14}C -hexadecane as a function of surfactant application in batch vessels containing soil. Subsamples of experimental treatments at several time points were subjected to DNA extraction, PCR amplification of a portion of the 16S rRNA gene, followed by separation of the PCR products using denaturing gradient gel electrophoresis (DGGE). In addition, enrichment cultures were established to obtain isolates of hexadecane- and surfactant-degrading organisms. Results from microbial community analysis as a function of time suggest significant shifts in specific members of the microbial population caused by application of hexadecane or surfactant. Moreover, surfactant applications greater than the CMC completely inhibited ^{14}C -phenanthrene and ^{14}C -hexadecane mineralization, reduced the apparent microbial diversity, and selected microorganisms not observed in sub-CMC treatments. Our results reveal the complexity of potential effects of surfactant application on microbial populations in soil, and suggest that while supra-CMC applications may not result in gross toxicity to all microorganisms, they most certainly select

for specific microorganisms that may not be capable of degrading hexadecane or phenanthrene.

Key words: degradation, hexadecane, phenanthrene, alcohol ethoxylates

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Jefferson A



**MULTI-SPECIES BIOFILMS
 FOR REACTIVE-BARRIER
 FORMATION**

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An innovative approach for the hydraulic control of contaminated groundwater is the application of biologically produced extracellular polysaccharide (EPS) subsurface barriers (i.e. static biobarriers). Manipulation of porous media permeability in this manner has been found to be effective under laboratory conditions and is currently planned for field-scale application. A developing, advanced application of the biobarrier technology is the use of reactive-bacterial populations to produce reactive biobarriers. Reactive-biobarrier technology offers a means of simultaneously degrading a contaminant while reducing contaminant migration. Since recalcitrant compounds, such as trichloroethylene (TCE), show little natural attenuation, the development of a TCE-reactive biobarrier could result in a significant advancement in bioaugmentation technology.

Reactive biobarriers can be developed in two ways: 1) using a single bacterial population to reduce the hydraulic conductivity of a formation and simultaneously degrade the contaminant; 2) using two species to develop a reactive

barrier, one species to produce the biofilm and reduce the hydraulic conductivity, the other species to carry out the desired reaction(s). The single-species method requires that the bacterial population produces copious amounts of biofilm while carrying out the desired reaction. The dual-species reactive biobarrier requires that the two species co-exist and persist in a biofilm formation. In order for coexistence to occur, the biofilm producing population must serve as an immobilizing matrix for the nonbiofilm-producing reactive population.

In order to optimize TCE degradation in a dual-species biofilm, a series of porous media columns (2.54cm diameter, 25.4cm long, 1mm glass beads) were constructed. Three experiments will address the initial establishment of a reactive population in a dual-species biofilm using these columns. The first experiment involves the inoculation of a reactive-bacterial culture into each column (*Burkholderia cepacia* PRITOM31c, a TCE-degrading bacterial strain and a non-biofilm former). After three days of nutrient addition, a biofilm-producing bacterial strain (*Klebsiella oxytoca* or *Pseudomonas fluorescens*) is introduced into each column. After a week, the columns are destructively sampled to determine the different bacterial populations and reactive population activity throughout the column. These results will be compared to experiment 2 (biofilm-forming population is inoculated prior to the reactive population) and experiment 3 (both biofilm and reactive populations inoculated simultaneously) to determine which biofilm-forming population and inoculation method will provide the maximum reactive population and maximum TCE-degrading potential. Optimizing the initial population of a contaminant-degrading bacterial strain may enhance its long-term persistence and activity in a multi-species biofilm, thus providing the basis for a successful dual-species, reactive biobarrier.

Key words: biofilm, biobarrier, multi-species, subsurface, trichloroethylene



CHEMICAL- AND BIOLOGICAL-OXIDATION PATHWAYS OF MTBE AND ITS OXIDATION BY-PRODUCTS USING COMBINATIONS OF H_2O_2 , O_3 AND UV UNDER OXYGENATED AND OXYGEN-LIMITED CONDITIONS

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Methyl tertbutyl ether (MTBE) is a fuel-oxygenating agent which has commonly been found in groundwater aquifers. Unfortunately, MTBE is biorecalcitrant and, therefore, costly to treat. Coupling of chemical and biological treatment processes offers a potentially viable treatment alternative of MTBE and is the focus of this research. Due to its structure, MTBE is not easily oxidized to readily biodegradable by-products.

The purpose of this ongoing study is to determine the oxidation byproducts and pathways of methyl tertbutyl ether (MTBE) using hydroxyl-radical-mediated reactors under a variety of conditions. Specifically, we are determining the oxidation pathways for MTBE using UV/ H_2O_2 , under oxygen-rich and oxygen-depleted conditions, and using a variety of ozone-based advanced oxidation pathways. Varying the advanced oxidation conditions has shown to significantly affect the nature of the oxidation by-products, and the oxidant dosages required for MTBE removal. Depending on experimental conditions, primary oxidation by-products include t-butyl formate, t-butanol, acetone, formic acid, methyl acetate, and a suite of by-products randomly methylated by methyl radicals under oxygen-depleted conditions. This research will report on the optimum advanced oxidation system and potential for achieving readily biodegradable by-products leading to the development of an integrated chemical-biological treatment system.

Key words: MTBE, groundwater, oxidation



EFFECT OF MEDIA TYPE AND CHARGE ON TCE COMETABOLISM IN A FLU- IDIZED-BED BIOREACTOR

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Fluidized-bed biological reactors (FBBRs) are used in water and wastewater treatment due to their ability to efficiently remove a variety of contaminants such as oxygen demand, nitrogen, and hazardous organics. In recent years, FBBRs have been studied by researchers for their ability to treat water contaminated with chlorinated solvents including trichloroethene (TCE). Proper selection of FBBR biofilm support media type and charge (bed-volume fraction) is critical for establishing a biomass of sufficient quantity and activity to transform TCE. Aerobic biodegradation of TCE is via cometabolism, which requires a supplemental growth substrate, thus, media selection involves consideration of efficient conversion of growth substrate to cometabolic activity for TCE degradation.

In this study, five types of sandy media (quartz, garnet, ilmenite, hematite, and magnetite) were tested in small-scale FBBRs under different conditions of charge and media diameter. Also, biofilm growth and TCE degradation were examined for three nutrient solutions containing phenol as the growth substrate: mineral salt waters (MSW), groundwater with excess nutrients (GWN), and amended groundwater with minimal nutrients (AGW). It was determined that NGW and MSW were suitable for the operation of a FBBR without loss of TCE-degradation rate. Biofilms cultivated on the different media were harvested and batch-assayed for their maximum specific TCE-degradation rates (k_c). It was found that quartz sand with 30-35 mesh particle size and 20% column sand charge was optimum for achieving high removal efficiency of TCE in FBBRs. The k_c was 197 mg-TCE/

g-VSS/d. When implemented in a continuous operating laboratory FBBR at a flow of 1 L/min and detention time of 4 minutes, TCE removals up to 80% were obtained.

Key words: trichloroethene, fluidized bed, bioreactor, sand media, cometabolism, phenol



EFFECTS OF AN ALTER- NATE GROWTH SUBSTRATE ON *IN SITU* BIOREMEDIATION OF POLYCYCLIC AROMATIC HYDROCARBONS

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Addition of an alternate growth substrate may enhance the bioremediation of recalcitrant organic compounds in contaminated groundwater aquifers by improving the growth conditions for a degradative microbial community and increasing the bioavailability of hydrophobic compounds by sorption to biomass. Effects of acetate as an alternate growth substrate were evaluated for a polycyclic aromatic hydrocarbon (PAH) mixture with respect to biodegradation rate, exopolymer composition, and partitioning of PAH between biomass and bulk-liquid phases. Aerobic batch cultures and sand columns were seeded with an inoculum obtained from PAH-contaminated soil from an active oil refinery site and enriched with naphthalene, phenanthrene, and pyrene. Experimental cultures were developed using acetate in varying doses up to 100 weight percent of the feed PAH carbon content. Half-order biodegradation rate constants were determined for a mixture of 10 mg/L naphthalene, 0.86 ml/L phenanthrene, and 0.086 ml/L pyrene. Results indicated that a 30 wt. percent acetate C amendment compared to no-acetate amendment increased the naphthalene biodegradation rate slightly from 2.6 to 2.8 $\text{mg} \cdot \text{L}^{-0.5} \cdot \text{h}^{-1}$, increased the phenanthrene biodegradation rate from 0.16 to 0.20

$\text{mg}^{0.05}\text{L}^{-0.5}\text{h}^{-1}$, and reduced pyrene biodegradation from 0.027 to 0.021 $\text{mg}^{0.05}\text{L}^{-0.5}\text{h}^{-1}$. PAHs were found to partition strongly to microbial biomass versus the aqueous phase (biomass-water distribution coefficients ranging from approximately 790 to 8,900) indicating that microbial biomass would tend to the capture dissolved PAHs in the subsurface environment. Acetate amendment altered the protein and carbohydrate composition of biomass. The biomass-water partition coefficient, K_{B-W} , was found to decrease with acetate amendment for naphthalene, and K_{B-W} generally increased with acetate amendment for phenanthrene and pyrene. Results suggest that the overall effects of acetate on biodegradation rate are a combined effect of microbial selection, biomass sorption, and release of PAHs from exopolymer decay. Flow-through sand column studies using pulsed addition of acetate indicate the utility of this process for enhanced subsurface bioremediation of PAHs in groundwater.

Keywords: biofilm, bioremediation, PAH, exopolymer, partitioning



BIODEGRADATION OF DE-ICING COMPOUNDS IN COLUMNS SIMULATING A RANGE OF NATURAL CONDITIONS

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Concern is building about the problem of releases of de-icing chemicals applied to airplanes into the environment near airports. The mixture most commonly used to de-ice aircraft is a combination of approximately 88% glycol, 2.5% surfactants and corrosion inhibitors (including methylbenzotriazole), and water. The glycol is therefore released into the environment at very high concentrations (on the order of 1,000 to 100,000 mg/L), which represent a significant oxygen demand. The

glycol is readily degradable by common soil bacteria, but if this glycol enters streams, the dissolved oxygen could be completely removed, thereby impacting aquatic life. Another problem associated with the de-icing compounds is the toxicity of the surfactants and corrosion inhibitors; surfactants have been found to be toxic to fish and water fleas while the methylbenzotriazole is toxic to microorganisms.

Studies are ongoing to determine the fate of de-icing compounds in the environment. Specifically, the fate of the compounds in “near runway” soil is of interest. Since glycol can be readily degraded, issues of interest are the impact of microbial growth on the soil characteristics. Experiments were conducted by feeding aqueous solutions of propylene glycol (PG) into columns (7 cm dia. x 15 cm tall) packed with sand; the sand was pre-seeded with natural bacteria that were enriched from Denver International Airport soil by growth on PG. Changes in the hydraulic conductivity of the sand were measured over time using constant head tests. Effluent PG, ammonia, and biomass concentrations were measured. At the end of a given growth period, the columns were sacrificed to determine the total mass of biogrowth on the sand and its distribution in the column. Of most interest was the significant decrease in the conductivity of the sand that occurred due to the growth of the bacteria. Up to three orders of magnitude decrease occurred over a period of 4 months, at which point shear balanced with growth. This “plugging” of the soil could be significant in field applications since with the lower conductivity there would be less infiltration. This could lead to spreading of the contamination and more overland flow, or a reduction of the biodegradation capacity due to oxygen or nitrogen limitation which could lead to PG contamination of the groundwater.

Experimental conditions were varied to simulate a range of environmental conditions:

1) Nitrogen available for biogrowth was limited relative to the carbon available from

the PG; nutrient limitation would be common in natural soils due to the high carbon loading from the PG.

2) The flowrate of water through the columns was varied to test for the effect of shear on the biofilm growth.

3) Influent PG concentrations were varied, representing a range of environmental dilution.

4) Tests with PG vs. the entire de-icing fluid mixture were run to compare inhibition effects due to the additives.

5) Frequency of PG exposure was varied to simulate periods of high loading and absence of loading (since aircraft de-icing operations are intermittent).

Initial studies with intermittent PG feeding (spike load of 100 mg PG that was recirculated every 2 days) found slow conductivity changes. During a 5-day period without PG, the hydraulic conductivity of the sand increased 2 orders of magnitude due to endogenous degradation of biomass, which decreased the biofilm filling the soil pores. The conductivity re-dropped by 2 orders of magnitude within 5 days by increasing the PG loading to 100 mg fed every 12 hours. This indicates that loading amount and frequency will be important in the clogging of the soil. The results of the intermittent feeding study will be compared to continuous feeding, and controlled periods without PG will be used to determine the rate at which the biofilm decays.

Another parameter of interest is oxygen. The columns became oxygen-limited, particularly at higher PG loading (400 mg PG every two days, with an inlet concentration of 1600 mg/L). Anaerobic biomass grew in the columns, but detailed measurements of the anaerobic activity are needed.

Understanding these issues will aid in predicting the fate of de-icing compounds in the environment, and engineering processes to reduce their environmental impact.

Key words: biofilms, porous media, de-icing fluid



MODELING THE BIODEGRADATION OF MIXTURES USING PSEUDOCOMPOUNDS

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Most studies of biodegradation kinetics have focused on single-substrate degradation by a pure culture. However, waste streams and contaminated sites typically contain diverse mixtures of pollutants that are degraded by a community of microorganisms. Modeling the biodegradation kinetics of mixtures of organic compounds is a difficult task, since complex interactions can occur in a mixed system due to such factors as inhibition of growth, substrate utilization patterns, and cometabolism. The focus of this laboratory research study was to reduce this complexity by grouping chemicals together and treating the groups as individual "pseudocompounds" thus reducing the number of compounds to model.

This work used a chemical mixture containing 13 mono- and di-substituted benzenes, phthalic esters, and polynuclear aromatic hydrocarbons, and a microbial culture isolated from Lowry Landfill Superfund Site. The first laboratory experiments were conducted on the entire chemical mixture to determine which chemicals to group into pseudocompounds. Cluster analysis was applied to kinetic parameters to determine the groupings or pseudocompounds. Using this approach, chemicals with similar degradation profiles were grouped together. A Monod-based model was proposed for predicting the degradation kinetics of the mixture. The Monod kinetic parameters of each pseudocompound were obtained through batch growth experiments. Interactions between pseudocompounds were determined through binary pseudocompound experiments. Using the growth and interaction parameters determined through experiments on individual

pseudocompounds, model fits and predictions were compared to actual mixture degradation kinetics. Model predictions of the biodegradation of mixtures of chemicals at concentrations similar to those used to obtain the single pseudocompound and interaction parameters were good. The overall percent variation explained for predicting the concentration of the four pseudocompounds and biomass ranged from 93-95% in these experiments. Changes in the mixture composition were made to evaluate the flexibility of the model. A mixture was created by randomly increasing or decreasing the chemical concentration of each component in the mixture by 50 %. Again the model proved adequate with 97% of the variation explained. Other mixture experiments demonstrated that additional work must be done to account for the inhibitory effects of chlorobenzene and the effect of substrate inhibition. Two random mixtures ($\pm 25\%$ and $\pm 50\%$ perturbations) were created with an increase in chlorobenzene. This increase in Chlorobenzene caused a strong inhibitory effect that could not be captured by the model. A random mixture containing concentration perturbations of $\pm 100\%$ demonstrated the need to account for substrate inhibition in the model.

This work was supported by grant number 5 P42 ES05949-05 from the National Institute of Environmental Health Sciences, NIH.

Key words: biodegradation, mixtures, modeling, lumping, pseudocompounds



ANAEROBIC/AEROBIC TREATMENT OF POLY- CHLORINATED BIPHENYLS IN SOIL

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Environmental polychlorinated biphenyl (PCB) contamination is often derived from spills or leaks of one or more of the Arochlor mixtures, which contain congeners with a range of degree of chlorination. In this situation, both anaerobic and aerobic treatments have been shown to partially degrade PCB mixtures. However, neither an anaerobic nor aerobic degradation scheme alone is ideal. Sequential anaerobic-aerobic treatment for PCB contamination is promising, yet little is known about specific parameters important for their successful bioremediation. Most of the work in this area has focused on a "black box" approach to enhancement of PCB transformation by sequential processes with little insight into the actual microbial processes at work. The roles played by different types of microorganisms inhabiting mixed-culture, dechlorinating communities is still unknown. Our research goal is to move beyond a "black box" approach by directly correlating changes in the microbial community to the observed enhancement of PCB transformations due to variable manipulation. These correlations will allow for development of better remediation strategies of PCB-contaminated soil.

In this laboratory-scale investigation, initial slurry microcosm studies of two different soils demonstrated dechlorination of several hexachlorobiphenyls to penta- and tetrachlorobiphenyls by indigenous organisms in both soils. No ortho dechlorination was observed in either soil, and the dechlorination pattern was strongly dependent on the congener being degraded in addition to the electron

donor utilized. Aerobic microcosm experiments demonstrated the presence of microorganisms able to degrade >50% of tri- and tetrachlorinated congeners as well as biphenyl over the course of three weeks. Microcosms not amended with biphenyl showed decreased dechlorination rates compared with those amended with biphenyl during the aerobic phase. Additional batch microcosm experiments are underway to determine (1) the effect of addition of an electron donor during the anaerobic phase on PCB dechlorination, (2) the effect of analog enrichment with biphenyl during the aerobic phase on degradation of PCBs and (3) the effect of varying treatment phase length of anaerobic and aerobic treatment phases. To correlate changes in microbial community composition and functional gene quantities with observed changes in PCB transformation, a combination of genotypic (quantitative PCR) and phenotypic (phospholipid fatty acid analysis) microbiological techniques is being utilized. PLFA patterns provide broad-based quantitative data on shifts in community composition. Information from PFLA analysis is being used to determine the amount of viable microbial biomass and provide insight into the microbial community composition. A quantitative polymerase chain-reaction method is also being utilized to track specific microbial genera and functional genes to better describe the effect of system perturbations on community dynamics. Changes in microbial community composition will in turn be used to understand and correlate changes in PCB bioremediation.

This work was supported by grant number 5 P42 ES05949-05 from the National Institute of Environmental Health Sciences, NIH.

Key words: PCBs, biodegradation, anaerobic, aerobic, phospholipid fatty acid analysis



REDUCTIVE DECHLORINATION OF PCBs IN SOIL

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Successful attempts to dechlorinate PCBs in the laboratory have utilized contaminated soils and sediments as sources of microorganisms. It has not been possible to isolate organisms with the ability to dechlorinate any of the PCB congeners. Anaerobic processes remove chlorine atoms from meta- and para- positions with preference for chlorine atoms with one or more immediately adjacent chlorine atoms. Thus, reductive microbial dechlorination of heavily substituted congeners can occur under anaerobic conditions.

Under aerobic conditions, unsubstituted and mono- to tetra- substituted chlorobiphenyls are metabolized via oxygen addition, dehydrogenation to a catechol structure, ring cleavage and reactions leading to benzoic acid and/or monochlorobenzoic acid. A two-step sequence of microbial processes is indicated, i.e., reductive dechlorination followed by aerobic removal of residual chlorine atoms from the biphenyl backbone. It was postulated that substantial dechlorination of weathered, commercial PCB formulations can be achieved, *in situ*, through the activity of endogenous anaerobic microorganisms.

Samples of soil contaminated with PCBs were acquired in a manner to preserve the activity of endogenous anaerobic microbial consortia. Soils were tight and clayey in character. Samples were composited, diluted with sand to enhance permeability, and contacted with medium in four semi-continuous flow, packed-bed reactors. Medium flow was continued, under nitrogen, for about four months; reactors were sacrificed and duplicate samples taken for chemical analyses. Total

PCBs and PCB-congener distributions were determined for initial soil composites and reactor packing after anaerobic treatment.

Anaerobic medium was prepared from dehydrated Thioglycollate solids dissolved in distilled water; nitrate ion (sodium nitrate) was the terminal electron acceptor. Partial heat sterilization was used to minimize biomass formation in feed systems. Results of total and congener analyses are discussed in detail. Changes in congener distributions, during anaerobic treatment, appear to confirm that microorganisms present in contaminated soil can contribute to reductive dechlorination of PCBs.

Key words: anaerobic, bioremediation, dechlorination, soil, polychlorinated biphenyls (PCBs)



EVALUATION OF GENE TRANSFER AS A MODE OF PLASMID DISPERSAL IN 2,4-D CONTAMINATED SOIL

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Gene augmentation can be used to enhance remediation of contaminated soils; however, little is known of the transport of genes through vadose zones. Column studies were used to evaluate the dispersal of plasmid pJP4 under unsaturated flow conditions in 2,4-dichlorophenoxyacetic acid (2,4-D)-contaminated soil. Soil microcosms amended to the same contaminant level were used to assess the potential for gene transfer during the course of the column runs. Plexiglass columns 30.5cm in length with an inner diameter of 7.5cm were packed ($P_b = 1.4 \text{ g/cm}^3$) with a sandy loam soil amended with 1,000 mg of 2,4-D g dry soil⁻¹. Unsaturated flow was maintained by the application of tension at the

base of the column with concurrent application of distilled water at the top of the column. Moisture content was monitored throughout the study using tensiometers inserted into the column at two depths. Soil within the top 2.5cm of the column was inoculated with an *E. coli* harboring plasmid pJP4 at 10⁶ CFU g dry soil⁻¹. The column was destructively sampled from bottom to top by removal of the soil in layers after various lengths of time. Soil from each layer was homogenized and donor organisms and indigenous recipients of plasmid pJP4 were enumerated via plating on selective media. Concentrations of 2,4-D in each soil layer and in the column effluent were monitored using HPLC analysis. Culturable donor organisms were detected in layers extending to 10.5cm from the top. Community DNA was also extracted from the soil layers and PCR analyzed for the *tfdB* gene of pJP4 as well as the *lamB* gene of *E. coli*. Studies showed that after a one-week column run, 2,4-D was no longer present within the top 15.5 cm of the column, which correlated with gene dispersion. These results suggest that plasmid transport in conjunction with plasmid transfer to indigenous recipients may be an applicable remediation strategy.

Key words: gene transfer, plasmid dispersal, unsaturated



MERCURY METHYLATION IN MARINE SEDIMENTS: AN ASSESSMENT OF COUPLED BIOCHEMICAL PROCESSES AND POTENTIAL FOR SEDIMENT REMEDIATION

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Anoxic, slurry incubations were performed to examine the relationship between mercury methylation rates (MMR) and sulfate reduction rates (SRR) in salt marsh sediments from the southeastern United States. The effects of temperature, addition of low-weight molecular organics, and microbial inhibitors were examined. Initial rates of mercury methylation are correlated with the rates of sulfate reduction. Significantly lower MMRs are observed after an initial 12h of exposure, following inorganic mercury addition, suggesting that sorption or precipitation of mercury reduced the availability of mercury for methylation. Results on parallel assessment of pore-water mercury levels will be discussed in this regard.

MMR results for various concentrations of inorganic mercury indicate that saturation kinetics occur. Using this kinetic framework, a model for MMR based on SM and inorganic Hg concentration will be presented and verified with experimental results. The use of this model in predicting the MMR reported in independent studies of the effects of temperature and substrate/inhibitors will be presented. The model provides a reasonable estimate of MMR observed in the initial 12h of the slurry incubations. However, the sequestering of inorganic mercury into less reactive pools by sorption to surfaces or incorporation into other phases, alters the amount of bioavailable Hg and hence MMRs. The ongoing assess of the bioavailability of Hg in the sediments will be

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discussed relative to extension of these observations to field sites.

Key words: mercury, methylation, sediments, sulfate reduction



THE ROLE OF MICROORGANISMS IN METAL TRANSFORMATION AND REMEDIATION

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The bioremediation of sites contaminated with both metals and organics is often inhibited by the toxicity of the metal. Using 2,4-dichlorophenoxyacetic acid, 2,4-D, and cadmium as copollutants, several cadmium-resistant bacterial isolates were examined for the ability to detoxify cadmium to sufficient levels to allow for 2,4-D degradation to occur. Degradation of 500 ppm 2,4-D in soil and broth by the cadmium-sensitive 2,4-D degrader *Alcaligenes eutrophus* JMP134 in the presence of cadmium occurred following cadmium detoxification by a cadmium-resistant isolate. Four cadmium-resistant isolates, representing the genera *Pseudomonas*, *Bacillus* and *Xanthomonas*, individually detoxified up to 32 ppm bioavailable cadmium in pure culture and soil under laboratory and field conditions. The observed mechanisms of cadmium-resistance found using transmission electron microscopy and staining included intracellular sequestration and extracellular sequestration by microbial polymers. The presence of the *cadA* gene, thought to be common in cadmium-resistant bacteria, was detected in only one isolate. This study demonstrated that bioremediation of co-contaminated systems can be facilitated upon inoculation with a metal-resistant microbial population to reduce metal toxicity.

Key words: metals, bioremediation, degradation, soil contamination



IDENTIFICATION OF SPECIFIC METHYLATION RATES FOR SPECIES OF SULFATE-REDUCING BACTERIA IN PURE CULTURE AND IN ORGANIC ACID-AMENDED SEDIMENT SLURRIES

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Sulfate-reducing bacteria (SRB) have been implicated as the primary biological producers of methylmercury (CH_3Hg^+) in mercury-contaminated sediments. However, the degree to which phylogenetic groups of SRB methylate mercury has not been determined. In this study, representatives from the SRB phylogenetic groups, i.e., *Desulfovibrio*, *Desulfobulbus*, *Desulfococcus*, *Desulfabacterium*, and *Desulfobacter*, were grown in the presence of inorganic mercury (Hg^+). Production of methylmercury, as well as the sulfate reduction rates, were quantified on a per cell basis. In pure culture systems there were significant differences in MMRs among the phenotypes. *Desulfobacterium* species generated the highest concentrations of methylmercury on a per cell basis. *Desulfovibrio* and *Desulfobulbus* species generated limited quantities of methylmercury when normalized on a per cell basis.

The effects of phenotype variations in sediments were studied using SRB cultures grown under fermentative conditions. The production of methylmercury was minimal with no definitive increases in concentration over time. Organic acids were added to sediment slurries in an effort to stimulate specific consortia capable of using the specific organic acid as an electron donor. Sediment slurries were treated with lactic and acetic acid 20 days prior to inorganic mercury addition. SRB phylogenetic groups present in slurry incuba-

tions were identified using 16S rRNA hybridization probes. These cultures were then incubated without the supplemental addition of organic-acid substrates to assess the effects of phenotype variations on SRRs and MMRs. Methylmercury concentrations, sulfate reduction rates, total mercury concentrations in slurry water, carbon substrate concentrations, and cell counts were quantitated in the sediment-slurry systems. These kinetic results will be presented with an integrated model to demonstrate the effects of the indicated parameters on mercury methylation processes in sediments systems. Results of both the pure culture and amended-slurry experiments suggest that SRB phylogenetic groups have significantly different potentials to methylate mercury. Thus, *in situ* rates of methylation in sediments are species dependent, driven indirectly by the availability of specific organic substrates. The bioavailability of mercury is thereby species dependent. This *species-dependant bioavailability* is a critical parameter in assessing remediation processes and the net mercury flux into the water column from contaminated sediments

Key words: methylmercury, sulfate reducing bacteria, phenotypes, sediments, 16S rRNA



STUDY ON HEAVY METAL UPTAKE BY ELSHOLTZIA HAICHOWENSIS SUN AND COMMELINA COMMUNIS LINN. USING HYDROPONIC CULTURE

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A great deal of work has been conducted outside China on accumulation of heavy metal by plants. Some research work has also been done in China on uptake of metals by plants. However, distribution, ecology, and phytochemistry of wild plants in natural environments of heavy metal mines within P. R. China and their relationships with supporting substrates are poorly understood. Several indicators that have been used by Chinese geologists for ore exploration for decades are of great value and worth further study. Among them are *E. haichowensis* and *C. communis*, which are widely distributed on copper mining wastes and copper-contaminated soils of the areas along the middle and lower streams of the Yangtze River.

We have recently completed a study of the uptake of copper, zinc, and Cd by the two plants using hydroponic culture method. The strength nutrient solution, which was used as a control, had the following composition (mM): 3 KNO₃, 2 Ca(NO₃)₂, 0.5 MgSO₄, 0.01 FeNa⁺ EDTA, 1 NH₄H₂PO₄, 9 X 10⁻³ MnSO₄, 46 X 10⁻³ H₃BO₃, 50 X 10⁻³ KCl, 1.5 X 10⁻³ CuSO₄, 1.5 X 10⁻³ ZnSO₄, 0.14 X 10⁻³ (NH₄)₆MO₇O₂₄ · 4H₂O, adjusted to pH 6.5 with 1 mol/L KOH. The control treatment had no Cd added. Further treatments called low metals had (mM) 3 CuSO₄, 5 ZnSO₄, and 0.10 CdCl₂; middle metals had (mM) 6, 10, and 0.15 of Cu, Zn, and Cd; and high metals had (mM) 9, 15, and 0.2 of Cu, Zn, and Cd, respectively. The twenty-day-old seedlings of the plants were

transferred into the hydroponic pots and grew there for a week before application of heavy metal. After application the plants were allowed to grow for another thirty days during which the solutions were renewed every two days. The plants were then harvested, recorded for biomass and analyzed with AAS following wet-ashing treatment.

The analytical data show a highly significant positive correlation between biomass of shoots and roots, and the concentrations of Cu, Zn, and Cd for *E. haichowensis* but less positive correlation for *C. communis*. It is found that the concentrations of Cu, Zn, and Cd in both roots and shoots for both plants increase with more applications of heavy metal concentrations. But there is a slight difference in uptake of heavy metals between the two plants. For *E. haichowensis*, the concentration of Cu in the roots increases with application of heavy metals at the beginning and later decreases when a certain level of heavy metals in the hydroponic pots is reached, while the concentrations of Cu, Zn, and Cd in the shoots have no remarkable variations. This suggests that it can be used as an indicator for ore exploration and a pioneer species for revegetation. For *C. communis*, the concentrations of Cu, Zn, and Cd increase linearly in both shoots and roots with the application of heavy metals in the pots, implying that it can serve not only as a good indicator for metal ore exploration but also as a pioneer species for phytoremediation. It is also found that the concentrations of heavy metal among different treatments in the roots indicate much greater variation than the shoots.

Key words: heavy metals, uptake, plant, hydroponic culture

Program Two
Thursday, May 27, 1999
Phytoremediation
Jefferson B



TOXICITY OF CHLORINATED ALIPHATICS TO POPLAR CUTTINGS AND CELL CULTURES

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Trichloroethylene and other chlorinated aliphatics are among the most commonly reported groundwater contaminants in the United States. Hybrid poplar trees are often used in phytoremediation efforts and may provide an effective yet inexpensive method of cleaning up groundwater containing various chlorinated aliphatics. However, these solvents may be toxic to plants at high concentrations. Increased knowledge of toxicity limitations and mechanisms will allow the selection of sites and plant species most appropriate for phytoremediation. An understanding of general trends correlating chemical characteristics with toxicity would be useful in predicting acceptable levels of untested compounds.

Hybrid poplar (*Populus deltoides* x *nigra* DN34) cuttings were grown hydroponically in sealed laboratory reactors and exposed to various concentrations of a chlorinated solvent. Phytotoxicity was assessed by monitoring leaf chlorosis, transpiration rate, and change in cutting weight. Axenic cell suspension cultures of the same poplar hybrid were established in liquid nutrient media. These cells were exposed to various concentrations of a chlorinated solvent and toxicity levels were determined by monitoring cell death. A series of chlorinated ethenes and ethanes with a broad range of octanol-water-partitioning constants was used. Toxicity of solvents to cuttings was

compared with toxicity to cell cultures. The effects of various chemical parameters on toxicity were also assessed.

Key words: phytoremediation, toxicity, chlorinated aliphatics, poplar trees



ANALYTICAL TECHNIQUES AND UPTAKE STUDIES OF EXPLOSIVES-CONTAMINATED WETLAND PLANTS

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Phytoremediation of explosives compounds has been implemented at the Iowa Army Ammunition Plant near Burlington, Iowa. An engineered wetlands system utilizing plants such as arrowhead, water plantain, and reed canary grass has been installed to remediate contaminated soil in the streambed and banks of Brush Creek. Up until the late 1970's, a man-made dam turned Brush Creek into a holding basin for explosives contaminated wastewater from the nearby Line 1 production facility. Determining the success of the ongoing remediation effort has been the focus of research into the fate of explosives compounds such as 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX) in wetland plants.

In an effort to better quantify field concentrations of RDX in plant tissues, a novel acetone-based extraction technique utilizing an ultrafiltration cleanup process has been developed. Plant extracts spiked with RDX were initially green in color due to the large quantity of chlorophyll and photosynthates that were removed from the leaves by the acetone. The final stage of the technique produced a clear, colorless solution ready for extraction with acetonitrile and subsequent HPLC analysis. Recoveries were 88 ± 15 percent for RDX.

An uptake experiment using U-¹⁴C RDX was performed in hydroponic solution in small flasks containing parrot feather and reed

canary grass. Results for parrot feather indicate that over 80% of the U- ^{14}C RDX was uptaken within 21 days. Plant extracts revealed that RDX was transported to the upper portions of the plants. Extracted samples were 80 ± 15 percent of the total radioactive content (determined via burning and recovery of $^{14}\text{Co}_2$) indicating very little transformation of RDX in the tissues. But, mass balance results showed only 30-50% of the applied label was recovered as RDX, indicating that volatile metabolites may have been formed.

Lastly, a gas chromatography/mass spectrometry (GC/MS) method has been developed to unequivocally identify and quantify RDX and its metabolites in a variety of matrices. Other explosives are easily quantified with the technique as well. The technique is performed with a Finnigan GCQ system running in negative ion/chemical ionization mode with methane as the reagent gas.

Key words: phytoremediation, explosives, wetlands, RDX



PLANT GROWTH CONDITIONS ALTER THE UPTAKE OF TRICHLOROETHYLENE BY HYBRID POPLAR

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Several recent reports of plant uptake of trichloroethylene (TCE) have concluded that plant uptake and transpiration of TCE are significant fate processes. However, most data indicates minimal uptake and translocation. A laboratory system that provides a realistic plant growth environment while obtaining high-mass recoveries is necessary to accurately determine plant-contaminant interactions and to minimize experimental artifacts. We constructed four continuous-high-flow, sealed, plant-growth-chamber systems to determine the fate of

volatile organic compounds in plants. Experimental variables evaluated include exposure duration, TCE concentration, and root-zone oxygen status. Mass recoveries of ^{14}C have consistently been >92% during studies ranging from 10 to 26 days. Transpiration stream concentration factors (TSCFs) have varied by an order of magnitude (0.02 to 0.19) and appear to be a function of exposure concentration, peaking at 10 mg/L. Root zone oxygen status did not impact plant uptake. TCE metabolites have been found only in the higher exposure treatments (10 and 70 mg/L TCE), with evidence of increased accumulation over time. We are now studying the effect of extended exposure duration on the uptake of TCE at low concentrations. Results of the current study and those conducted previously will be summarized with emphasis on the interaction between exposure duration, phytotoxicity, uptake, translocation, and metabolism.

Key words: phytoremediation, trichloroethylene, plant uptake, TSCF



AN EXPERIMENTAL STUDY OF PHYTOREMEDIATION OF METHYL-TERT-BUTYL ETHER (MTBE) IN GROUNDWATER

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The feasibility of phytoremediation of groundwater contamination with methyl-tert-butyl ether (MTBE) was experimentally examined using a six-channel system planted with alfalfa plants. Two bacterial strains capable of degrading MTBE were each added to two out of six channels. A solution of 0.844 mM MTBE was continuously fed into each channel at 1 L/day until a stable MTBE concentration level in the groundwater was established; then the feeding was switched back to distilled water. The channel ground-

water effluent MTBE concentration and the soil gas MTBE fluxes were monitored from the beginning of the MTBE solution feeding until no MTBE was detected. Integration of the gas flux data indicated that the four vegetated channels with introduced bacteria had less MTBE recovered from the soil surface than channel 3 which was vegetated but without any introduced bacteria. The total mass balance for MTBE showed that the fractions of MTBE which were not recovered in the planted channels were 10-25% higher than in the unplanted channel, suggesting that, due to the presence of the plants, MTBE might have been undergoing enhanced rhizosphere biodegradation.

Key words: phytoremediation, MTBE, biodegradation, mass balance



BIODEGRADATION OF JET FUELS IN THE PRESENCE OF VEGETATION

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Aliphatic hydrocarbons are the major constituents of many petroleum-type mixtures and appear to be widely distributed in the environment. Soils contaminated with jet fuels, which are primarily comprised of aliphatic hydrocarbons, may be toxic to plants. In general smaller hydrocarbon molecules are more toxic to plants than are larger hydrocarbons within the boiling range of 150-275°C. In this study, the biodegradation of jet fuels is being studied in the presence of vegetation. A two-channel soil chamber with alfalfa plants is contaminated with approximately 1330 mg of

jet fuel kg⁻¹ of soil, and four cylindrical soil columns are also contaminated with 2000 mg of jet fuel kg⁻¹ of soil. Two of those columns are planted with horseradish and the other two are unvegetated. Jet fuel biodegradation and chronic toxicity on plants in the soil chamber and columns will be studied over the period of three months. A separate four-week batch-biodegradation study is being conducted in 20 mL scintillation vials with soils contaminated with 2000 mg of jet fuel kg⁻¹ of soil. Treatments include soil amended with 5% raw and cooked horseradish tubers every week, soil amended with 20% raw and cooked horseradish tubers at the beginning, soil with no amendment, and sterilized soil with no amendment. Microbial activity and biodegradation will be monitored at weekly intervals for a month. This paper will present the experimental details and preliminary results of these studies.

Key words: alkanes, horseradish, phytoremediation, microbial activity



PHYTOREMEDIATION OF VEHICLE WASH SEDIMENTS

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Many military bases have vehicle wash facilities where combat and other equipment are washed with high-pressure water hoses after training maneuvers. While doing so,

sediments with variable concentrations of petroleum hydrocarbons accumulate in concrete basins. Landfill disposal or land applications are conventional treatment methods to handle these sediments. However, growing vegetation may enhance either the rate or endpoints of dissipation of the petroleum hydrocarbons in sediments. Other environmental benefits likely include reduction of soil erosion due to wind and water. We are testing two vegetative treatment systems consisting of a mixture of tall fescue and western wheat grass and a mixture of tall fescue and legumes designed to treat approximately 136 m³ of petroleum hydrocarbon-contaminated sediments generated by the Central Vehicle Wash Facility at Fort Riley, Kansas. Contaminated sediments were spread in a 30-cm deep layer. The two vegetation treatments, along with an unvegetated control, were seeded in September 1997 in a randomized block design with four replications. This paper will describe the vegetation treatment system design and present results of analyses of total petroleum hydrocarbon concentrations and plant growth for sampling events through the first year of this two-year field trial.

Key words: petroleum hydrocarbons, phytoremediation, vegetation

Program Three
Tuesday, May 25, 1999
Zero-Valent Metals
Jefferson A



**CORRELATION ANALYSIS
 OF RATE CONSTANTS FOR
 DECHLORINATION BY IRON
 METAL**

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Cleaving the carbon-chlorine bond via dehalogenation is the basis for a number of abiotic remediation technologies, such as those involving vitamin B12 or iron metal [1-3]. However, despite the important role of dehalogenation in these technologies, there have been few successful linear free energy relationships (LFERs) to predict contaminant dehalogenation rates. Kinetic data on dechlorination by Fe⁰ have become quite abundant [4], and they now make up one of the most extensive data sets available for pursuing correlation analysis of contaminant dehalogenation rates. We have used previously reported kinetic data for dehalogenation of alkanes and alkenes by Fe⁰ to develop LFERs based on estimated one-electron reduction potentials and LUMO energies calculated from semi-empirical and ab initio routines using CAChe molecular modeling software.

We have performed correlation analysis using this Fe⁰ data set in order to (i) explore the reliability of the available data, (ii) develop LFERs for predicting dechlorination rates by Fe⁰, and (iii) improve our understanding of the fundamental factors controlling reduction kinetics by Fe⁰ and dehalogenation kinetics in general. Satisfactory correlations were ob-

tained with a variety of measures of electron affinity as the descriptor variable. The resulting LFERs: (i) reveal qualitatively interesting patterns in reactivity and (ii) are useful for predicting the reactivity of compounds for which limited experimental data are available. Comparison of new kinetic data with model predictions reveals a remarkably robust LFER, considering the diversity of compounds and conditions that are included in the training set. The analysis also has implications regarding the reduction of solutes by Fe^0 and the degradation of chlorinated aliphatics by competing reduction pathways.

References

1. Lesage, S., S. Brown, and K. Millar, Vitamin B-12-catalyzed dechlorination of perchloroethylene present as residual DNAPL. *Ground Water Monitoring and Remediation*, 1996. 16(4): p. 76-85.
2. Matheson, L.J. and P.G. Tratnyek, Reductive dehalogenation of chlorinated methanes by iron metal. *Environmental Science & Technology*, 1994. 28(12): p. 2045-2053.
3. Gillham, R.W. and S.F. O'Hannesin, Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water*, 1994. 32(6): p. 958-967.
4. Johnson, T. L., M. M. Scherer, and P.G. Tratnyek, Kinetics of halogenated organic compound degradation by iron metal. *Environmental Science & Technology*, 1996. 30(8): p. 2634-2640.

Key words: LFER, QSAR, dehalogenation, zero-valent iron



NITRATE REMOVAL WITH INDUSTRIAL IRON POWDER

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This research project is designed to study the feasibility of removing nitrate in ground-water using cheap industrial grade iron powder (about 0.5 mm in size). The iron powder was sieved from shavings and fillings from iron products. The cost was about \$0.08/lbs. Batch and column studies were conducted to determine nitrate removal efficiencies. In addition, several batch studies were conducted to evaluate the possible mechanisms for removing nitrate in water samples.

Batch experiments were conducted in 160 ml dilution bottles with 5% (w/v) of the iron powder. The initial pHs of these samples were 2.3, 6.5 and 11.2. pHs were adjusted using sodium hydroxide and hydrochloric acid. The results indicate that nitrate removal is dependent on the initial pH. To evaluate the possible mechanisms, batch studies were designed to evaluate several mechanisms proposed in iron remediation processes found in the literature. This was done by evaluating variables such as Fe^{2+} , Fe^{3+} , nitrate, pH, and redox variations in regular intervals for a period of 3 days. The results tend to indicate that most nitrate reduction occurs when magnetite (Fe_3O_4) was formed. Initially iron oxide or hydroxide was formed (brown precipitate). Minimal nitrate removal was observed. As pH increases and redox drops, magnetite was formed and significant nitrate removal was observed. In the case where pH was low, magnetite was formed within a few hours. The formation of magnetite was confirmed by the literature, and an analysis of the black precipitate formed in the batch samples. The analysis confirmed the presence of both Fe^{2+} and Fe^{3+} .

To simulate an iron wall treatment, acrylic tubes with a diameter of 1.5" and a height of 12" were constructed as continuously fed reactors. Mixing two parts of fine sand with one part of iron powder prevented plugging. Removal rates appeared to dependent on detention time. With a hydraulic detention time of about 7-8 days, about 99% of the nitrate was consistently removed for a period of 4 months.

Based on the preliminary results obtained from this research, it appeared that iron powder could reduce nitrates in nitrate-contaminated water. It appeared that a possible mechanism for nitrate removal might involve the formation of magnetite (Fe_3O_4). For field testing, it is recommended that iron powder be mixed with sand to form a treatment wall to prevent plugging and improve removal rates.

Key words: iron, iron powder, nitrate, remediation, groundwater



PREPARATION, CHARACTERIZATION, AND USE OF Z_nO NANOPARTICLES

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One of the most popular methods for preparing metal oxide nanoparticles is using sol-gel chemistry. This is a relatively simple and inexpensive method for preparing rather large quantities of this nanoparticle powder. There are three basic steps involved in this method. The first includes finding or preparing a molecular precursor, usually a metal alkoxide. The second step involves hydrolyzing this precursor and forming a gel. The third step is dehydrating this gel to form a metal oxide powder. Grams of this powder can be made using this general method. One of the most recent metal oxide powders we have

formed by this method is zinc oxide. The zinc oxide formed by this synthesis has a crystallite size of 3 nm, and a surface area of 120 m²/g. Whereas commercially made zinc oxide has a crystallite size of 42 nm and a surface area of 4 m²/g. This zinc oxide has been characterized by elemental analysis, TEM, BET, XRD, IR, and TGA. The zinc oxide nanoparticles, like other metal oxide nanoparticles, shows a significantly increased chemical reactivity. Due to the increased chemical reactivity, these metal oxides show potential for use as destructive adsorbents for toxic chemicals.

Key words: nanoparticles, zinc oxide, metal oxide powder, sol-gel chemistry

Program Three Tuesday, May 25, 1999 Metals Remediation Jefferson A



CHROMIUM(VI) REMOVAL BY MODIFIED PVP-COATED SILICA GEL

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This research involved synthesizing of a reactive polymer, long alkyl quaternized poly(4-vinylpyridine) (PVP) and coating it on the surface of silica gel to produce a granular sorbent to remove Cr(VI) from water.

Batch experiments were conducted to determine the kinetics, sorption isotherm, effect of pH, and influence of other anions on the chromium adsorption. The research demonstrated that the synthesized long alkyl quaternized PVP-coated silica gel (referred to as coated gel) could successfully remove chromium(VI) from solution.

The absorption of Cr(VI) by the coated gel was strongly influenced by the pH. The maximum sorption occurred at about pH 4.5-5.5 under the test conditions. The removal efficiency almost reached 100% when the initial Cr(VI) concentration was 2.5 mg/L with 2.5 g/L of coated gel at pH 5.0. The concentrations of Cr(VI) had a pronounced effect on the rate of sorption. Compared with the ion exchange, the sorption kinetics of Cr(VI) was fast (about 5h). The equilibrium sorption data fitted well to the Langmuir isotherm model. The sorption of Cr(VI) was influenced to some extent by other anions. The relative effect of anions in decreasing order for sorption of Cr(VI) on coated gel was $\text{SO}_4^{2-} > \text{Cl}^- > \text{CH}_3\text{COO}^-$. Chromium adsorbed on the coated gel was easily recovered under certain conditions. NaOH was a good desorption reagent; the desorption efficiency of Cr(VI) could reach 90%. The desorption rate was very fast. After desorption, the coated silica gel could be reused.

Key words: chromium(VI), removal, recovery, coated gel, sorption



CHARACTERIZATION OF CHROMIUM (VI) BIOREDUCTION AND CHROMIUM (III) BINDING TO ALFALFA BIOMASS

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Chromium (VI) is a common waste product generated from industrial processes such as electroplating, wood preservation, and metal finishing, and is highly toxic as compared to chromium (III). Current disposal and treatment methods, such as ion-exchange

resins, are costly and pose a great health risk to the public. A more environmentally sound and cost-effective method of phytofiltration using alfalfa biomass may be a plausible answer for the removal of both chromium ions from solution. Previous studies have shown alfalfa to have a high affinity for chromium (III) at pH 5 and 6 under single-metal and mixed-metal conditions. Flow studies performed using silica-immobilized alfalfa biomass were conducted and X-ray microfluorescence (XRMF) was used to show conclusive evidence of chromium (III) binding. Studies performed using X-ray absorption near edge structure (XANES) provided direct evidence that alfalfa biomass reduces chromium (VI) to chromium (III). Time and temperature studies conducted at pH 2 and 5 were also utilized to study the reduction process of chromium (VI) to chromium (III). This study showed that chromium (III) binding increased as the temperature increased under single- and mixed-metal conditions. However, chromium (VI) binding does not follow the same temperature-dependent trend. This will be further investigated along with the pathway of the bioreduction process and additional studies involving XANES and EXAFS will be conducted. This information will lead to the finalization of an environmentally friendly and cost-effective phytofiltration system using alfalfa biomass.

Key words: XANES, XRMF, alfalfa, metal binding, phytofiltration, chromium



SPECTROSCOPIC STUDIES OF GOLD (III) BINDING TO ALFALFA BIOMASS

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A need to develop environmentally friendly technologies to retrieve precious metals has arisen due to the current mining methods, which involve the use of harsh chemicals that endanger the community's health. Alfalfa biomass has shown in previously performed experiments that it has a substantial ability to bind gold(III) from aqueous solutions in a rapid and pH-independent manner. Furthermore, the gold(III) solutions that reacted with the alfalfa biomass turned purple, indicating gold(III) reduction to gold(0). Transmission electron micrographs (TEM) of the samples confirmed the bioreduction process. Flow experiments with silica-immobilized alfalfa biomass were done and X-ray microfluorescence (XRMF) analysis performed to have direct evidence of gold binding. Also, time and temperature dependence experiments, at pH 2.0 and pH 5.0, were conducted to study the gold(III) to gold(0) reduction process. The results obtained show that this is a time, temperature, and pH-dependent process. X-ray absorption near edge spectroscopy (XANES) and extended X-ray adsorption fine structure (EXAFS) data corroborated the reduction of gold(III) to gold(0). We have no knowledge of the actual mechanism of the bioreduction process. We are currently, however, performing experiments *in situ* to determine the pathway involved by using XANES and EXAFS techniques.

Key words: XANES, EXAFS, XRMF, alfalfa, gold, metal binding, phytofiltration



COPPER(II) AND LEAD(II) BINDING BY ALFALFA BIOMASS: USE OF CHEMICAL MODIFICATION AND X-RAY ABSORPTION SPECTROSCOPY TO DETERMINE THE METAL-BINDING MECHANISM

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Traditional methods currently employed to remediate heavy metal-contaminated waters prove to be cost prohibitive. Therefore, more cost-effective methods of remediating heavy metals from contaminated waters need to be developed. The use of plant materials as a metal adsorbent may be a possible solution. Previously performed experiments have shown that alfalfa shoot biomass can bind an appreciable amount of heavy metal ions, even from multi-contaminate-containing solutions. Although the alfalfa biomass has shown to be very effective at removing heavy metal ions from aqueous solution, more research is needed to understand the metal-binding mechanism. In order to determine the contribution of carboxyl, amino, and sulfhydryl ligands to the metal-binding process, these groups were chemically modified. Batch experiments were performed with the modified biomass and suggest that carboxyl groups play the most significant role in the binding of copper(II) and lead(II). In addition, X-ray absorption spectroscopic analysis (XANES) may corroborate these results. These studies are important for determining the ligands that may be involved in the binding of metal ions to the alfalfa biomass, thus aiding in the innovative removal and recovery of metal ions from contaminated waters through phytofiltration.

Key words: XANES, metal ligands, heavy metal binding, alfalfa



BERKELEY PIT INNOVATIVE TECHNOLOGIES PROJECT

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The Berkeley Pit, an abandoned open-pit copper mine located in Butte, Montana, has been filling with water since the early 1980s. To date, over 25 billion gallons of water are contained within the pit, creating a lake over 800 feet deep. According to the latest modeling efforts, by the year 2021, the gradient of the groundwater flow will reverse directions, thus allowing the contaminated water to disperse out of the pit. At that time, the water will require treatment to prevent any further contamination of adjacent aquifers.

The Berkeley Pit Innovative Technologies (BPIT) Project is managed by Montana Tech of the University of Montana (Montana Tech) through a subcontract with MSE Technology Applications, Inc. (MSE-TA) which implements the Mine Waste Technology Program (MWTP). The purpose of the BPIT project is to provide a test bed for innovative and/or high-risk technologies for remediating Berkeley Pit water. The project focuses on bench-scale testing of remediation technologies to help define alternative remediation strategies for the Environmental Protection Agency's future cleanup objectives for the Berkeley Pit water. To date, 11 technology providers have performed bench-scale demonstrations at Montana Tech.

Key words: technology, pit lakes, geochemistry, remediation



HEAVY METAL BINDING BY *MUCOR ROUXII* BIOMASS GROWN UNDER COPPER-STRESSED CONDITIONS

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Inactivated strains of *Mucor rouxii* cultured at high- and trace-copper concentrations were investigated for their ability to bind heavy metal ions from solution. The heavy metal ions tested included Cu(II), Pb(II), Cd(II), Ni(II), Zn(II), Cr(III), and Cr(VI). Overall, the *Mucor rouxii* cells grown under higher copper concentrations bound more Cu(II), Pb(II), and Cd(II) ions. No significant differences between the different biomasses were observed for the binding of the other metal ions. In addition, important morphological changes were observed in the fungal cells cultured at higher copper concentrations. This may indicate that the copper-stress produces additional binding sites for certain toxic metal ions. The adsorption by the fungal biomass of most metal cations increased as the pH was increased. However, the binding of Cr(VI) showed more binding at lower pHs. X-ray absorption spectroscopic studies indicated the presence of Cr(VI) and Cr(III) adsorbed onto the *Mucor rouxii* biomass. Thus, Cr(VI) may be reduced to Cr(III) and then Cr(III) may also be binding to the fungal biomass. Batch and flow experiments also demonstrated that inactivated and immobilized *Mucor rouxii* biomass was an efficient process for heavy metal removal and recovery from aqueous solution, in addition to the reuse of the biomass. Also, Ca(II) and Mg(II) ions showed not to interfere in the binding of Cu(II) and Pb(II) by the fungal biomass.

Key words: Mucor rouxii, heavy metal binding, morphological alterations



BERKELEY PIT LAKE FROM TOP TO BOTTOM

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An interdisciplinary team of Montana Tech researchers, being funded by the Mine Waste Technology Program (MWTP), has currently completed studying several aspects of the Berkeley Pit Lake system to better understand the system as a whole. The information obtained from the studies may be used to predict future qualities of the water, to evaluate the natural rate of remediation, to determine if partial *in situ* remediation may be practical prior to expensive pump-and-treat remediation, and to predict water quality for similar bodies of water in the United States. The following research has been completed on the Berkeley Pitlake as part of this project: Biological Survey of Berkeley Pit Water; Sediment/Pore Water Characterization; Sulfate-Reducing Bacteria, Surface Oxidation Reactions; and Organic Carbon. The projects were funded through the Mine Waste Technology Program (MWTP). The MWTP is sponsored by the EPA through the DOE, and implemented by MSE Technology Applications, Inc., in Butte, Montana. The underlying theme of all MWTP projects is remediation and/or control of current or future mine waste problems.

Key words: remediation, pitlakes, technology, geochemistry, biology

Program Three

Wednesday, May 26, 1999

Adsorption

Jefferson C



NANOCRYSTAL METAL OXIDE-CHLORINE AD- DUCTS: SELECTIVE CATA- LYSTS FOR CHLORINATION OF ALKANES

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Nanocrystals of MgO and CaO adsorb chlorine gas exothermally in large amounts. Dissociative chemisorption takes place where chlorine atoms are trapped on highly basic surface oxide anion sites, probably at edge and corner sites, mainly. These adducts are active for the catalytic chlorination of methane to form chlorinated methanes, and 2,3-dimethylbutane to give monochlorinated products at the tertiary site. No light is required for the reactions, showing that the nanocrystal-Cl₂ adducts behave as trapped Cl atoms, which are intermediate in reactivity between Cl₂ and free Cl atoms.

Key words: chlorine gas, methane



SORPTION-DESORPTION ASYMMETRY OF ORGANIC COMPOUNDS IN NATURAL SEDIMENTS

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The ability to accurately determine the effects of pollutants upon individual organisms or on local ecosystems is important for estab-

lishing realistic endpoints for cleanup and to estimate actual long-term environmental risk. The fundamental need for environmental risk assessment is to understand adsorption and desorption processes as they relate to fate and transport of organic contaminants in the environment.

It is often desirable to have a standard experimental protocol to assess the risk of contaminants in soil. A protocol to uniformly contaminate and desorb sediment was tested with phenanthrene and the sediment from Bayou Manchac in south Louisiana. Significant amounts of sorbed phenanthrene remained in the sediment following desorption by XAD-2 in a dialysis bag. Six research groups at Rice University, Louisiana State University, and Southern University are currently studying the biological response and availability of desorption-resistant organic pollutants.

Typically, desorption of hydrophobic organic compounds includes reversible and an irreversible fractions; the irreversible compartment has a finite maximum capacity for specific chemical-sediment combinations; and the desorption behavior associated with this compartment is independent of chemical and sediment properties. An irreversible sorption-desorption isotherm has been proposed to model these unique behaviors associated with the irreversible compartment. In this research, effectiveness of the irreversible adsorption-desorption isotherm has been examined with the desorption of five chlorinated benzenes from four sediments. The desorption results covered wide solid and aqueous-phase concentration ranges and were well modeled with the irreversible isotherm. Through laboratory studies and field observations, we have begun to demonstrate that the response of an ecosystem or any at-risk population is not controlled by the total concentration of a contaminant in which a receptor resides, but instead only by that fraction which is biologically available. The physical-chemical and biological mechanisms that have signifi-

cant impact on environmental risk assessment will be discussed.

Key words: sediment, criteria, adsorption, desorption, availability



DEVELOPMENT OF ADSORPTION ISOTHERMS AND BREAKTHROUGH CURVES FOR CYANAZINE AND S-TRIAZINE METABOLITES IN SYNTHETIC AND NATURAL WATERS

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The purpose of this study is to assess both the technical and the economic viability of treating cyanazine and selected s-triazine metabolites using PAC versus GAC in Missouri's public water treatment plants. The compounds included in the full matrix include cyanazine, atrazine, hydroxyatrazine, deethylcyanazine, deethylatrazine, deisopropylatrazine, and didealkylatrazine. The specific objectives of the study include: 1) development of adsorption isotherms for the study compounds via batch isotherms; 2) examination of the effects of pH (7 vs. 10), temperature (15 vs. 21 °C), source water (deionized vs. Missouri River water), carbon form (PAC vs. GAC), and carbon type (PACs: Watercarb, Hydrodarco B, and Calgon WPH; GAC: pulverized F400); 3) examination in column studies of the effects of competitive adsorption between different s-triazines and between s-triazines and natural organic matter; and 4) performance of an economic analysis to assess relative treatment costs (versus atrazine) for each compound studied for both GAC and PAC.

Higher capacities for cyanazine were generally achieved at higher pH (10 vs. 7), and at low temperature (15°C vs. 21°C) for each carbon examined. Unfiltered Missouri River water caused a significant decrease in carbon capacities. Results for the filtered Missouri

River water isotherms for all study compounds under all matrix conditions will soon be available. Almost all of the isotherms developed for the study compounds were highly *favorable* (i.e., convex from the top) with Calgon WPH and Hydrotarco B. The isotherms developed with Watercarb, however, were much less favorable.

This research, which will be completed in April 1999, has resulted in several preliminary conclusions. Capacities for atrazine and cyanazine of Watercarb PAC (commonly used in Missouri) is much lower than that of Calgon WPH or Hydrotarco B. If problems are encountered meeting newly promulgated MCLs for cyanazine, utilities may have the option of switching their PAC supplier (or dosages) to allow maintaining compliance, rather than having to consider using GAC. The decision whether or not to switch PACs will be on a case-by-case basis and is related primarily to costs (i.e., \$/mg removed = \$/g carbon) / q(mg/g)).

Key words: cyanazine, atrazine, adsorption, isotherms



NANOCRYSTALLINE-METAL OXIDES AND MIXED-METAL OXIDES AS EFFECTIVE ADSORBENTS FOR VOLATILE ORGANIC COMPOUNDS

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Nanocrystals of MgO, CaO, Al₂O₃ and iron-containing composites of different oxides were prepared by aerogel (AP-samples) or conventional (CP-samples) methods. High surface areas/gram were obtained, often as high as 500 m²/g. These materials were investigated as adsorbents for typical volatile organic compounds that are representative of air pollutants. As a result of their high surface areas and their enhanced surface reactivity, nanocrystalline MgO, Al₂O₃, and iron-containing composite materials have

shown remarkably high capacities to chemically adsorb such organic compounds. Compared to high surface-area activated carbon, the most widely used material in this application, our nanocrystalline materials have exhibited higher capacities and the ability to destructively adsorb rather than physisorb these chemicals. FT-IR investigation of acetaldehyde adsorption on AP- and CP-MgO indicates that a multilayer dissociative adsorption took place. Adsorption of other organic compounds was also investigated including acetone, propionaldehyde, benzaldehyde, trimethylacetaldehyde, ammonia, dimethylamine, N-nitrosodiethylamine, and methanol. In addition, long-term air exposure did not have detrimental effects on the adsorption properties of AP-MgO.

Key words: nanocrystals, adsorption, chemical adsorption, physisorbed



DESTRUCTIVE ADSORPTION OF WAR AGENT MIMICS BY NANOPARTICLE MAGNESIUM OXIDE

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A series of war agent mimics has been destructively adsorbed by specially produced nanoparticle MgO. 2-Chloroethyl ethyl sulfide (2-CEES), mimic of mustard gas, is dehydrochlorinated to ethyl vinyl sulfide, MgCl₂ and H₂O at room temperatures. Reaction ratios are optimized at 10:1 surface oxides-to-2-CEES with a destruction of 88% over 12 hours. Hexafluoropropylene (HFP), a mimic of perfluoroisobutylene, is destructively adsorbed with nanoscale magnesium oxide powders producing environmentally safe MgF₂, CO, CO₂ and graphite. The reaction occurs best at 450°C with a 2:1 surface oxide-to-HFP ratio. Studies are also being performed on the destruction of chloroacetonitrile (mimicking CICHN) at a range of temperatures. Analysis is

accomplished using FT-IR, gas chromatography, powder XRD, and elemental analysis. Comparisons to reactivity of "conventionally prepared" high-surface-area MgO and commercially prepared MgO will also be made.

Key words: nanoparticles, MgO, adsorption, war-agents



VAPOR SORPTION OF AIR POLLUTANTS BY METAL OXIDES

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Vapor sorption data for volatile organic compounds (VOCs) have been obtained using a quartz crystal balance. The data were taken at room temperature, which is below the boiling points of the analyses of interest, and some indoor air pollutants including methanol, ketones, chlorinated alkanes, etc. Nanoporous metal oxides were pretreated and used as highly efficient adsorbents, and comparisons are made when VOCs were introduced at relatively high pressures. Adsorption isotherms are also prepared to study the monolayer coverage on the sample surface of different morphologies, mainly with alcohols and nitriles. Results of these details will be presented and discussed.

Key words: adsorption, metal oxides, pollutants

Program Three

Wednesday, May 26, 1999

Biobarriers

Jefferson C



ANIMAL WASTE CONTAINMENT IN ANAEROBIC LAGOONS LINED WITH COMPACTED CLAYS

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Animal waste containment practice has recently drawn immense interest from public and regulatory agencies in agriculture-oriented states such as Kansas and North Carolina. In this study, soils from Kansas, which were used to construct a hydraulic barrier at the bottom of the lagoons, were analyzed. The wastewater in the lagoons contains significant amounts of contaminants (ammonia, nitrate, and chloride, for example) from animal feed operations. Lagoons, when designed improperly, may leak contaminants to the underlying soil and aquifers. As a result, it is important to predict and monitor the quality of the soil underlying these lagoons and the influence of leachate on groundwater. In this study, soils from southwest Kansas were studied with two different kinds of wastewater: i) from cattle waste, ii) from swine waste. The contaminant transport behavior, as well as changes in the hydraulic conductivity properties, for three different molding water contents were monitored. The contaminant transport through two hypothetical layers (1st layer: clay liner, 2nd layer: featured soil) and the impact on the aquifer as a result of this transport were analyzed.

Key words: animal waste lagoons, clay liners, fate, transport of solutes



BIOLOGICAL CLOGGING OF COMPACTED-CLAY LINER

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There have been several studies of water quality near animal waste lagoons reported in the literature. Lagoons constructed at sites with coarse-grained soils are often provided with a compacted clay liner to prevent excessive seepage from the lagoon and limit groundwater contamination below the lagoon. In this research, soil column experiments were conducted to study biological clogging of the compacted clay liner caused by the accumulation of microbial biomass by monitoring the influent and effluent. The microbial growth in soil columns and hydraulic conductivity reduction along the soil columns were studied. The goals of the project are to find out the effects of biological systems on compacted clay liners which will lead to more efficient compacted clay liner design and to develop a set of mathematical models to predict biological clogging of lagoon liners.

Key words: lagoons, clay liners, microbial biomass



A MODEL TO PREDICT BIOLOGICAL CLOGGING IN POROUS MEDIA

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Biofilm growth in porous media due to naturally existing microorganisms can cause reductions in hydraulic conductivity in any natural subsurface. Quantitative and mechanistic evaluation of biological clogging is a matter of recent interest. A model is developed to predict biological clogging as a gradual pore-

volume reduction process due to biomass accumulation and formation of biofilm on the pore walls. This involves kinetic expressions for predicting growth of microorganisms in terms of limiting substrate concentration. The porous media is idealized as an ensemble of capillary tubes. Model predictions are compared with experimental observations, and a sensitivity analysis is conducted.

Key words: biomass, hydraulic conductivity, clogging, porous media

Program Three Wednesday, May 26, 1999 Fate and Transport Jefferson C



ANALYSIS OF HORIZONTAL WELLS FOR PUMP-AND-TREAT REMEDiation

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The technology to drill wells horizontally was developed by the petroleum industry for crude oil production starting in the 1940s and it reached commercial viability in the 1980s. These horizontal wells are being used with increased frequency for remediation of contaminated groundwater. Computer simulation has been performed to gain insight into the groundwater flow associated with horizontal wells. Accurate simulation of this flow requires a three-dimensional model; a model based on the boundary element method was used for this investigation. The results indicate that horizontal wells can be very effective in pump-and-treat remediation of contaminated groundwater that exists within specific vertical regions of an aquifer; however, the placement of the well is critical in the remediation design. Ongoing research includes development of advanced boundary elements that will allow

the head specified boundary condition in the well to be satisfied more accurately. It is expected that this development will improve the capabilities of the computer model and increase our understanding of the flow associated with horizontal wells. The methodology used to investigate the flow associated with horizontal wells could also be applied to computer simulation of phytoremediation; this application will be discussed.

Key words: three-dimensional, horizontal well, pump-and-treat, remediation



MODELING PERMEABILITY CHANGES DUE TO PARTICLE TRANSPORT

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Groundwater flow is a very important issue in geoenvironmental engineering. Groundwater contains colloid particles; some of them are pollutants, like toxic metals, organics, and radionuclids. As these fluid suspensions migrate through subsurface porous media, some will deposit in the pores, and therefore, clog the pores, making the subsurface layer less permeable. However, the determination of the fundamental soil property, the permeability, needed in groundwater flow modeling, is still puzzling geoenvironmental engineers.

The objective of this paper is to model the migration and deposition of particles in pores, to determine how the coefficient of permeability changes with time.

In the modeling, the pore-size distribution of porous media and particle-size distribution of pore fluid suspensions are used to model particle migration and deposition mechanisms. Due to the clogging of pores, pore-size distribution and probability of particle deposition are all time dependent. Their changes are

analytically expressed. Two important parameters, critical velocity of pore fluid and ionic condition of pores, are taken into account. Finally, a numerical algorithm is proposed, utilizing the physically based model, to obtain permeability as a function of time.

In order to validate the model, several experiments are conducted and the results are compared with the model predictions; good agreement is found between experimental observations and model predictions.

Keyword: particle migration, accumulation, permeability



TRACER SENSITIVITY TO ENTRAPPED NONAQUEOUS-PHASE LIQUIDS: INTERMEDIATE SCALE EXPERIMENTS IN HETEROGENEOUS POROUS MEDIA

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Characterization of distribution of non-aqueous-phase liquid wastes in the subsurface is required for effective remediation. Characterization efforts rely heavily on core-scale evaluation of material properties and NAPL saturation distribution. As alternative tracer tests provide parameter values based on the continuous system, many published field tracer tests relied on extensive sampling networks to evaluate the tracer concentration spatial distribution. Practical limitations force most field investigations to rely on temporal data from a limited number of samplers. This study investigates the sensitivity of a conservative tracer-sampling network to the entrapment of NAPLs in a two-dimensional system. A series of intermediate-scale tracer experiments were

performed in a heterogeneous porous media. Homogeneous and heterogeneous zones were created in a 10 X 1.5 X 0.05 meter tank using six sands. Tracer tests performed prior to the introduction of any NAPL provide the baseline response of the heterogeneous porous media. Following each of two NAPL spills, tracer tests were performed to obtain the impacted solute flux characteristics. The effect of the NAPL entrapment was compared to variability between realizations using flow and transport models calibrated with the experimental data. Analysis of the results reveals a distinct impact on solute transport characteristics in the two-dimensional heterogeneous experiments. The knowledge gained in this research will help us to design better field-tracer schemes and sampling strategies at NAPL-contaminated field sites.

Key words: tracers techniques, NAPL detection, site characterization



CHELATING EXTRACTION FOR REMOVAL OF RADIONUCLIDES FROM CONTAMINATED SOILS

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Soil contamination involving radionuclides is a common problem encountered at many contaminated sites of the U.S. Department of Energy (DOE). Chelating extraction is well suited as a remediation technique for radionuclide-contaminated soils. The ACT*DE*CONSM technology (using a combination of chelation and carbonate chemistry in an alkaline-oxidative environment) has previously been shown to effectively remove plutonium (Pu) from clayey/soil/sediment at the Mound site, to level compatible with the Ohio-EPA risk-based cleanup limit. While applica-

tion of ACT*DE*CON on Mound's Pu-contaminated soils underwent pilot-scale demonstration, DOE requested that further study be conducted to evaluate the application of ACT*DE*CON to clean up other sites within the DOE complex which are contaminated with other radionuclides among which are uranium, thorium, and radium. The primary objective of this work was to develop a predictive tool for the selection of chelators and other components of the ACT*DE*CON solution for the target radionuclide contaminants at Mound and other DOE sites, and to assess chelation remediation efficiency based on a minimum of essential test results.

This laboratory investigation involved using a computerized solution-phase equilibrium model to select appropriate chelating agents for use in this study. Relevant model input parameters included acid-base equilibrium constants of the chelators, complexation constants of the chelators with radionuclides, and radionuclide speciation constants with natural ligands (OH^- , HCO_3^- , CO_3^{2-} , SO_4^{2-} , etc.). These parameters were used to develop a chemical equilibrium model to predict the complexation ability, selectivity, and recoverability of a large number of chelators toward the target radionuclide contaminants. The modeling indicated the following chelating agents offered potential in effectively removing the target radionuclide from the soils:

Radium: Ethylenediaminetetraacetic acid (EDTA), diethylenetrinitrilopentaacetic acid, (DTPA), nitrilotris(methylene)triphosphonic acid (NTTA), and 5-sulfosalicylic acid

Thorium: EDTA, DTPA, NTTA, N-2 actamidoiminodeacetic acid (ADA), and 2-aminoethanethiol

Uranium: EDTA and DTPA

Chelating agents selected for use alone or in combination with the other ACT*DE*CON components were EDTA, DTPA, NTTA, and ADA. Removal of the target radionuclides from three separate soils were studied. The results of the extraction were modeled for

different soil characteristics. Results from this study are summarized below:

- EDTA and DTPA were the most effective chelating agents for removing thorium and uranium from soils.
- The presence of ACT*DE*CON solution significantly enhanced the removal of thorium and radium from contaminated soils, due to the presence of bicarbonate/carbonate ions, which act as mild complexing agents.
- All of the chelating agents tests (EDTA, DTPA, NTTA, and ADA) were ineffective in removing uranium from all of the contaminated soils tests (at least for the operating conditions used), due to the extremely low concentration of uranium present in the soils.
- The presence of ACT*DE*CON solution did not significantly improve the removal of uranium from contaminated soils, although it did cause a slight increase in the removal efficiencies of all the chelating agents studied.
- A removal predictive model that incorporates various chelating agents was developed to address the removal of thorium from contaminated soils. Its predictions agree with experimental measurements within a standard deviation of 11%.

*Key words: radionuclides, ACT*DE*CON, EDTA, DTPA*

Program Three
Thursday, May 27, 1999
Analytical Methods
Jefferson C



ORGANOMETAL SPECIATION ANALYSIS WITH SUPERCRITICAL FLUID CHROMATOGRAPHY COUPLED TO ICP-MS

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Supercritical fluid chromatography with ICP-MS detection has been used in this research group for elemental speciation with much success. Specific applications include the use of SFC for the speciation of organometal compounds of tin, chromium, arsenic, antimony, lead, and more recently mercury. Organomercurial compounds are used for a number of industrial and agricultural applications including fungicides, paints, and pharmaceuticals. It is well established that many of the mercury compounds known are highly toxic, however, the toxicity of the organomercurials depends on the species of the compound. For this reason, the speciation of organomercurials becomes of general interest.

Mercury compounds are known to be difficult to analyze because of the memory effects they produce; therefore, different techniques have been tried. The most used analytical technique for this type of speciation analysis is gas chromatography with a variety of detection methods such as electron-capture, atomic absorption spectroscopy, atomic emission spectroscopy, atomic fluorescence spectroscopy, mass spectrometry, and ICP-MS. However, GC can only be used for the analysis of relatively thermostable compounds, and some mercury compounds are non-volatile at the temperature of use. Using SFC for the analysis of organomercurials overcomes this problem.

With SFC, diorganomercurials can be analyzed without prior derivatization treatment, but monorganomercurials and inorganic mercury must be converted into compounds of lower polarity or require the use of modifiers in the carbon dioxide phase. The latter use of modifiers in the mobile phase with capillary columns can cause a considerable reduction in the capacity factors. Therefore derivatization *via* a complexation reaction is a better option prior to the analysis of monorganomercurials and inorganic mercury. This complexation reaction can be done using a simple two-phase reaction with diethyldithiocarbamate.

The derivatized organomercurials together with the diphenyl mercury chloride were injected using time-split injection into the SFC system with FID detection. The conditions found for the separation were 100°C with a pressure ramp of 10 atm/min. The initial pressure was 100 atm with a hold time of 1 min. The final pressure was 360 atm. The resolution of the 3 peaks was satisfactory. The main problem we encountered with the FID detector was the memory effect of the column. This might have been due to overloading of the column since the FID detector is not as sensitive as ICP-MS. The other problem found was the noise produced by the detector due to the use of chlorinated solvents, which degraded the stainless steel parts of the detector. The use of ICP-MS as a detector eliminated all these problems.

Key words: supercritical fluid chromatography, mercury compounds



FROM SAMPLE PREPARATION TO DETECTION FOR ELEMENTAL SPECIATION STUDIES

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Successful elemental speciation studies are dependent on several steps. Proper sample preparation is crucial to assure that the detected and determined species represent those of the original sample. Chromatographic separation is usually required to separate complex samples into their elemental species at appropriate resolution. Finally, the detection scheme must be sensitive to low levels for certain sample types and preferably be able to provide qualitative information as well.

Recent studies in these laboratories have been focusing on these various aspects of elemental speciation studies. Solid Phase Microextraction (SPME) methods provide excellent opportunities for sample preparation and preconcentration. New approaches with ion-pairing reagents to access a wider range of species' polarities will be discussed. Microwave extraction studies with arsenic in fish hold high potential for retaining species integrity while preserving low levels of detection. Capillary chromatographic methods offer high potential for high resolution -- high-peak capacity methods. Recent studies with capillary electrophoresis and supercritical fluid chromatography illustrate the potential of these low-volume, low-flow techniques. In addition, these separation methods provide optimal means for sample introduction to low-power plasmas. These have the advantage of providing low-level detection plus qualitative information. The rf glow discharge and the reduced-pressure TCP are two such sources.

Key words: speciation, sample preparation, plasma spectrometry, chromatography, trace metals



SPECIATION ANALYSIS OF TRACE ARSENIC AND SELENIUM BY HYDRIDE-GENERATION SAMPLE INTRODUCTION COMBINED WITH LASER-INDUCED FLUORESCENCE AND LASER-ENHANCED IONIZATION DETECTION

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Arsenic (As) and selenium (Se) are important environmental pollutants whose environmental cycling and toxicity are strongly determined by their chemical forms. Both elements are generally more mobile and more hazardous to living organisms when present as oxidized species. For this reason, environmental measurements of As and Se should include comprehensive descriptions of concentrations and speciation information. Hydride generation (HG) is a sample introduction technique that is used to volatilize metalloid elements as vapor-phase hydrides from solution-phase samples and results in considerable improvements in sensitivity. As these procedures are selective for specific oxidation states, they can also be used to determine the speciation of the element in the sample material. Hydride generation techniques developed for the speciation of As and Se are being performed in various atomizers where detection is accomplished by laser-induced fluorescence (LIF) spectrometry. Research emphasis is on developing approaches that can be used to perform measurements of low concentrations of these elements (parts per billion and less) in small amounts of sample materials and also to determine speciation. Limits of detection are currently on the order of 200 picogram (absolute mass) for each element. Current applications of these techniques are to the characterization of As and Se distributions in soils and poplar trees in order to understand the changes in speciation that are associated with phytoremediation

activities. The development of atmospheric sampling techniques combined with HG sample introduction and LIF detection is also being pursued for the measurement of As and Se in particulate matter to evaluate the concentrations and sources of these elements at hazardous waste sites.

Key words: arsenic, selenium, phytoremediation, speciation, hydride generation



ULTRATRACE ANALYSIS OF ARSENIC AND SELENIUM BY LASER-INDUCED FLUORESCENCE SPECTROMETRY TECHNIQUES

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Arsenic (As) and selenium (Se) are two metalloid elements that have high biological activity and are of considerable environmental concern. Both elements are commonly found at elevated concentrations at hazardous waste sites. However, at elevated levels, measurements of these elements are often difficult due to low sensitivity, limited range of response and high susceptibility to interferences. Laser-induced fluorescence (LIF) spectrometry is an analytical method that combines extremely high sensitivity and a large linear range of response with high selectivity. For this reason, it provides exceptionally good analytical performance for trace and ultratrace measurements of elemental analyses. Ultrasensitive LIF spectrometry techniques have been developed for the measurement of As and Se at the parts per billion (ppb) and sub-ppb levels. The highest sensitivity has been achieved using LIF detection combined with electrothermal atomization. In the ETA-LIF approach, atomization is accomplished in a graphite furnace. Near 100 % atomization efficiency is achieved in the furnace atomizer, which facilitates the mea-

surement of small (mg mass) samples. Current limits of detection are on the order 0.02 ppb for both As and Se in 10-microliter volume samples. Studies are also underway to develop alternative atomization systems to facilitate the transition of the ETA-LIF technique to a field transportable system. ETA-LIF techniques are being applied to the determination of As and Se in a variety of sample materials in order to study their occurrence and distribution of these elements in normal and polluted environmental systems. Particular emphasis is being placed on the study of soil As at hazardous waste sites and the impact of phytoremediation by poplar trees on the soil distributions and biogeochemical cycling of this element.

Key words: arsenic, selenium, phytoremediation, ultratrace analysis



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This study was conducted by the Missouri Department of Natural Resources through a grant provided by the US Environmental Protection Agency to develop fluorometric methods to distinguish different types of leachates and leachate-impacted waters from unaffected waters.

The premise upon which this study is based is that some fluorescent by-products of the degradation of waste may be useful in detecting leachate in the environment. Most leachates exhibit strong fluorescence in the range of 250 to 450 nanometers (nm). Leachates such as landfill leachate, hazardous waste, petroleum, domestic sewage, animal waste, and other leachate produced from

decaying sawdust may display similar fluorescent characteristics with regards to their organic contaminants. The focus of this study was to determine the effectiveness of specific techniques in identifying fluorescent indicators of different leachates in raw (untreated) surface water and groundwater. The intent was to determine if a fluorescence signature could be developed to identify these different types of contaminants using an inexpensive technique.

Two fluorescence spectrophotometer methods were developed. One method involved synchronously scanning the excitation and emission spectra of raw water samples. The second method involved three-dimensional contouring of the fluorescence of raw water samples.

Samples were collected in conjunction with split samples for analysis by conventional wet chemistry techniques. The intent was to compare the fluorescent signature classification with more standardized methods in order to determine the effectiveness of the fluorescence methods.

Initial results indicate that samples can be distinguished from background water in dilutions of up to 100 to 1 where other organic sources are not present. Fluorescence signatures for different leachates were identified.

Key words: fluorescence, fingerprinting, signature, inexpensive, diverse

Posters

Jefferson D,E,F



ENHANCED ANAEROBIC DEGRADATION OF TETRACHLOROETHENE AND 1,1,1-TRICHLOROETHANE USING A LACTATE-ENRICHED METHANOGENIC CULTURE IN THE PRESENCE OF ZERO-VALENT IRON

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Recent research into anaerobic biotic degradation of chlorinated organic chemicals has emphasized the importance of hydrogen as an electron donor to the success of achieving desired end products. Previous investigation has determined that zero-valent iron may be utilized to reduce water to hydrogen to provide an electron donor for the dechlorination of both tetrachloroethene (PCE) and 1,1,1-trichloroethane (TCA). The current investigations focused on batch studies of both an unacclimated lactate enrichment culture and a second culture acclimated to PCE at concentrations of approximately 50 mM.

The PCE-acclimated lactate enrichment culture showed an enhanced ability to degrade PCE in the presence of iron filings, as compared to the culture alone or the iron alone in nutrient media. While results of the acclimated culture without iron showed the fastest rate of PCE disappearance, the overall dechlorination was less complete as 1,2-cis-DCE and vinyl chloride are the significant end products. Under both iron conditions, a significant portion of PCE transformed in the system may be accounted as ethene and ethane. Subsequently, zero-valent iron appears to be significant in the dechlorination of PCE under the conditions studied.

Batch studies will also be conducted to analyze the role of zero-valent iron in TCA

dechlorination in conjunction with the unacclimated lactate enrichment culture. Initial experiments indicate a similar enhancement of the observed end products as with the acclimated culture.

Key words: anaerobic, bioremediation, iron, tetrachloroethene, 1,1,1-trichloroethane



MICROBIAL-Fe(0) INTERACTIONS DURING TREATMENT OF GROUNDWATER CONTAMINANT MIXTURES

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Fe(0) barriers promote favorable conditions for treating mixtures of redox-sensitive pollutants (e.g., carbon tetrachloride, Cr(VI), and NO_3^-). In addition to contaminant reduction by Fe(0), such *in situ* barriers can induce anaerobic biodegradation through the depletion of O_2 and the production of water-derived H_2 during Fe(0) corrosion. This work investigated how the nature of the contaminant mixture affects specific contaminant degradation rates in bioaugmented and sterile Fe(0) systems. We also studied the effect of bacterial colonization of the Fe(0) surface on abiotic removal rates, and the effect of the Fe(0) surface area concentration on bacterial activity.

Contaminant interactions were studied in 120-ml unseeded reactors containing 60 ml of buffered medium, a 60-ml headspace of N_2/CO_2 (80:20, v:v), 10 g of Fe(0) (Master Builders® medium/coarse), and various combinations of carbon tetrachloride, Cr(VI), and NO_3^- . Degradation rates for each compound (dependent variables) were analyzed as a function of the presence or absence of other contaminants (independent variables) by Analysis of Variance. Contaminant interactions, such as competition for reactive Fe(0) sites, were not statistically significant in abiotic experiments. This suggests that Fe(0) was not limiting at the tested surface area concentration (ca. $4 \times 10^5 \text{ m}^2/\text{m}^3$).

Similar batch reactors were used to study how microbial colonization of the Fe(0) surface affects abiotic removal rates. Cr(VI) was used as a model pollutant to determine if bacterial attachment to the Fe(0) surface hinders direct contaminant reduction by Fe(0). Treated microcosms were previously seeded with the hydrogenotrophic denitrifier *Paracoccus denitrificans*, which grew in the presence of H₂ and NO₃⁻. *P. denitrificans* cannot transform Cr(VI), which permits isolating the effect that bacteria have on Fe(0) reactivity. Microbial colonization of the Fe(0) surface was verified by electron microscopy. Under the tested conditions, Cr(VI) removal rates were statistically undistinguishable in seeded versus unseeded reactors. Apparently, any detrimental effect associated with bacteria-blocking Fe(0) reactive sites was offset by bacterial-enhanced corrosion of Fe(0), which would enhance the flow of electrons (i.e., cathodic depolarization).

The effect of Fe(0) dose on microbial activity were also studied in 120-ml reactors, containing 60 ml of mineral medium, 60 ml N₂/CO₂ headspace, and various amounts of Fe(0) (i.e., 0, 1, 1, 5, 10, 50, 100, or 500 g). This experiment was conducted with a mixed culture of hydrogen-consuming sulfate reducers. Fe(0) does not react with sulfate. Yet, its corrosion by water produces hydrogen, which stimulates microbial sulfate reduction. Thus, this model system isolates the effect of Fe(0) surface area concentration on microbial activity. Increasing the Fe(0) dose initially stimulated sulfate reduction, possibly due to a higher production of H₂. Nevertheless, very high Fe(0) doses had an inhibitory effect due to a corrosion-induced increase in pH beyond the tolerance range of the bacteria. This suggests that an optimum Fe(0) area concentration exists for combined microbial-Fe(0) treatment systems. This optimum, however, is probably system specific and depends mainly on the buffering capacity of system.

Key words: Fe barriers, anaerobic biodegradation, microbial reaction



SIGNIFICANCE OF GREEN RUST MINERALS IN ABIOTIC REDOX TRANSFORMATIONS

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Historically redox cycling of trace elements in the environment has been considered primarily the result of biotic transformation pathways. The significance and potential for abiotic transformation pathways in natural systems, specifically reduction by green rust (GR) minerals, is still unclear [1]. Green rust minerals are mixed-valent iron hydroxide minerals consisting of layers of positively charged hydroxide sheets with interlayers containing anions such as chloride, sulfate, and carbonate. GR minerals have recently been identified in hydromorphic soils lending support to its existence and role in redox transformations in natural systems [2,3]. The reduction process changes both the transport characteristics and the properties of the contaminant. Therefore, determination of the governing process, biotic or abiotic, is essential for designing efficient remediation technologies and predicting the fate of trace elements in the environment.

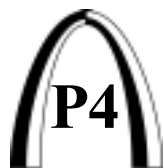
To this end, we are investigating the reduction of nitroaromatic compounds and chlorinated solvents by GR minerals. GR minerals are extremely sensitive to oxidation; hence, they are only stable in anoxic environments such as hydromorphic soils. To avoid exposure to oxygen, the synthesis is accomplished in an anoxic glove box by the precipitation of green rust from iron salt solutions maintained at a slightly basic pH [4]. The purity of the minerals will be confirmed with x-ray diffraction (XRD). Kinetic data on the reduction of contaminants by GR minerals will be collected from batch reactor systems. Both the concentration of the contaminant and Fe(II) content of the green rust mineral will be

monitored with respect to time to evaluate the rate of contaminant reduction and rate of mineral transformation. The resulting kinetic data provides a framework for assessing the significance of abiotic transformations by GR minerals in both natural and engineered systems.

References

1. Oremland R.S., Lovley D., Myneni S.C.B., Tokunaga T.K., Brown G.E. (1998) "Green Rust" in the Lab and in the Soil. *Science*. 281, 1111a.
2. Abdelmoula M., Troland F., Bourrie G., Genin M.R. (1998) Evidence for the Fe(II)-Fe(III) Green Rust "Fougerite" mineral occurrence in hydromorphic soil and its transformation with depth. *Hyperfine Interactions*. 32, 233-238.
3. Trolard F., Genin M.R., Abdelmoula M., Bourrie G., Humbert B., Herbillon A. (1997) Identification of green rust mineral in a reductomorphic soil by Mossbauer and Raman spectroscopies. *Geochimica*. 61, 1107-1111.
4. Taylor R.M. (1985) A Rapid Method for the Formation of Fe(II)Fe(III) hydroxycarbonate. *Clay Miner*. 20, 147-151.

Key words: green rust, abiotic seduction, reduced iron minerals, catalysis, iron oxides



NITRATE REDUCTION BY IRON METAL: THE RATE-LIMITING STEP

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Nitrate is a priority pollutant because of the associated health risks such as methemoglobinemia. Groundwater resources throughout the United States, particularly in the North Central region, are contaminated with nitrate (Nolan, et al., 1997). Many of the existing technologies for the removal of nitrate are marginally cost effective or may result in more concentrated waste streams that present a disposal problem. Recently, reduction by iron

metal is showing great promise as a viable remediation technology for groundwater contaminated with nitrate.

It is important to understand the rate-limiting step controlling the reduction of nitrate by iron metal. We are using an iron rotating disk electrode (RDE) to determine whether the reduction of nitrate at the iron surface is limited by mass transport to the surface or chemical reaction (Scherer, et al., 1997). Based on the slow rates of nitrate reduction observed in batch experiments (Till, et al., 1998), we expect to observe little, if any, mass transport limitations.

Additional experiments are being conducted to evaluate the effect of temperature on the reduction of nitrate by iron metal. A series of batch reactor experiments will be run over a temperature range of 8 to 33°C. The batch experiments will be performed in triplicate for abiotic reactors and biotic reactors seeded with a pure culture of *Paracoccus denitrificans*. The kinetics of nitrate reduction, the formation of intermediates, and the resulting end products will be monitored with ion chromatography. The results will provide a better understanding of the effects of a cooler environment, such as the groundwater environment. In addition, the results will be evaluated with the Arrhenius equation to determine the activation energy of the iron-nitrate reaction. A low activation energy will indicate that the reduction rate is diffusion, or mass-transport controlled. A high activation energy, on the other hand, will indicate that the reduction rate is limited by chemical reaction.

References

- Nolan, B.T., B.C. Ruddy, K.J. Hitt and D.R. Helsel. 1997. Risk of Nitrate in Groundwaters of the United States—A National Perspective. *Environmental Science and Technology*, 31, 2229-2236.
- Scherer, M.M., J.C. Westall, M. Ziomek-Moroz, and P.G. Tratnyck. 1997. Kinetics of Carbon Tetrachloride Reduction at an Oxide-Free Iron Electrode. *Environmental Science and Technology*, 31, 2385-2391.

Till, B.A., L.J. Weathers, and P.J.J. Alvarez. 1998. Fe(0)-Supported Autotrophic Denitrification Environmental Science and Technology, 32, 634-639.

Key words: zero-valent iron, RDE, mass transfer



EFFECT OF SURFACE OXIDES ON THE LONGEV- ITY OF IRON PERMEABLE REACTIVE BARRIERS

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The use of zero-valent iron as a reductant in permeable reactive barriers (PRBs) is a promising technology for remediating contaminated groundwater. The process of contaminant degradation is analogous to a corrosion reaction where electron transfer occurs from the iron metal surface to the dissolved contaminant. Oxidative dissolution of the iron metal results in the formation of an oxide layer on the metal surface. The oxide layer may act as a physical barrier to electron transfer (similar to the role of an oxide film on a passivated electrode) and inhibit electron transfer from the iron metal to the contaminant (1). However, despite the likelihood of a passivating oxide layer forming in iron PRBs, little loss of efficiency has been observed in field-scale implementations of iron PRBs (see, for example, ref. 2).

Several hypotheses that may explain the observed longevity of iron PRBs include: (i) localized corrosion, such as pitting or crevice corrosion, which provides direct access to the underlying iron; (ii) semi-conductor properties of the oxide which allow electrons to transport through the oxide layer via the oxide conduction band, impurity bands or localized states; or (iii) formation of a highly reactive surface oxide (1). For example, the rate of reduction of carbon tetrachloride by a reduced iron oxide

(green rust) has been shown to be similar to that observed in iron PRBs (1,3). To examine the role of oxide formation in PRBs, we are conducting batch and column experiments of chromate and chlorinated solvent reduction by iron metal. Contaminant disappearance rates will be measured as a function of time and length of experiment to evaluate long-term performance under a variety of conditions. The results will improve our understanding of the mechanisms of contaminant degradation as iron walls age. In addition, the results may explain discrepancies observed between laboratory and field rates for contaminant degradation by iron PRBs (2, 4).

References

- (1) Scherer, M. M.; B.A. Balko; and P.G. Tratnyek, The role of oxides in reduction reactions at the metal-water interface, in Kinetics and Mechanisms of Reactions at the Mineral-Water Interface, D. Sparks and T. Grundl, Editors. In Press, ACS Symposium Series No. 715, American Chemical Society; Washington, DC.
- (2) O'Hannesin, S.F.; Gillharn, R.W. Groundwater, 1998, 36, 164-170.
- (3) Erbs, M.; Hansen, M.C.B.; Olsen, C. E. Environ. Sci. Technol. 1999, 33, 307-311
- (4) Johnson, J.L.; Scherer, M.M.; Tratnyek, P. G. Environ. Sci. Technol. 1996, 30, 2634-2640.

Key words: iron metal, green rust, corrosion



BIOAUGMENTATION OF ZERO-VALENT IRON FOR THE ENHANCED TREAT- MENT OF CHLORINATED ALIPHATIC COMPOUNDS

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Carbon tetrachloride (CT), tetrachloro-
ethene (PCE) and 1,1,1-trichloroethane (1,1,1-
TCA) are known to degrade under
methanogenic conditions through reductive
dechlorination. It is also known that these
chlorinated aliphatics will be reductively dechlori-
nated by zero-valent iron under anaerobic
conditions. Hydrogenotrophic methanogens
have been demonstrated to grow from the
cathodic depolarization of zero-valent iron. It
has been hypothesized that the conjunctive use
of a methanogenic consortia supported on an
iron media (bioaugmenting the iron) will in-
crease the extent and rate of dechlorination of
the chlorinated hydrocarbons over systems
using iron alone. This hypothesis was tested in
continuous-flow column reactors with common
steel wool as a support media for an acetate or
lactate enrichment culture. Data for the acetate
enrichment indicate that the iron-methanogen
combination results in enhanced removal of CT
and perhaps of 1,1,1-TCA. Results with PCE
are not as promising. Experiments with the
lactate enrichment culture demonstrate an
enhanced removal of PCE and 1,1,1 - TCA with
the iron-methanogen combination. Additional
studies with mixtures of CT, PCE, and 1,1,1
-TCA indicated the potential advantages of
bioaugmenting zero-valent iron. In mixtures, the
rate and extent of dechlorination was generally
enhanced in seeded columns. This research
should be helpful in developing remediation
strategies for sites contaminated with chlori-
nated aliphatic compounds.

*Key words: anaerobic, bioremediation, iron,
chlorinated hydrocarbons*



ZERO-VALENT IRON ADSORPTION KINETICS AND DECHLORINATION OF POLYCHLORINATED BYPHENYLS

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Iron, in its varying forms, is widely
studied and has been proven effective in the
degradation of contaminants in groundwater,
industrial process waters, landfill leachate, soil,
sediment, and slurries. Iron is convenient to
work with because it is inexpensive, abundant,
non-toxic, and easily handled. Iron is also
versatile in its ability to participate in both
reductive and oxidative reactions.

The Environmental Research Center
(ERC) is studying iron and its relationship with
polychlorinated biphenyls. Electrochemical
peroxidation (ECP), an enhancement of
Fenton's Reagent, utilizes sacrificial steel
electrodes and low-amperage current to supply
soluble ferrous iron, and with the addition of
hydrogen peroxide, this process has been
proven to degrade contaminants by producing
hydroxyl radicals, which are voracious oxidiz-
ers. Research into the adsorption kinetics of
polychlorinated biphenyls onto the steel elec-
trodes during the ECP process lead to adsorp-
tion studies involving zero-valent iron filings
as well as electrodes.

Adsorption of PCBs on iron electrodes
was determined by conducting ECP experi-
ments with the electrodes submersed in an
aqueous PCB solution of Aroclor 1248 for a
period of five minutes. PCB concentrations in
the aqueous phase were measured following
the five-minute treatment and the electrodes
were individually extracted to determine the
concentration of PCBs that were adsorbed.
After 5 minutes, ~10% of the PCBs in the
aqueous solution were adsorbed on the steel
electrodes.

Much greater adsorption was found when
zero-valent iron filings were added to the
aqueous PCB solution. Experiments were

conducted using 1%, 5%, and 10% iron filings in 120 mL of the aqueous PCB solution and aqueous subsamples were taken from each at 0.25, 1, 4, and 24 hours. The iron filings were extracted after 48 hours. Within 15 minutes, approximately 70% of the PCBs were adsorbed to the iron, and by 48 hours, virtually all of the PCBs were adsorbed to the 5% and 10% iron.

Biphenyl was identified in the extracts of the iron filings after 48 hours of submersion at all three concentrations, 1%, 5% and 10% iron, and its concentration increased linearly with iron %. Biphenyl production is interpreted as a product of PCB dechlorination, which occurred during adsorption to zero-valent iron.

Key words: iron, polychlorinated biphenyls, adsorption, dechlorination, biphenyl



NITROGEN TRANSFORMATIONS IN WASTES FROM ANIMAL PRODUCTION OPERATIONS

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Nitrogen is an important element in animal waste management because high concentrations of nitrate are often a problem in groundwater. The fate of nitrogen in feedlots and lagoons which contain the wastes is of concern during active operation and when the facility is closed temporarily or permanently. One approach receiving attention is the transformation of the nitrogen in the waste to nitrogen gas. Another is to make use of vegetation as a sink for nitrogen, incorporating the nitrogen into plant biomass. Mass balances can be used to consider the merits of potential approaches and research strategies. Recently,

processes have been identified which indicate that ammonia and nitrate can be combined to form nitrogen gas under anaerobic conditions where nitrate is the electron acceptor. Denitrification of nitrate to form nitrogen gas is also an anaerobic process. However, nitrate is formed from animal wastes under aerobic conditions. Thus, management of dissolved oxygen in lagoons and in closure operations is important. The results of a review of the literature and an analysis of several management alternatives will be presented.

Key words: mass balance, nitrogen, transformation, lagoons, animal waste



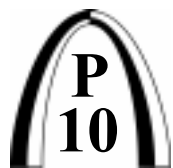
EFFECT OF BACTERIAL EXTRACELLULAR POLYMERS ON PAH DESORPTION AND MINERALIZATION IN SOIL

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The sorption and hydrophobicity of polycyclic aromatic hydrocarbons (PAH) limit their availability to microorganisms, and contribute to the difficulty encountered in bioremediation of PAH-contaminated soil. Prior research has shown that bacterial extracellular polymers bind PAH and act to enhance PAH mobility in soil systems. In this research, the extracellular polymer produced by a bacterium isolated from soil was employed in laboratory studies with a model PAH, phenanthrene. The experimental results show that the selected polymer enhances the water solubility,

dissolution, and mineralization rate of phenanthrene. A mathematical model was developed to describe the effect of the extracellular polymer on phenanthrene dissolution and biodegradation. Using independently determined parameters, the model gives a satisfactory prediction of phenanthrene mineralization at polymer concentrations of 50 and 100 mg TOC/L. In soil systems, experimental results show that the polymer both increases the rate of desorption, and enhances the rate of mineralization of soil-bound phenanthrene. A model is proposed for describing desorption and biodegradation of soil-bound phenanthrene in the presence of extracellular polymer. This model employs a statistical gamma distribution to describe the heterogeneity in PAH mass transfer rates from soil to water, and assumes instantaneous binding of phenanthrene to polymer and of polymer to the test soil, while microbial growth is described by Monod kinetics.

Key words: PAH, extracellular polymers, desorption, biodegradation



IN SITU BIOREMEDIATION OF PCB BY COMBINATION OF THE ALFALFA PLANT AND SELECTIVE MICROORGANISMS

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We have studied 2',3,4 PCB degradation capability of selective microorganisms, alone or in combination with alfalfa plants. Two genetically engineered bacteria, *Commanonas sp.* and *Rhodococcus sp.*, *Sinorhizobium melilon* and *P. chrysosporium* were our test microorganisms. The contaminated soil samples were from Woodspond. Ten treatments were set up in duplicate: treatment #1, our control was sterile soil spiked with 100 ppm of 2',3,4 PCB (pure congener); #2 and #3

were, respectively, *Commanonas sp.* plus Woodspond soil and *Rhodococcus sp.* plus Woodspond soil; #4 and #5 were, respectively, *Rhodococcus sp.* plus alfalfa plant plus *S. meliloti* and Woodspond soil and *Commanonas sp.* plus Woodspond soil plus alfalfa plus *S. melilon*; #6 was Woodspond only without any microorganisms, #7 and #8 were, respectively, sterile PCB-free soil spiked with 100 ppm of 2',3,4 PCB plus *Commanonas sp.* and sterile PCB-free soil spiked with 100 ppm of 2',3,4 PCB plus *Rhodococcus sp.*; #9 and #10 were, respectively, sterile PCB-free soil spiked with 100 ppm of 2',3,4 PCB plus fungal spores and sterile PCB-free soil spiked with 100 ppm of 2',3,4 PCB plus fungal spores plus *S. meliloti* plus alfalfa. Complete PCB (100 ppm) depletion, measured by GC-MS, was observed with all microorganisms alone, after three weeks incubation period. The PCB depletion was proportional to the growth measured by CFUs count for *Commanonas sp.*, *Rhodococcus sp.* and *S. meliloti* and the mycelial extension for *P. chrysosporium*, indicating a possible use of the pollutant by these microorganisms as a source of carbon and energy. Moreover, we noticed extensive PCB depletion (approx. 100%, within a week) from the contaminated soil when *Commanonas sp.* and *Rhodococcus sp.* were combined with alfalfa plants. *S. melilon* and alfalfa depleted the pollutant to a lesser extent 70-80% within the same period. Whereas alfalfa did not appear to have any positive effect on *P. chrysosporium*'s PCB-depletion capabilities. Our study showed that concomitant use of microorganisms and plant could result in a tremendous quantitative improvement of *in situ* PCB cleanup from contaminated soil/sediment in a time-saving manner. (Supported by NIGMS-N1H and U.S. Army to SKD).

Key words: PCB, alfalfa, bioremediation, commanonas sp., Rhodococcus sp.



EFFECT OF PLANT ROOT EXUDATES ON SOIL MICROBIAL COMMUNITIES

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Phytoremediation is a low-cost option for the clean up of contaminated soils. Although numerous studies have demonstrated increased degradation of hazardous organic compounds in the soil surrounding plant roots (the rhizosphere), little is known about the mechanism by which this occurs. In this study, the role of root exudates in this phenomenon was explored; specifically, the influence exudates have on soil microorganisms.

Corn (*Zea mays* L.) was grown in soil and in an aseptic, hydroponic culture. Rhizosphere and bulk soils were analyzed for microbial numbers and for mineralization of 2,4-Dichlorophenoxyacetic acid (2,4-D). Sterile root exudates were collected from the hydroponic corn and applied to microbial cultures (originally isolated from non-rhizosphere soil). Changes over time in the microbial community were determined by direct and plate counts, by microbial lipid analysis of biomass and activity, by BiologTM GN analysis, and by their ability to mineralize radiolabeled 2,4-D.

Results from the soil-grown corn study indicate an increased number of microorganisms in the rhizosphere (compared to bulk) and, more significantly, higher rates and extents of 2,4-D mineralization. This same effect was produced by the addition of root exudates to the microbial cultures. Increases were observed in both microbial numbers and mineralization rates, although there was a lag time before changes occurred. In addition, Biolog shifts did not immediately follow exudate amendment of microbial cultures. This suggests an actual change in the community structure under exudate pressures and perhaps

reflects the selection for a degrading community.

Current studies are pursuing the component of the exudate responsible for changes in community structure and increased degradation. Exudates are being fractionated, chemically characterized (by HPLC, CHN, and GC/MS), and applied to microbial cultures and actual soils.

Key words: corn (Zea mays), root exudates



DESIGN OF A GRAPHICAL USER-INTERFACE DECISION SUPPORT SYSTEM FOR A VEGETATED-TREATMENT SYSTEM

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The use of vegetation in remediating contaminated soils and sediments has been researched for a number of years. Positive laboratory results have lead to the use of vegetation at field sites. The design process involved with field sites and the associated decision processes is being developed. As part of this development, a computer-based, graphical user interface (GUI) decision support system (DSS) was designed to be used by practicing environmental professionals. The steps involved in designing the GUI, incorporation of the contaminant degradation model,

and development of the DSS will be presented, along with a demonstration of the developed product.

Key words: decision support system, graphical user interface, phytoremediation, field site



EFFECT OF BENZOTRIAZOLES ON SUNFLOWERS

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Benzotriazole and methybenzotriazole are primarily used as rust inhibitors in antifreeze and airplane de-icersolutions. They comprise approximately 1% of antifreeze and up to 10% of de-icers. Hydroxybenzotriazole has been proposed for use in large quantities in the paper pulp industry. It has been shown that benzotriazole and methybenzotriazole are toxic to most plants even at concentrations below 0.1 mg/mL. On the other hand, white-rot fungus was found to significantly degrade all three benzotriazoles at concentrations up to 1 mg/mL. This is presumably due to lignin peroxidase. Some plants are known to produce large amounts of peroxidase. Therefore, an experiment was established to add 100 mL of 0.05 mg/mL of each benzotriazole compound every day to sunflower plants growing in vermiculite. The plants were able to tolerate this level. The contaminant concentration in the runoff from the vermiculite was approximately 0.05 mg/mL. This suggests that the contaminants move freely through the sunflowers. No contaminant could be found in the sunflower leaves after extraction. This suggests that sunflowers are able to degrade the benzotriazoles. A steady dosage of 0.1 mg/mL was found to kill the benzotriazole- and methybenzotriazole-treated sunflowers after approximately one week. The hydro-

xybenzotriazole-treated sunflowers were able to survive the 0.1 mg/mL concentration.

Key words: benzotriazoles, toxicity, sunflowers, white-rot fungus



TRANSPORT OF TRICHLOROETHYLENE THROUGH WOODY TISSUES

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The uptake and distribution of trichloroethylene (TCE) was examined in intact poplar and willow plants grown hydroponically. Following a two-day exposure during which plants used ~200-400 mL of water contaminated with about 10 mM TCE, samples of the stem tissue were analyzed for accumulated TCE. A distinct concentration gradient of TCE was observed with relatively low levels accumulated in the uppermost parts of the plant. Portions of the stem close to the source contained TCE levels several-fold higher than that of the input water. A sorption coefficient of ~30 and a reasonable rate of radial diffusion during axial transport could explain the TCE distribution. A direct estimate of the transverse diffusion coefficient and the importance of the bark of the stem was obtained by soaking intact or peeled stem sections for four days in a TCE-contaminated solution, followed by monitoring the out-diffusion from the tissue until equilibrium was attained. Half-times for out-diffusion were in the range of 1-2 hours for peeled stems of 6-7 mm diameter but were 5-8 hours for intact stems of comparable size. This result indicates that the bark provides a significant resistance to out-diffusion of TCE. Some modeling results will be presented.

Key words: trichloroethylene, diffusion, sorption, poplar trees



THE INFLUENCE OF SOLUTION MATRIX ON THE PHOTOCATALYTIC DEGRADATION OF 2-CHLOROBIPHENYL IN TiO_2 SLURRIES

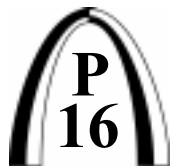
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The effects of solution matrices, i.e., pH, inorganic ions, and humic acids, on the TiO_2 photocatalytic degradation of 2-chlorobiphenyl (2-CB) were investigated. A lower-solution pH was found to be favorable for the degradation in the pH range of 3 to 11. Chloride ions showed no rate effect at pH 4 but significant rate-inhibition effects were observed at pH 7 and 10. The inhibition by chloride ions at pH 10 was more than that at pH 7. Carbonate/bicarbonate showed an inhibition effect on the degradation at pH 10 and pH 11. Magnesium ions inhibited the degradation under alkaline conditions but showed no rate effect at pH 4. Humic acids were found to inhibit 2-CB degradation. The inhibition effect was leveled off at the concentration of 5 mg/mL.

Key words: photocatalytic degradation, Titanium dioxide (TiO_2), 2-Chlorobiphenyl (2-CB)



REVEGETATION OF HEAVY METAL-CONTAMINATED MINE TAILINGS (CHAT)

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Mined areas near the city of Galena, Kansas, are a continuing source of Pb, Zn, and Cd contamination that move off-site in response to erosion by wind and running water. Revegetation of the mine tailings (*chat*) could limit the spread of these heavy metals. In this study, six treatments with four replications were imposed on 24 test plots in order to evaluate their effectiveness in the growth of fescue grass and containment of the heavy metals. Treatments included ¹an unmanured and unseeded control; ²a manured, unseeded control; ³a manured, seeded control; ⁴two manured, seeded treatments inoculated with *mycorrhiza* fungi; and ⁵a manured and seeded treatment with periodic application of benomyl fungicide. Fescue grass has been established in all seeded plots; by end of the third growing season (October 1998), the vegetative cover for all seeded treatments averaged 28.5%, with the benomyl fungicide treatment being significantly higher than the second *mycorrhiza* fungi treatment (36% and 21.5%, respectively). There were no significant differences between treatments for basal cover (which averaged 10.4%). The presence of vegetation has not significantly affected heavy metal distribution in the exchangeable, carbonate, Fe- and Mn-oxide, organic, and residual fractions of the chat, but the presence of manure has significantly concentrated Pb in the organic fraction

at the expense of the exchangeable and carbonate fractions. In addition, the addition of manure has significantly concentrated zinc in the organic fraction at the expense of the exchangeable and residual fractions, and has significantly concentrated cadmium in the organic fraction at the expense of the exchangeable fraction.

Key words: chat, heavy metals, revegetation, organic fraction



INVESTIGATION OF METAL-ION BINDING BY AGRICULTURAL BY-PRODUCTS

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The objective of this study was to optimize the conditions for metal adsorption by oat (*monida*) and wheat (*delicias*) biomass in order to determine their potential use for the adsorption of toxic metal ions from waste waters. The optimal metal binding pH and binding times were determined for Cu(II), Pb(II), Cr(III), and Cr(VI). Separate binding capacity experiments were performed with the native biomass which resulted in the binding of 5.1 mg Cu(II)/g; 19.0 mg Pb(II)/g; 2.5 mg Cr(III)/g; 4.3 mg Cr(VI)/g; 2.4 mg Zn (II)/g; 2.9 mg Ni(II)/g; and 4.3 mg Cd (II)/g for oat biomass. Wheat biomass was able to bind 5.0 mg Cu(II)/g; 9.8 mg Pb(II)/g; 0.7 mg Cr (III)/g; 0.9 mg Cr (VI)/g; 1.4 mg Zn (II)/g; 2.2 mg Ni (II)/g; and 5.2 mg Cd (II)/g. In addition, it was found that biomass exposure to NaOH increased the metal binding. Experiments performed to optimize the NaOH modification process revealed a 30-minute biomass exposure to 0.1M NaOH as the optimal conditions. Also, additional chemical modification experiments are being performed to further enhance the binding of both cations and anions. Further information will be presented on the binding mechanisms of metal ions to these agricultural

products. This information could be useful for the remediation of heavy metal ions from wastewater by agricultural by-products.

Key words: oat biomass, wheat biomass, heavy metal binding, chemical modification, binding mechanism



ADSORPTION OF HEAVY METAL IONS BY BIOMASS OF *SOLANUM ELAEGNOFOLIUM* (SILVERY NIGHT-SHADE)

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A screening previously performed for metal concentration in desert plants indicated that *Solanum elaeagnofolium* (Silvery Nightshade) had the potential to be used as a biomaterial for heavy metal recovery. The Cu (II), Pb (II), and Zn (II) binding properties of native and NaOH modified biomass of *Solanum elaeagnofolium* were studied. Batch experiments were conducted with oven-dried and ground stems and leaves of *Solanum elaeagnofolium* to characterize the metal binding properties. These experiments included pH profile, time dependency, and metal binding capacity to the biomass. Results for this work have indicated that optimal metal binding pH occurred at pH 5.0 for Cu (II), Cd (II), Pb (II), and Zn (II) within a 10-15 minute time period. Binding capacity experiments showed that native *Solanum elaeagnofolium* was able to bind the following amounts (ma metal/g biomass): 13.1 mg Cu (II)/g, 19.0 mg Cd (II)/g, 21.7 mg Pb (II)/g, 6.9 mg Zn (II)/g. However, NaOH modified biomass of *Solanum elaeagnofolium* showed an increase in metal binding for most of the metal ions studied. By treatment with HCl, nearly 90 percent or greater of the bound metal ions were recovered. These results indicate that NaOH can be used to chemically modify the biomass of *Solanum elaeagnofolium* to recover copper, lead, and zinc ions from aqueous solution. In

addition, silica immobilized *Solanum elaeagnifolium* was used in columns for flow studies which show that Silvery Nightshade could be used to remediate heavy metal contaminated waters in a cost-efficient manner

Key words: Solanum elaeagnifolium, heavy metal binding, chemical modification



EFFECTS OF POLYCHLORINATED BIPHENYL-CONTAMINATED SEDIMENT ON LARVAL AMPHIBIAN GROWTH AND DEVELOPMENT

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Amphibian decline has been well documented across the Northern USA and Canada. Mortality and deformities among frogs have been attributed to increased exposure to UV-B emissions, pathogens, introduction of exotics, and environmental pollutants. We have evaluated sediment removed from the St. Lawrence River (SLR), where frogs which were once abundant but are no longer found. The sediment was found to contain 600 ppm polychlorinated biphenyls (PCBs). Embryos of the Northern Leopard Frog (*Rena pipiens*) were collected from a single laboratory clutch and exposed to high or low concentrations of sediment from the SLR or a control sediment from Fall Creek (FC) in Ithaca, N.Y., or no sediment at all (C). Dechlorinated municipal water was added to all aquaria and 75% of the water was changed twice weekly, leading to decreasing levels of PCB in the water column and sediment over time. At day 51, SLR-H and SLR-L tadpoles weighed 5 and 3 times that of controls, and also had markedly increased snout-vent lengths.

As a tadpole in SLR-H went through metamorphic climax, forelimb emergence order was reversed and there was a delay in the development of its mouthparts. The remarkable weight gain and advanced metamorphoses seen in SLR tadpoles compared to

controls suggest alterations in the levels of prolactin and thyroxine. The relationship between these hormones and bio-available PCBs is currently under investigation.

Key words: amphibian, metamorphosis, polychlorinated biphenyls, sediment



MANAGING SEDIMENT CONTAINMENT FACILITIES TO PROMOTE PCB SEPARATION AND DEGRADATION

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Due to their relatively lower cost, sediment containment technologies are currently favored over treatment technologies as methods of managing the large amounts of PCB-contaminated sediments removed during dredging. Millions of cubic yards of PCB-contaminated dredged material will be produced as harbors and rivers are dredged for navigational and/or remedial purposes. In New York alone, dredging is on going, planned, or proposed for the St. Lawrence, Grasse, Raquette, and Upper Hudson Rivers and New York Harbor. Recent policy decisions suggest that much of the sediment contaminated by PCBs will be placed in containment facilities. However, since containment does nothing to reduce the PCB concentration in the sediments, it should be considered a temporary remedial measure that will require indefinite monitoring and maintenance. The environmental liability is postponed to the future generations. We contend that by designing, operating, and managing containment facilities to promote organochloride separation and destruction, we can use them as treatment facilities. The physical properties of PCBs in many anaerobic sediments will facilitate this.

Anaerobic microbial degradation of PCBs in sediments has been described from numerous locations and in the laboratory. In general, the removal of meta- and para- positioned chlorines from the PCB molecule by the

anaerobes produces lower or/hydrochlorinated congeners. These congeners are considerably more volatile, soluble, and mobile than the original congener. Because of their enhanced solubility and volatility, lower or/hydrochlorinated congeners dominate the PCB fraction in water, biota, and air near the anaerobically dechlorinated sediments. When water in contact with contaminated sediment evaporates, large quantities of PCBs can be released. These vapor PCBs can travel large distances; it is likely much of the PCB contamination in the Arctic and Antarctic are the result of this volatilization of PCBs from contaminated sites in temperate regions.

PCB-contaminated sediment is hard to treat inexpensively and effectively due to the sorption of the contaminant into the particulates; however, aqueous and vapor phase PCBs are easily destroyed with existing advanced oxidative technologies (AOTs). We suggest the design of a containment facility that can enhance the physical separation processes (solubility, volatility) and treat the resulting aqueous and vapor phase contaminants. A conceptual approach for containment cell management includes three treatment phases: 1) anaerobic, 2) aerobic, and 3) residual. Anaerobic processes would be used to optimize microbial dechlorination and solubilization. Aerobic treatment would combine any biological (aerobic biodegradation) or physical benefits derived from aeration, land-farming, composting, solar heating, or other processes. The residual phase would involve continued *in situ* treatment by chemical (hydrogen peroxide addition) or passive (phytoremediation) means. During each phase, the leachate and volatiles produced would be treated by AOTs and recycled. The ultimate objective would be a residual contaminant fraction with limited mobility and bioavailability.

Key words: PCBs, containment, degradation, dredging, sediment



INITIAL INVESTIGATION OF ANALYTICAL EXTRACTION TECHNIQUES FOR THE DETERMINATION OF BIOAVAILABILITY OF PESTICIDES IN SOIL

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The inadvertent ingestion of contaminated soil can be a major source of pesticide exposure, especially in young children. Analytical techniques explored in the past have been designed to quantitatively determine the total contamination level of environmental solids. The actual level of a pesticide that is available for absorption into the biological system may be much lower than the overall contamination level due to the interaction of each compound with the soil matrix. This bioavailability is dependent on the chemical species involved as well as the soil type. We report a comparison of the recoveries of pesticides from soil and sand using different analytical extraction techniques. The methods to be compared are Soxhlet Extraction, Microwave-Assisted Extraction and Microwave Extraction with Solid-Phase Microextraction. Future comparisons of the results of these analytical extractions with data from physiological tests may lead to the development of a bioavailability determination technique that will avoid the use of animals or complex models of biological systems.

Key words: bioavailability, pesticides, soil, extraction



PEROXIDASE-MEDIATED BINDING OF PHENOLS TO SOILS

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Horseradish peroxidase-catalyzed binding of phenol and o-cresol to two soils was investigated. Soils belonging to the Hayne series (very fine sandy loams) were collected from a field and a forested site near Manhattan, Kansas. The two soils are derived from the same parent material but contain different amounts and types of soil organic matter. Experimental investigations looked at binding of the two target phenols when present in solution alone and when present as a mixture. Results were expressed in terms of quickly desorbable, slowly desorbable, and non-desorbable or bound fractions of the contaminant.

Key words: soil, soil organic matter, phenol binding, sorption



METAL AND ARSENIC BIOAVAILABILITY IN SMALL MAMMALS INHABITING SMELTER- ASSOCIATED TAILINGS AND AERIAL DEPOSITION AREAS FOLLOWING DIFFERENT REMEDIATION TREATMENTS

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Risk-based decision making associated with chemically contaminated waste sites generally emphasizes the reduction or elimination of actual or potential toxic exposures to receptor populations of concern. Wildlife inhabiting contaminated sites can be front-line indicators of chemical exposure and effects due to their intimate association with site-related contaminated media. This association provides a sensitive means of detecting exposure and effects-associated adverse responses. Measures of exposure and adverse responses in wildlife inhabiting contaminated areas can provide a means for testing predictive models of exposure and effects, and determining the effectiveness of proposed remedial actions.

The Anaconda Smelter Superfund site in Deer Lodge County, Montana, encompasses over 100 square miles that have been affected by 100 years of milling and smelting operations. Stack emissions, tailing accumulations, and wind dispersal have resulted in the distribution of metal-contaminated wastes over a wide area. Wastes include approximately 230 million cubic yards of concentrated smelter tailings, 30 million cubic yards of furnace slags, 500,000 cubic yards of flue dust, and many square miles of contaminated soils. Principle contaminants of concern at the site are arsenic, cadmium, copper, lead, and zinc that occur in a variety of forms and a wide range of concentrations. A number of techniques at several scales and locations have been tested to assess remediation and stabilization options for the COCs on the site. The *in situ* treatment option includes tillage, lime/fertilizer amendments, and seeding with selected native grasses and has led to development of grassland habitat with abundant small mammal populations. Similar habitat has been formed following coverage of contaminated areas with clean soils and subsequent planting with native grasses.

The goal of this preliminary study was to evaluate small mammal populations inhabiting some of these sites and collect data on general

abundance, and exposure and accumulation of the principle contaminants of concern. We used Sherman live traps to collect *Peromyscus maniculatus* and *Microtus pennsylvanicus* inhabiting differentially remediated areas at the Anaconda Smelter site. Livers, kidneys, and whole bodies were analyzed for the five principle contaminants of concern. Additional data will be collected on biochemical and physiological endpoints, rodent population demographics, and population and community health. In addition to testing the accuracy of established exposure models, these data will aid in comparing bioavailability of metals to wildlife inhabiting remediated portions of the smelter site and will be incorporated into a baseline data set that can be used in biomonitoring efforts as the site is further remediated.

Keywords: wildlife, smelter, small mammal, metals, remedial options



GEOGRAPHIC DISTRIBUTIONS OF EXPOSURE AND PHYSIOLOGICAL RESPONSES OF RACCOONS TO POLYCHLORINATED BIPHENYLS ON WILDLIFE MANAGEMENT AREAS IN WESTERN KENTUCKY, USA

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Raccoons (*Procyon lotor*) are potentially useful sentinels for environmentally persistent contaminants distributed from point sources through runoff and erosion. We investigated the spatial distribution of raccoon exposure and effects of polychlorinated biphenyl and heavy metals on a wildlife refuge surrounding

an industrial facility and a reference wildlife refuge along the Ohio River in Western Kentucky. Sixty-seven raccoons were captured, twenty-nine necropsied, and twenty-seven fitted with radio-transmitters. Fat biopsy, liver, and brain samples were analyzed for twelve individual PCB congeners. Total PCB residues ranged from 0.116 - 39.543 PPM (wet wt.) in fat biopsy samples, 0.27 - 7.237 PPM (wet wt.) in necropsied fat samples, 0.0 - 0.395 PPM (wet wt.) in liver tissues, and 0.0 - 0.344 PPM (wet wt.) in brain tissues. There was little difference between PCB residue levels in raccoon tissues from either site, but variation was quite high. Backwater from the Ohio River was thought to be a major source of PCBs on the reference area. Females from the potentially contaminated site tended to have higher PCB concentrations than reference females and this was thought to result from denning within the industrial complex in a condemned building known to have elevated PCB concentrations. Liver enzyme induction, porphyrin alterations, differential cell counts, and hormone levels, as well as demonstrations of exposure and effects-distribution mapping, will also be presented.

Key words: raccoon, wildlife, PCB, GIS



A MODEL FOR TRIBAL RISK ASSESSMENT

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Current risk assessment practices use scientific and technical processes to evaluate potential consequences associated with impact to human health and ecosystems. Risk management is the process of evaluating, selecting, and implementing alternative action, based on political, social, economic, and scientific information to reduce risk. To be effective in solving environmental problems on Native

American lands, risk assessment and management practices must integrate tribal cultural and ecological knowledge. Individual tribes must take active roles in redefining concepts of risk and setting limitations on the extent of external agents they will allow to impact their environments. A model for risk management needs to include the following elements: 1) background research that explores oral and written historical sources, cultural and ecological resource applicability, archeology, and scientific records; 2) an examination of the current state of the tribal environment; 3) alternative solutions to environmental contamination which incorporate traditional, cultural, and ecological knowledge; 4) implementation; and 5) continuous monitoring that is in harmony with the tribe's cultural and psychological identity. Examples of tribes engaged in the above activities include the Oglala Lakota Nation, Prairie Band of Potawatomi of Kansas, and the Mekoryuk, Noatak, and Fort Hope Villages of Alaska.

Key words: Native/Alaskan American, cultural risk assessment, minority colleges, minority lands



DESORPTION AND AQUEOUS EXTRACTABILITY OF POLYCYCLIC AROMATIC HYDROCARBON MIXTURES ON SOIL

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There is an urgent need to develop an accurate method to assess the risk associated with contaminated soils and complex mixtures. Perhaps more importantly, this method should provide a means of defining acceptable residue levels to allow a more cost-effective approach

to site remediation. Contaminated media at Superfund sites typically consist of complex mixtures of organic and inorganic chemicals. Especially difficult to characterize are the mixtures of polycyclic aromatic hydrocarbons (PAHs) which are often found at wood preserving, coal gasification, and refinery sites. Mixtures, particularly those derived from petroleum sources, often behave toxicologically and physically in a manner not predicted by the properties of their individual components. This aspect is particularly important in studies of bioavailability.

This focus of this study was to compare the behavior of simple and complex PAH mixtures when applied to silty loam soil and aged for a year. The complex mixture was a wood-preserving waste (WPW) creosote spiked at a level of 5% (wt/wt). The simple mixture was composed of phenanthrene, anthracene, pyrene, and chrysene. These PAHs were added at a level that approximated those found in the WPW soil. Both soils were extracted on days 0, 60, and 180 of aging with eight possible methods. The first was a model stomach solution, the second was a model intestinal fluid, and the third was a model gastric fluid with the stomach and intestinal fluids used in series. The fourth was distilled water, the fifth was phosphate buffered water at pH 7, and the sixth was a 1:1 solution of the phosphate buffered water and methanol. The seventh method measured desorption kinetics in water with Tenax TA beads. Finally, the soils were extracted with 1:1 hexane:acetone in an automated soxhlet device.

The desorption measurements with Tenax beads quantifies the amount of each PAH in refractory (unavailable) and labile (available) states. This presentation will focus primarily on pyrene as a model PAH since its behavior fell between that of the other PAHs examined. On day 0, 84% (95% C.I.: 72% to 97%) of the pyrene in the model mixture was labile while 79% (95% C.I.: 71% to 87%) of the pyrene in the WPW soil was in the labile fraction. Following 60 days of aging, 70% (95% C.I.: 58%

to 83%) of the pyrene from the model chemical soil was labile and 71% (95% C.I.: 68% to 74%) of the pyrene from the WPW soil was labile. After 180 days of aging, the pyrene in the model chemical soil continued to decrease in availability with 69% in the labile fraction (95% C.I.: 50% to 89%). In contrast, the pyrene in the WPW soil became slightly more available than it was on day 60 with 74% in the labile phase (95% C.I.: 63% to 85%). The reason for this change is not known but may be related to alterations in the creosote matrix over this 6-month period. These differences illustrate the importance of employing actual complex mixtures in studies of bioavailability rather than relying on single compounds or simple mixtures alone.

Key words: complex mixtures, bioavailability, PAHs, desorption



AN EXPERIMENTAL APPROACH TO CONVERGENT-FLOW TRACER TESTS IN HETERO- GENEOUS MEDIA

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Careful characterization and use of flow and transport parameters, such as transmissivity, dispersivity, and porosity, is critical for accurate numerical simulation of contaminant migration and subsequent assessment of potential hazards to humans and the accessible environment. In the field, convergent-flow tracer tests can be used to characterize hydraulic parameters in an aquifer. Often, the resulting breakthrough curves are analyzed with the assumption of radial symmetry. With this approach, the computed dispersivity estimates can vary significantly with changes in the

tracer-injection position. In an attempt to explain these variations, some authors have interpreted this so as to imply that porosity is tensorial in nature. Research by Xavier Sanchez-Vila and Jesus Carrera (1997) concludes that the above 'directional porosity' interpretation is an improper characterization of hydraulic conductivity and anisotropy. Further, they proved theoretically that directional effects in porosity and dispersivity show up in a natural way when one considers a heterogeneous transmissivity field with an anisotropic correlation structure. This research experimentally validates their conclusions and facilitates a better understanding of dispersivity in highly anisotropic media. To validate their conclusions, we ran several 2D convergent-flow tracer tests in a horizontal tank. The media consists of four different sands packed in blocked grids such that the overall system is highly anisotropic and heterogeneous. Stochastic simulations are not used to generate the grid in order to avoid a multi-normal transmissivity field. In these experiments, water is pumped from a port centrally located and reaching to the vertical mid-point in the tank while maintaining a constant head on the sides of the tank. When steady state is reached, a conservative tracer (Bromide) slug is injected into one of several ports. Successive readings are taken at the point of outflow until a complete breakthrough curve is obtained. This procedure is repeated at other injection port locations and the effective porosity and longitudinal dispersivity are computed from each breakthrough curve via inversion. With this data, we validate the conclusions of Sanchez-Vila and Carrera and show that porosity is not a directional parameter and that directional flow effects are incorporated in the transmissivity tensor.

Key words: directional, porosity, tracer, dispersivity, anisotropy



EFFECT OF FLOW RATE AND INFLUENT PARTICLE CONCENTRATION ON CLOGGING OF SOIL FILTERS

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The existing soil filter design criteria don't address the clogging of filters due to transport of fine colloid-sized particles in natural and contaminated environments. Traditionally, the design criteria for soil filters are empirically based and are expressed in terms of the ratio of the sizes of the base particles and the filter particles. In this study, an attempt has been made to understand the reduction in hydraulic conductivity of the porous medium due to the flow of colloid-sized particles. Well-characterized, locally available filter sand and processed Ottawa sand were used in this study to represent the porous media. Fine kaolinite particles and polystyrene microspheres, both processed, were mixed in the influent to represent the fine colloids. The influents at a specific concentration were sent through the porous medium up to 1700 pore volumes at different flow rates. It was found that the hydraulic conductivity of the porous medium reduced considerably in all the test cases. No definite trend in the change of hydraulic conductivity was observed as the influent flow rates were increased. The experimental results of hydraulic conductivity reduction and the observed effluent particle size distribution will be presented to highlight the effect of pore-size distribution of the porous media.

Key words: soil filter, clogging, pore fluid, transport, porous media



BIOLOGICAL CLOGGING IN POROUS MEDIA AND THE EFFECTS OF USING IODINATED RESINS

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Clogging of porous media caused by the accumulation of microbial biomass and extracellular polysaccharide (EPS) greatly influences water transport in subsurface environments. An understanding of the relationship between increase in microbial biomass and the reduction in the hydraulic conductivity of the soil is of importance to the simulation of the transport of biological contaminants in soil filter systems.

In this research, soil column experiments were conducted to examine the influence of biomass accumulation on the soil hydraulic conductivity. Experiments were conducted with autoclaved soil columns using an influent of *P.aeruginosa* culture and *in situ* experiments in which the soil columns were packed with *P. aeruginosa* using an influent of rich-nutrient medium. Similar sets of experiments were conducted using a mixture of soil and iodinated resin to evaluate the effect of the resin on their capability to destroy the bacteria. Plate counts of the effluent collected at different intervals during the experiment showed that there were no bacteria, but the permeability of the soil columns decreased, as was also observed in the columns with soil alone. Experiments using dead cells with the iodinated resin alone revealed that the hydraulic conductivity was also decreased using dead cells.

Key words: biological clogging, biomass, iodinated resin



BIOMETHYLATION OF ARSENIC IN CONTAMINATED SOILS AND SOLID WASTES

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Biomethylation of arsenic from soils is a naturally occurring phenomenon wherein indigenous fungi and bacteria methylate inorganic arsenic form volatile, biomethylated forms of arsenic. Utilization of biomethylation as a remediation method for soils and wastes heavily contaminated with arsenic has not been shown. An experiment was conducted on calcine and lead slag waste materials (smelter wastes) high in total arsenic (10,920 and 3,160 mg kg⁻¹, respectively) and lead (8,430 and 12,610 mg kg⁻¹, respectively) concentrations to determine if biomethylation could be promoted as a remediation method to lower soil arsenic levels. Contaminated materials were supplemented with ground soybean meal (60,000 mg kg⁻¹), glutamine (1%), and vermiculite (1:4, by volume); kept moist with distilled water; and then incubated under aerobic and anaerobic conditions. After a 20-week incubation period, the calcine waste demonstrated 5.3 mg of arsenic lost via biomethylation (0.0005% of the total calcine arsenic). An experiment conducted on an uncontaminated soil spiked with a known amount of arsenic was performed to determine if the biomethylation conditions were adequate to promote biomethylation. Biomethylation resulted in 19.8 mg of arsenic volatilized over a 20-week period (0.002% of the total calcine arsenic). Another experiment was conducted to determine if the high lead concentrations inhibited the biomethylation process. The calcine waste material was supplemented with reagent grade lime to raise the pH to 7.4 and reduce the bioavailable fraction of lead. Biomethylation

resulted in the formation of 96.8 mg of volatilized arsenic (0.009% of the total calcine arsenic), a > 17-fold increase. Further optimization of this enhanced biomethylation technique may present a cost-effective remedial technology for some arsenic-contaminated soils and solid wastes.

Key words: bioremediation, biomethylation, arsenic



MINE WASTE REMEDIATION AT THE ANACONDA SMELTER NPL SITE

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The Anaconda Superfund Site is one of the largest by acreage in the country. It is located in southwest Montana near Butte adjacent to the town of Anaconda. Current investigations have identified over 20,000 acres considered for remediation. The complexity of the site is also significant. Numerous issues include the following concerns: groundwater, surface water, contaminated soils, mine tailings, smelter flue dust, stream corridors, and other miscellaneous wastes. Also of concern are the remedial process coordination issues such as the following: institutional controls, groundwater monitoring, vegetation monitoring, delisting, data management, technology management, stormwater management, wetland delineation and creation, operation and maintenance, and historical preservation.

This presentation will give a brief overview of past investigations and studies and focus on current remediation plans. A detailed approach to coversoiling tailings material and highly contaminated soils will be presented.

This approach includes the locating of borrow materials (up to 12 million cubic yards) and the conceptual design of coversoiling tailings and waste materials along with the reclamation of some of the borrow sites as wetlands. Another focus of the presentation will be the remediation of several thousand acres of moderately to severely contaminated soils. This remediation effort will include several reclamation techniques needed to remediate many different types of contamination. It will address those soils with a 0 to 2-inch surface contamination as well as those soils having contamination as deep as 18 inches. A brief outline of the process developed to assess remediation needs for contaminated soils will also be presented.

Key words: reclamation, metals, soils, tailings



THE POTENTIAL FOR BIOSTABILIZATION OF COAL TAR IN THE AQUEOUS ENVIRONMENT

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Coal tar is a multicomponent dense non-aqueous-phase liquid (DNAPL) typically associated with subsurface contamination at former manufactured gas plant facilities. Coal tar is composed of several hundreds of polycyclic aromatic hydrocarbons (PAH) compounds, such as naphthalene and phenanthrene. Once released into the subsurface, the PAH compounds are released from the coal tar DNAPL to water, creating a long-term groundwater contamination problem. Because of the complex and often unpredictable migration of DNAPLs in heterogeneous subsurface systems, it is often technologically impossible to achieve complete removal or destruction of all of the DNAPL mass present at a site, particularly when large DNAPL pools are entrapped within fine-grained media. *In situ* biodegrada-

tion surrounding the DNAPL source may stabilize the DNAPL-contaminated sites. The focus for this research is on the potential for near-source biostabilization of DNAPL pools composed of multicomponent coal tar.

Biostabilization refers to microbial activity in the vicinity of the DNAPL source area that can result in: (1) consumption of aqueous-phase pollutants released from the DNAPL source, resulting in plume prevention; (2) consumption of the more soluble post-degradation DNAPL residue; and (3) lowered aggregate toxicity of the aqueous plume due to a combination of the above two processes. The goal of this project is to develop rapid-screening tests to quantitatively evaluate the potential for biostabilization of DNAPLs. The protocols will be tested by assessing the biological treatment of DNAPL coal tar in batch biometer reactors under aerobic conditions, employing a mixed consortium of bacteria obtained from Johns Hopkins University and Michigan Tech University. The bacteria used for biotreatment have been identified as a consortium of *Stenotrophomonas maltophilia*, *Pseudomonas fluorescens/putida*, and *Pseudomonas stutzeri*.

DNAPL biostabilization is assessed by monitoring four parameters in the biometer batch reactors: (1) microbial activity determined by cell counts, oxygen consumption and CO₂ evolution; (2) aqueous phase contaminant concentrations surrounding a pool of DNAPL coal tar; (3) aggregate toxicity of the aqueous phase; and (4) composition of the DNAPL residue. The four parameters are assessed in well-mixed biometers representative of aboveground slurry systems with no mass transfer constraints, as well as in quiescent, unmixed systems representative of the subsurface.

Preliminary results from these experiments indicate lower level of microbial activity; lower aqueous-phase contaminant concentration and aggregate toxicity in unmixed quiescent systems with low mass transfer rates and reduced bioavailability in quiescent sys-

tems; and this combined with low-level microbial activity surrounding coal tar pools, can facilitate toxicity reduction and risk management at subsurface sites contaminated with DNAPL coal tar.

Key words: coal tar, DNAPL, biostabilization, microbial activity, contaminants



CHROMIUM(VI) ELIMINATION FROM CONTAMINATED GROUNDWATERS USING REDOX-REACTIVE BIOBARRIERS

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We are seeking to develop an alternative to traditional subsurface barrier technologies, which in most cases involves the excavation of trenches and the re-filling of these trenches with reactive material such as zero-valent iron filings. The costs of establishing a barrier in such a manner can be prohibitively high depending on the necessary depth of the barrier.

The metabolism of Metal-Reducing Bacteria (MRB) could be used to create zones of reduced indigenous metals (e.g., ferrous iron from ferric iron) in the path of contaminated groundwater forming permeable redox-reactive subsurface barriers. Microbially reduced iron can reductively dechlorinate organic pollutants, reduce nitroaromatics, and/or precipitate heavy metals and radionuclides from contaminated waters.

In order to efficiently treat aquifers, either indigenous MRB have to be stimulated, or - to bioaugment aquifers in a cost-effective way - pre-cultivated or genetically engineered MRB have to be injected and transported over large distances in the subsurface. Starvation of MRB provides an effective means of transporting bacteria through porous media while maintaining their full genetic potential.

Starved MRB were resuscitated with surface-associated iron minerals in batch and column experiments producing Fe(II) in the process. In both batch and column studies, the produced Fe(II) remained surface-associated and reduced Cr(VI), a common groundwater contaminant, to Cr(III). Cr(III) precipitated on the existing surfaces, forming stable end products and thereby eliminating the chromium compounds from the water phase. Current research efforts are focusing on the possibility of re-activating depleted zones of redox-reactive metals with MRB.

Key words: transport, biobarrier, starvation, chromium



ENERGY RECOVERY POTENTIAL OF SELECTED LANDFILLS IN THE U.S.A.

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Biodegradation of organic waste in sanitary landfills results in generation of a mixture of gases, comprising methane (about 50%), carbon dioxide (45%) and other gases (5%). Modern landfills, built in compliance with the Hazardous and Solid Waste Amendments Act of 1984, are designed to collect methane for potential use in space heating of buildings and structures and as fuel for producing electricity. Ideally, any landfill that has an annual capacity of 75,000 tons of in-place waste represents a valuable energy resource that should be harnessed for the above uses rather than flaring or burning. Anytime the methane concentration in the landfill gas exceeds 15%, it will support flame and at a concentration of more than 35%, energy recovery becomes economical.

The presentation discusses the process of gas formation, design of a landfill gas collection system, and the potential for methane gas generation of selected landfills in six states—

California, Iowa, Missouri, Nebraska, New York, and Wisconsin. According to a preliminary estimate by the EPA (1996), a disposal facility, where the quantity of landfilled waste is between 75,000 and 999,000 tons per year, is capable of producing enough electricity to meet the energy requirement of 5,000 to 20,000 homes. It is further estimated that these candidate landfills could collectively generate 1295 MW of electric power, yielding \$2.2 million in economic benefits per day in the six states. Environmental and other advantages associated with methane recovery along with the EPA's Methane Outreach Program are also reviewed.

Key words: biodegradation, sanitary landfills, gas formation, methane gas

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