

Program One
Tuesday, May 23, 2000
Bioremediation of Petroleum
Hydrocarbons



**THE ROLE OF THE VA-
DOSE ZONE IN THE
NATURAL ATTENUA-
TION OF GAS CONDEN-
SATE HYDROCARBONS**

¹Kerry Sublette, ¹Steve Harmon, ¹Rick Yates,
²Gary Trent, ³Ravi Kolhatkar, ⁴Greg Thoma,
and ⁵Kathleen Duncan, ¹Center for Environ-
mental Research & Technology, University of
Tulsa, 600 S. College Ave., Tulsa, OK 74104;
²Environ Services, Tulsa, OK; ³Amoco Re-
search Center, Naperville, IL; ⁴University of
Arkansas, Fayetteville, AR; ⁵University of
Oklahoma, Norman, OK; ¹Phone:
(918) 631-3334, E-mail: steven-
harmon@utulsa.edu.

Leaking underground concrete sumps used to store produced water have contaminated groundwater with gas condensate hydrocarbons at a gas production site near Ft. Lupton, Colorado. The source of contamination has been removed; however, a plume of hydrocarbon contamination extends some 46 m from the original source location. This is an agricultural area and the water table is rather shallow (about 1.4 m on average) and fluctuates seasonally over 0.3 to 0.6 m. Further, this site is in close proximity to a potential surface receptor, the South Platte River.

Amoco Production Co. and the University of Tulsa have conducted extensive monitoring of the groundwater at this site for over 4 years in conjunction with microcosm studies to ascertain the rate and extent of intrinsic bioremediation of hydrocarbons at the site. Geochemical indicators of biodegradation of hydrocarbons by indigenous microorganisms include oxygen depletion, increased alkalinity, sulfate depletion, methane production, and Fe⁺² production associated with hydrocarbon contamination. Sulfate-reducing bacteria and methanogens were also shown to be orders of

magnitude higher in contaminated sediments compared to noncontaminated areas. Lastly, metabolites of hydrocarbons degradation, including metabolites characteristic of anaerobic degradation of xylenes and toluene, have been found in contaminated groundwater.

Clearly some purely anaerobic degradation of toluene and xylenes occurs at the site based on the characteristic metabolites of anaerobic degradation detected. However, the relative importance of this mechanism to the overall attenuation of these or other BTEX compounds is unknown. In addition the site still contains scattered free product floating on the water table; therefore, there is also a significant inventory of aliphatic hydrocarbons at the site, which have not been shown to degrade under anaerobic conditions. Since the plume has been observed to be stable and the total hydrocarbon inventory seems to be decreasing, some significant role for oxygen is suggested. Since this is a relatively shallow aquifer, the vadose zone may act as a significant source of oxygen for hydrocarbon degradation. In order to investigate the role of the vadose zone in the natural attenuation of hydrocarbons at this site, an extensive characterization of the vadose zone has been carried out as a function of depth. The vadose zone was sampled in 15-cm increments from the surface to the water table in both contaminated and uncontaminated areas of the site. Each 15-cm sample was composited and analyzed for individual C₃+ hydrocarbons, hydrocarbon metabolites, methane, CO₂, total organic carbon (TOC), and total inorganic carbon (TIC). Methane, CO₂, TOC, and TIC were also subjected to ¹³C analysis. Samples were also analyzed to determine characteristics of microbial populations using phospholipid fatty acid analysis (PLFA), degrading gradient gel electrophoresis (DGGE), and gene probes for genes related to aerobic biodegradation of aliphatic and aromatic hydrocarbons. Results of these analyses and their implications with regard to the mechanisms of hydrocarbons' biodegradation in the vadose zone will be discussed.



BIO-SEP: AN ADVANCED BIOCATALYST SUPPORT SYSTEM FOR GROUNDWATER AND WASTE-WATER TREATMENT

¹Kerry Sublette, ¹Steve Harmon, and ²Carl Camp, ¹Center for Environmental Research & Technology, University of Tulsa, 600 S. College Ave., Tulsa, OK 74014; ²Du Pont, Wilmington, DE; ¹Phone: (918) 631-3085, ¹E-mail: kerry-sublette@utulsa.edu.

Bio-Sep is a porous, adsorptive polymeric biocatalyst support that has numerous applications in the treatment of groundwater and wastewater streams. Bio-Sep consists of 2-3 mm spherical beads engineered from a composite of 25% polymer for toughness and high durability and 75% powdered activated carbon for high shock resistance. The bulk density of the beads is approximately 0.16 g/cm³ with a porosity of 75%. The median pore diameter is 1.9 microns; however, large macropores (> 20 microns) also exist inside the beads. These unique beads feature a structure that allows microorganisms to colonize throughout the internal volume of the bead, resulting in high biomass density and high volumetric productivity. Volumetric productivities of over 10 times that of conventional activated sludge treatment have been demonstrated. The Bio-Sep biocatalytic process has been demonstrated with a wide variety of contaminants including hydrocarbons, methylene chloride, picric acid, ammonia, sulfidic caustic, phenolics, aldehydes and ketones, and amides. This paper will review the details of the Bio-Sep structure and applications of this biocatalyst support in environmental applications. Aspects of Bio-Sep bioreactor design, as well as potential bioprocessing applications, will also be reviewed.

Key words: Bio-Sep, biomass density, sludge treatment



USE OF MOLECULAR TECHNIQUES TO INVESTIGATE MICROBIAL POPULATIONS IN SOIL IMPACTED BY HYDROCARBONS AND BRINE

¹Kerry Sublette, ¹Lorrie Houston, ¹Steve Harmon, ²Kathleen Duncan, and ³Ravi Kolhatkar, ¹Center for Environmental Research & Technology, University of Tulsa, 600 S. College Ave. Tulsa, OK 74104; ²University of Oklahoma, Norman, OK; ³BP Amoco, Naperville, IL.

An investigation of the impact of a hydrocarbon spill or leak on soil ecology or the potential or progress of bioremediation of contaminated soil typically requires an enumeration and characterization of microbial populations in the soil. Most conventional methods for enumeration require culturing on a solid medium (viable plate counts) or in liquid medium (most probable number counts). However, it has been estimated that 90% of the microorganisms in soil are non-culturable. Molecular microbial techniques which do not depend on culturing give a more complete picture of the soil microbiology of an impacted site. For example, phospholipid fatty acids (PFLA) from microbial cell membranes and cell walls may be extracted with an organic solvent and characterized by GC/MS to yield information about the total viable biomass present, community structure, metabolic status, and environmental stress. Specific PLFA biomarkers can indicate the presence and numbers of sulfate-reducing bacteria (SRB), methane-oxidizing bacteria, fungi, eucaryotes, etc. DNA extracted from soils can be probed for specific genes such as those specific for aerobic degradation of aromatic or aliphatic hydrocarbons, ammonium oxidation, or sulfide reduction of SRB. Amplification of 16s ribosomal DNA by PCR and separation of the products using degrading gradient gel electrophoresis (DGGE) can allow determination of the number and relative abundance of eubacteria in soil samples. Subsequent sequencing of individual bands from the gel can

identify dominant organisms. Use of these techniques to characterize the microbial community in soil impacted by crude oil will be discussed.

Program One
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Bioremediation--PAHs



**MODELING
MULTI-SUBSTRATE BIO-
DEGRADATION KINETICS
OF BINARY
POLYCYCLIC AROMATIC
HYDROCARBON MIX-
TURES**

¹*Christopher Knightes and Catherine Peters,
Department of Civil and Environmental
Engineering, Princeton University, Princeton,
NJ 08544; ¹Phone: (609) 258-1552, ¹E-mail:
knightes@princeton.edu.*

Polycyclic aromatic hydrocarbons (PAHs) are an important class of environmental contaminants because of their suspected carcinogenicity. Because they are organic compounds, PAHs represent a feasible source of carbon and energy for naturally occurring microorganisms. Therefore, biodegradation is a feasible remediation strategy for PAH-contaminated sites. PAHs typically occur as complex mixtures, but more research has focused on sole-substrate biodegradation. The goal of this study was to investigate how multi-substrate Monod biodegradation kinetics can be used to model a binary mixture of PAHs and how the presence of an additional substrate impacts the biodegradation of the other substrate. Two series of experiments were performed, naphthalene and 1-methylnaphthalene, and naphthalene and phenanthrene. The biodegradation studies were performed as a series of independent batch aqueous experiments with two PAHs available as substrates for a PAH-degrading consortium. Parallel abiotic reactors were used to verify that abiotic losses were minimal. The Monod kinetic parameters and

yield coefficients used to model the multi-substrate system were estimated from independent sole-substrate experiments. From these experiments, it is demonstrated that multi-substrate biodegradation kinetics can be adequately modeled using previously determined sole-substrate parameterization. Furthermore, the multi-substrate model demonstrates two competing effects: enhancement and competitive inhibition. The compound with faster biodegradation kinetics (naphthalene) is not dramatically affected by the presence of a secondary substrate. The slower degraded compounds (1-methylnaphthalene and phenanthrene) have enhanced biodegradation by the biomass growth on naphthalene, but not as enhanced as would be seen if there were no competitive inhibition.

Key words: biodegradation, kinetics, multi-substrate, PAHs, mixtures



**ACCELERATED
BIOREMEDIATION OF
PAH-CONTAMINATED
SOILS BY PRETREAT-
MENT WITH FENTON'S
REAGENT**

¹*Kenneth Reardon and ²Shelley Allen, ^{1,2}De-
partment of Chemical and Bioresource
Engineering, Colorado State University,
Glover Room 100, Fort Collins, CO 80523;
¹Phone: (970) 491-6505, E-mail:
reardon@engr.colostate.edu; ²Phone: (970)
491-1123, E-mail:
shelley@engr.colostate.edu.*

Chemical oxidation and bioremediation are two remediation techniques commonly used to treat contaminated soil. Bioremediation can be an economically sound method of treating easily degradable compounds. However, many pollutants are not effectively degraded by bioremediation. Chemical oxidation, on the contrary, successfully degrades contaminants that are biologically recalcitrant, but is considerably more expensive than the biological treatment. By

combining these two technologies, a cheaper, more effective method should result. For the most effective combination, the optimal extent of chemical oxidation must be found.

In a laboratory-scale project, soils obtained from two different sites were used to study the combination of chemical oxidation and bioremediation. The primary contaminants in these soils were polycyclic aromatic hydrocarbons (PAHs) and pentachlorophenol (PCP), chosen because they are both recalcitrant and carcinogenic. The specific chemical oxidation process utilized in this study involved the addition of hydrogen peroxide along with a Fenton's-like reagent. This mixture was selected because it produces hydroxyl free radicals, which have an oxidizing potential second only to fluorine. In order to distribute the reagent properly into the soil, a Microenfractionator™, designed by H&H Eco Systems, Inc., was used. The Microenfractionator is essentially an efficient, rapid, and large-scale mixing device. It not only mixed the reagent homogeneously into the soil, but also decreased the mass transfer limitations brought about by sorbed contaminants. This decrease in mass transfer limitations increased the degradation rate by increasing the availability of the contaminants. Once chemically oxidized and well mixed, the soil was set aside to allow the indigenous microorganisms to biodegrade the remaining contaminants. The effect of hydrogen peroxide was tested at three concentrations: zero, one, and two percent (by weight).

Soil samples were taken at regular intervals over a six-week period. These samples were analyzed for pollutant levels, microbial population characteristics, and mutagenicity. The microbial population characteristics studied include total biomass, population composition, and degradation activity.

The highest overall degradation was achieved by the two-percent hydrogen peroxide, which was the highest concentration of hydrogen peroxide tested. This level of hydrogen peroxide also had the largest impact on the

microbial community. The concentration of microorganisms decreased by a factor of four after the hydrogen peroxide was added. However, the microbial population rebounded within a week. The addition of even a small amount of hydrogen peroxide produced better degradation than bioremediation alone.

Key words: bioremediation, oxidation, PAH, PCP, soil



ESTIMATION OF STYRENE INHIBITION AND INDUCTION KINETIC PARAMETERS ON A MIXED CONSORTIUM OF PAH-DEGRADING BACTERIA: IMPLICATIONS FOR MODELING AND DESIGNING BIOISOLATION SCHEMES

¹Eric Vestal, ²Angela Bielefeldt, ³Kendra Morrison, ⁴Anuratha Ramaswami, ⁵Tissa Illangasekare, ¹Division of Environmental Science and Engineering, Colorado School of Mines, Golden, CO 80401; ²Department of Civil, Environmental, and Architectural Engineering, University of Colorado, Boulder, CO 80309; ³U.S. EPA, 999-18th St., Suite 500, Denver, CO 80202; ⁴Department of Civil Engineering, University of Colorado (Denver), Denver, CO 80217; ⁵Amax Chair, Division of Environmental Science and Engineering, Colorado School of Mines, Golden, CO 80401; ¹Phone: (303) 273-3483, ¹E-mail: evestal@mines.edu; ²Phone: (303) 492-8433, ²E-mail: Angela.Bielefeldt@colorado.edu; ³Phone: (800) 227-8917, ³E-mail: Morrison.Kendra@epamail.epa.gov; ⁴Phone: (303) 556-4734, ⁴E-mail: aramaswa@carbon.cudenver.edu; ⁵Phone: (303) 384-2126, ⁵E-mail: tillanga@mines.edu.

Nonaqueous-phase liquids (NAPLs) trapped in the subsurface as pools pose serious long-term groundwater contamination problems. With traditional remediation methods, such as pump-and-treat, it is often impossible to achieve complete removal of NAPL pools

and such methods can even promote unwanted down-gradient migration (Cohen and Mercer, 1993). The long-term, ubiquitous presence of aromatic hydrocarbons in the environment has allowed microorganisms in the subsurface to develop the capability to metabolize them (Neff, 1979). Microbial metabolism of hydrophobic organic contaminants typically found in coal tar, such as poly-aromatics (PAHs) and styrene, makes bioremediation an attractive, low-cost cleanup strategy. Bioisolation presents an *in situ* technology that can potentially retard mass transfer of the more soluble components as well as reduce overall dissolved-phased organic constituents in contaminant plumes, thereby effectively isolating NAPL pools from downstream receptor locations. The design of bioisolation/biostabilization schemes requires modeling of net mass transfer, degradation, transport, and biogrowth. Microbial degradation kinetic rate constants are critical to the accurate modeling of these phenomena. If substrate material either inhibits or induces the microbial degradation, this can alter the accuracy of a Monod-type multicomponent, multi-electron acceptor kinetic expression used in the modeling phase of remediation design engineering. We have found that styrene, in concentrations greater than 15 mg/L, is toxic (enzyme inhibition) to a mixed consortium of PAH-degrading bacteria. There is also evidence that enzymatic induction can affect the measured degradation kinetics, depending on the growth history of the culture. The kinetic data we present is for a bacterial population of PAH degraders in the *Pseudomonadaceae* family that have been maintained in CSTRs and exposed to coal tar as well as naphthalene, phenanthrene, and 2-methylnaphthalene at aqueous solubility levels as well as styrene at 15 mg/L. We present the experimental method used to identify, measure, and uncouple the induction and inhibition, the parameter estimation (inversion) process for quantifying the inhibition constant and induction curve within the framework of the multi-component, multi-electron

acceptor Monod formulation, and the implications for long-term bioisolation strategies based on semi-coupled mass transfer, degradation, flow, transport, and biogrowth modeling.

Key words: biokinetics, bioisolation, modeling, PAH, NAPL

Program One Tuesday, May 23, 2000 Bioremediation--Applications



ANAEROBIC TREATMENT OF LANDFILL LEACHATE TO OPTIMIZE METHANE GENERATION

¹Syed Hasan, ²Suman Ghosh, and ²Namita Oswal, ^{1,2}Department of Geosciences, University of Missouri-Kansas City, 5100 Rockhill Road, Kansas City, MO 64110-2499; ¹Phone: (816) 235-2976, E-mail: hasans@umkc.edu.

A partially bi-phasic, laboratory-scale anaerobic digester was designed and utilized for optimum generation of methane, using a high strength landfill leachate with chemical oxygen demand (COD) of 15,500 mg/L at a loading rate of 200 mL/day. The apparatus comprises a downflow semi-continuous digester that was operated at mesophilic temperature (37 ± 0.5 °C) where the hydraulic retention time was maintained at 20 days. Modification to the conventional anaerobic digestion was attempted by creating an aerobic phase two days prior to the effluent's entry into the anaerobic system. This modification gave the digester sufficient buffering capacity to withstand limited environmental stress and prevented generation of excess acid that could lead to a sour condition and resulting failure. Simultaneous monitoring of selected volatile fatty acids helped in optimizing the reaction conditions and maintaining stability of the digester. Experimental results showed that the digester could be used successfully to treat

landfill leachate with high COD, and is capable of withstanding high loading rate and minor environmental shocks. The data showed a total COD removal of 79% and a methane yield of 0.032 m³/kg of COD removal. Methane content of the biogas varied between 35 and 39%.

Key words: bi-phasic anaerobic digester, landfill leachate, methane recovery



NITROGEN REMOVAL IN LABORATORY-SCALE CONSTRUCTED WETLANDS

¹Achintya Bezbaruah, ²Tian Zhang, and ³John Stansbury, ^{1,2,3}Department of Civil Engineering, 205 PKI, University of Nebraska-Lincoln at Omaha Campus, Omaha, NE 68182-0178; ¹Phone: (402) 554-3565, ¹E-mail: abezbaru@unomaha.edu; ²Phone: (402) 554-3784, ²E-mail: tzhang@unomaha.edu; ³Phone: (402) 554-3896, ³E-mail: jstansbury@unomaha.edu.

As an alternative to conventional biological wastewater treatment systems, the laboratory-scale subsurface constructed wetland was used in this study for COD and nitrogen removal in a single reactor. Two reactors, 11.5' x 0 5' x 3' each, have been constructed side by side, and located in a controlled environment chamber. The reactors are fed with primary settled municipal wastewater from a local treatment plant. The first reactor is for COD removal, nitrification, and heterotrophic denitrification, while the second one is for COD removal, nitrification, and sulfur/limestone (S/L) autotrophic denitrification. A polishing zone has been kept in both reactors and they are equipped with aeration pipes for optional compressed air aeration. Plants are not grown in the reactors so as to exclude their effect in the process. The parameters monitored are organic, ammonium, and hydraulic loading rates; and hydraulic retention times (HRTs), COD, NH₄⁺-N, NO₃⁻-N, DO, pH, etc. The wetlands have been operated at

several different temperatures and hydraulic retention times (HRTs).

Results so far obtained suggest ammonia-nitrogen removal and nitrification up to 65% in the first wetland. When compressed air aeration is not used, a stratified pattern of ammonia-nitrogen removal and nitrification has been observed, these being slightly faster at the surface than at the bottom. This suggests that DO may be one of the limiting factors for nitrogen removal in a constructed wetland. It seems that the limiting DO concentration is ca. 1 mg/l for nitrification to take place and hence, nitrogen removal. The temperature effect on COD and nitrogen removal has been investigated by evaluating the first-order reaction rate constant and temperature activity coefficient (q). The ammonia and nitrate removal rates do not increase much beyond 18°C. Sulfur-limestone autotrophic denitrification is very efficient (>95%), indicating that the rate-limiting step for nitrogen removal in the second wetland is nitrification. No SO₄²⁻ is detected in the effluent of the second wetland, although it is detected immediately after the S/L section. In both reactors, NO₃⁻-N removal increases with an increase of HRT, while COD is removed very efficiently (up to 98%) at all HRTs. Currently, the effect of the ratios of COD/ammonium and COD/nitrate-N on nitrification and denitrification in these wetlands are being investigated. The results of this study seem to indicate that subsurface constructed wetlands can be used to treat wastewater generated by small communities.

Key words: constructed wetland, ammonia, nitrate, nitrification, denitrification, COD



MECHANISM AND KINETICS OF NONIONIC SURFACTANT INHIBITION OF PENTACHLOROPHENOL BIODEGRADATION

¹Todd Cort and ²Angela Bielefeldt, ^{1,2}University of Colorado, Boulder, Department of Civil Environmental and Architectural Engineering, Campus Box 428, Boulder, CO 80309;

¹Phone: (303) 492-0139, ¹E-mail: cort@ucsu.colorado.edu; ²Phone: (303) 492-8433.

The use of surfactants has a great deal of potential to increase the biodegradation rates of hydrophobic organic compounds in contaminated environments by increasing the total aqueous solubility of these compounds. However, inhibitory effects of surfactants on the biodegradation process have frequently been reported. A variety of factors and mechanisms have been proposed to explain the inhibition process, including cellular toxicity from interaction of surfactant molecules with cell membranes (changing fluidity) or directly with membrane-bound proteins, direct inhibition of enzymes involved in the catabolic pathway either by association with the enzyme or with the substrate, decreased bioavailability due to sequestration of the substrate compound into surfactant micelles, or the accumulation of toxic intermediates due to incomplete metabolism incurred from substrate-surfactant interactions. The future utility of surfactant-aided bioremediation efforts relies on the ability to accurately predict the effect of surfactants on a given bacterial culture with a known set of organic contaminants.

Several potential mechanisms of surfactant-induced inhibition of pentachlorophenol (PCP) biodegradation were tested using a pure bacterial culture of *Sphingomonas chlorophenolicum* sp. Strain RA2. PCP and glucose degradation as well as endogenous decay rates were measured in aqueous batch systems in the presence of 10-5000 mg/L of the nonionic surfactant Tergitol NP-10 (TNP10). Concentrations of TNP10 over 200 mg/L inhibit biodegradation of PCP at concen-

trations below 100 mg/L. This inhibition was best described by the Monod kinetic equation where the effect of TNP10 inhibition is reflected in the half-saturation constant (K_s). The value of the K_s increased from between 1.4-13.5 mg/L with no surfactant present to 13.6-202 mg/L at the highest level of inhibition. At PCP concentrations above 200 mg/L, TNP10 reduced the substrate inhibition effect of PCP, resulting in faster PCP degradation rates at higher concentrations of TNP10. Measurements of surfactant confirm that TNP10 is not degraded by RA2. Calculations of a micelle partition coefficient (K_m) show that the differences in initial PCP degradation rates can be explained by accounting for the amount of PCP available to the cell in the aqueous solution. A model is discussed based on these results where PCP is sequestered into micelles at high TNP10 concentrations to become less available to the bacterial cell and resulting in observed inhibition. Under substrate toxicity conditions, the same mechanism serves to increase the rate of PCP biodegradation by reducing aqueous PCP concentrations to less toxic levels. TNP10 also enhanced the glucose degradation and endogenous decay rates between 500 and 5000 mg/L as measured by dissolved oxygen uptake and biomass growth. Tests of glucose degradation and endogenous decay confirmed that TNP10 does not inhibit RA2 via a mechanism of general cellular toxicity. These results suggest that TNP10 may have different effects on RA2, depending on the nature of the substrate.

Key words: pentachlorophenol, surfactant, bioremediation, kinetics, inhibition



TETRACHLOROETHENE (PCE) DEHALOGENATION BY SEQUENCING AN- OXIC/AEROBIC BIOREACTOR

Lei Wang and Robert Segar Jr., Department of Civil and Environmental Engineering, University of Missouri-Columbia, Columbia, MO 65211; Phone: (573) 882-0075; E-mail: segarr@missouri.edu.

As one of the important industrial solvents, tetrachloroethene (PCE) has been widely used worldwide. Since PCE is difficult to treat by aerobic biological processes, most research has been focused on anaerobic dehalogenation of PCE. A disadvantage of the anaerobic process is that the dechlorination is incomplete and the metabolites such as vinyl chloride, a carcinogen chemical, can accumulate in the reactor. To treat the less chlorinated ethenes, an aerobic process is necessary as the second stage. In this study, an anoxic/aerobic biological process was employed to treat PCE. An oxygen-tolerant and denitrifying bacteria was enriched from the mixed sludge taking from the primary and secondary digesters at the City of Columbia Municipal Wastewater Treatment Plant, Missouri. These bacteria were found to be very effective in dehalogenating PCE. At the same time, the phenol-induced bacteria were added to cometabolize TCE. The microorganisms were cultured in a sequencing anoxic and aerobic bioreactor. A fast and complete PCE dehalogenation was achieved by proper control of the nitrate-feeding concentration, substrate concentration, aeration, pH, and oxidation-reduction potential. A 24-hour cycle (22 hours for anoxic and 2 hours for aerobic) could completely reduce PCE with a feeding concentration of up to 100 $\mu\text{g/L}$. In the reactor, acetate, methanol, and phenol were growth substrates and electron donors, and nitrate and PCE were electron acceptors.

Key words: tetrachloroethene (PCE), trichloroethene (TCE), anoxic/aerobic, fluid-

ized-bed bioreactor, denitrifier, dehalogenation

Program Two Tuesday, May 23, 2000 Analytical Methods I



DETERMINATION OF TRACE-LEVEL GOLD(III) BINDING TO ALFALFA BIOMASS USING GFAAS WITH ZEEMAN BACK- GROUND

¹J.G. Parsons, ¹G. Gamez, ¹K.J. Tiemann, and ²J.L. Gardea-Torresdey, ^{1,2}Department of Chemistry and Environmental Science and Engineering, University of Texas at El Paso, El Paso, TX 79968; ²Phone: (915) 747-5359, ²E-mail: jgardea@utep.edu.

Due to current technologies used to extract gold from ores, increasing environmental pollution has occurred. Existing technologies for the extraction or recovery of gold include cyanidation which uses sodium cyanate (extremely toxic). Because of various accidents and wastes generated by the cyanidation process, an increasing need to develop new technologies to extract or recover gold from aqueous solution has arisen. Previous experiments performed in this laboratory have shown that alfalfa has the ability to reduce gold(III) to gold(0). These experiments have also shown that gold(III) at high concentrations is adsorbed by the alfalfa biomass independently of pH. pH profiles have been performed at trace levels for both native biomass and chemically modified biomass using a 100 ppb gold(III) aqueous solution. However, at trace-level gold(III) concentrations, the adsorption of gold(III) has been observed to be pH dependent. The observed trend in the binding by the native alfalfa biomass was highest at pH 3.0 (97%) and decreased (to approximately 50%) at pH 4.0 and pH 5.0. However, the esterified biomass had an opposite binding

trend, a low binding at pH 2.0 and 3.0 (50%) and a sharp increase in binding at pH 4.0 with a maximum binding at pH 5.0 (90%). Currently, experiments are being performed to see the effects of hard cations, such as calcium, magnesium, and sodium, on the binding of gold(III) to the alfalfa biomass. Results will be presented.

Key words: alfalfa, gold, Zeeman, GFAAS



ELECTROCHEMICAL AND X-RAY ABSORPTION SPECTROSCOPIC STUDIES OF CU(II) AND PB(II) BINDING TO ALFALFA BIOMASS

¹K.J. Tiemann, ¹G. Gamez, ¹J.G. Parsons, ¹K. Dokken, ¹I. Herrera, and ²J.L. Gardea-Torresdey, ^{1,2}Department of Chemistry and Environmental Science and Engineering, University of Texas at El Paso, El Paso, TX 79968; ²Phone: (915) 747-5359, ²E-mail: jgardea@utep.edu.

We have performed several studies to determine the electrochemical properties of Cu(II) and Pb(II) binding by alfalfa biomass using carbon paste alfalfa-modified electrodes. Experimental conditions such as alfalfa-carbon paste concentrations, solution pH, and metal preconcentration times were determined. Results of the electrochemical studies have shown that an increase in response was observed by increasing the concentration of alfalfa biomass with a maximum response at 30% (w/w). In addition, the response was found to escalate as the pH of the Cu(II) and Pb(II) solutions was raised from 2 to 6, which parallels the trends observed from previously performed batch experiments. X-ray absorption spectroscopic studies were also performed to determine the actual chemical binding sites that are involved with Cu(II) and Pb(II) binding by the alfalfa biomass. Results from these studies will be presented.

Key words: XANES, EXAFS, alfalfa, biosensor, metal binding, copper, lead



CAPILLARY ELECTROPHORESIS - INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR NUCLIDE DETERMINATIONS OF LANTHANIDES IN AN IRRADIATED TANTALUM TARGET MATERIAL

¹Jason Day, ¹Joseph Caruso, ²J. Sabine Becker, and ²H.J. Dietze, ¹University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221-0172; ²Central Laboratory for Analytical Chemistry, Research Center Jülich, Jülich, 52425, Germany; ¹Phone: (513) 556-9304, ¹E-mail: dayjn@email.uc.edu.

A nuclide analysis lanthanide elements was performed using capillary electrophoresis (CE) interfaced to a double-focusing sector field, inductively coupled plasma mass spectrometer (DF-ICP-MS). Peak areas were used to calculate isotope ratios and lanthanide oxide formation data. Isotope ratio determinations of samples with natural isotope ratios show good agreement with natural isotope values. Detection limits were in the low ng ml⁻¹ concentration range for the most abundant isotopes. This procedure was applied to a sample from a tantalum target material which had been irradiated with a high-energy proton beam for 500 days. Spallation nuclides in these samples were lanthanides in the concentration range of ~1 µg ml⁻¹ to low ng ml⁻¹. Additionally, spallation-product nuclide abundances are significantly different from natural isotope ratios. The CE separation method has the advantage of short analysis times and very small sample amounts (~35 nl).

Key words: lanthanide oxide formation, isotope ratios, CE separation method

Program Two
Tuesday, May 23, 2000
Analytical Methods II



PROCEDURE FOR OBTAINING REPRODUCIBLE FURFURAL ANALYTICAL RESULTS

¹John Huntington, Ph.D. and ²Phillip Stark, P.E., ¹Analytica Environmental Laboratories, Incorporated, 325 Interlocken Parkway, Suite 200, Broomfield, CO 80021; ²EnviroGroup Limited, 7208 South Tucson Way, Suite 125, Englewood, CO 80112; ¹Phone: (303) 469-8868, ext. 166, ¹E-mail: jhunting@analyticacroup.com; ²Phone: (303) 790-1040, ²E-mail: pstaark@envirogroup.com.

Furfural is a substance that is found in organic vegetative matter and many foods. Furfural is produced from biomass and is used as a solvent in numerous manufacturing processes. It is a listed hazardous waste. Analysis of the compound is complicated by a tendency to undergo oxidation, hydrolysis, and polymerization in the sample as well as laboratory standards.

Groundwater was analyzed for the presence of furfural due to an accidental industrial release. Initial analytical results gave extremely poor spike recoveries, poor precision, and poor accuracy. EnviroGroup Limited requested the assistance of Analytica Environmental Laboratories, Incorporated in developing a procedure for sample collection and sample analysis which would give more consistent and usable data.

Furfural background information, chemical properties, and current analytical methods are reviewed. A description is given of the investigative procedures that were used to understand the source of the difficulties and to develop a better method. The developed analytical method is described and compared

to previously used methods.

Key words: furfural, analysis



DETECTION OF SELENOAMINO ACIDS ENANTIOMERS IN SELENIUM-ENRICHED YEAST USING HPLC COUPLED TO ICP-MS

C.A. Ponce de Leon and Joseph Caruso, University of Cincinnati, Department of Chemistry, Mail Location 0172, Cincinnati, OH 45221-0172; ¹Phone: (513) 556-9304; ¹E-mail: poncedc@email.uc.edu.

Selenium is an important micronutrient for living organisms. Selenium is especially important because it is capable of being substituted for sulfur in amino acids. Selenium species are of special interest because of their anti-cancer properties, as shown by Clark et al., but selenium in high concentrations and in certain forms may be toxic. The natural abundance of selenium in nature is low; therefore, selenium enriched foods are produced. The microorganisms present in certain foods transform the selenium into different selenium species; thus, different foods contain different species. These selenium-enriched foods have been analyzed to elucidate the selenium species present. Techniques such as ion-exchange chromatography, ion-pair chromatography, reversed-phase chromatography as well as gas chromatography have been used for this purpose. These techniques have helped elucidate the selenoamino acids present in the samples, but the chiral properties of the organoselenium species have yet to be studied. This is of importance since in living organisms, only one of the enantiomers has activity. Chiral chromatography can separate the different enantiomers in a compound. Chiral-HPLC chromatography can be coupled with ICP-MS to give a very selective and sensitive technique.

This work will present the chiral analysis of selenoamino acids that may be present in selenium-enriched yeast. The yeast analysed

was enriched by two different procedures. The separation was carried out using a crown ether stationary phase. Also, the results obtained using different extraction methods will be presented.



**A SIMPLE, INEXPENSIVE
AND RAPID METHOD TO
DETERMINE TOXICITY
USING
A BACTERIAL INDICA-
TOR ORGANISM**

James Botsford, Department of Biology, New Mexico State University, Las Cruces, NM 88003; Phone: (505) 646-3726, E-mail: jbotsfor@nmsu.edu.

I have developed a technique for determining toxicity of all sorts of compounds. More than 200 chemicals have been assayed. I have compared results with my assay with results from 22 other assays and find I get comparable results. The method uses the bacterium *Rhizobium meliloti*, the bacterium that grows symbiotically with alfalfa and fixes nitrogen for the plant. The bacterium can reduce a thiazole tetrazolium dye, MTT, very readily and toxic chemicals inhibit the reduction of the dye. Large amounts of toxin inhibit the reduction severely; smaller amounts have a lesser effect so the test is quantitative. A spectrophotometer is used to estimate reduction of the dye. Divalent cations inhibit reduction of the dye. This can be eliminated by the addition of small amounts of EDTA.

The test is simple. High school students have contributed to the research. The test is inexpensive; the bacteria can be grown for almost nothing and the chemicals used are inexpensive and are readily available. The test is rapid; it takes less than an hour to carry out the reactions, plot the results, and calculate the toxicity of the sample. Any laboratory able to grow bacteria should be able to carry out the assay readily. We have compared this test with 22 other tests.

We have also compared these 22 tests with one another. Tests involving animals

tested in vitro simply are not as sensitive as tests using fish, *Daphnia magna*, or microorganisms. This work will be discussed in detail.

Key words: toxicity, compounds, Rhizobium meliloti

**Program Two
Tuesday, May 23, 2000
Analytical Methods III/Biosorption**



**ENVIRONMENTAL AP-
PLICATIONS OF CHIRAL
HPLC**

¹Wen-ye Lee and ²James Salvador, ^{1,2}Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968; ¹Phone: (915) 747-5849, ¹E-mail:

gloria@salvador.chemistry.utep.edu; ²Phone: (915) 747-5704, ²E-mail: james@salvador.chemistry.utep.edu.

Chiral pesticides are asymmetric and thus have a non-superposable mirror image or enantiomer. Most of the chiral pesticides are currently sold, used, and analyzed in enantiomer pairs as if they were just one single compound even though enantiomers have different biological activities and thus different environmental ramifications.

In our study, commercial chiral High Performance Liquid Chromatography (HPLC) was used to separate and quantify chiral pesticides. The separation of six locally used racemic pesticides will be reported. The degradation of these chiral pesticides in soil samples will also be presented.

Key words: pesticides, chiral, enantiomer



REMOVAL OF HEAVY METAL IONS FROM WASTE WATER BY ADSORPTION ON IMMOBILIZED MICROALGAE

A. Wilke, G. Bunke, and R. Buchholz, TU Berlin, Inst. of Biotechnology, Dept. Bioprocess Engineering, AckerstraBe 71-76, 13355 Berlin, Germany; Phone: ++49 (0) 30 314-72527, Fax: ++49 (0) 30 314-72573, E-mail: anwi@bibo.lb.tu-berlin.de.

The contamination of wastewater and soil with toxic heavy metal ions is a complex problem. The removal of this contamination has received much attention in recent years. From an environmental protection point of view, heavy metal ions should be removed at the source in order to avoid pollution of natural waters and subsequent metal accumulation in the food chain. Conventional methods for removal are chemical precipitation, chemical oxidation, chemical reduction, ion exchange, filtration, electrochemical treatment and evaporation. All these procedures have significant disadvantages, which are for instance incomplete removal, high-energy requirements, and production of toxic sludge or waste products that also require disposal. These methods often are very expensive. Alternative methods for heavy metal removal were developed in the last decade. One of them is the biosorption of heavy metal ions on biomass. Microalgae are known to have high capacities and selectivities in the uptake of heavy metals. Although the biosorption process has many advantages compared to conventional techniques, there are only a few established processes up to now. The use of screened microalgae to reduce the heavy metal concentration in wastewater effluents is the main subject.

A new biosorbent material, based on different microalgae with high metal capacities or selectivities, was obtained by a new immobilization process. For this procedure, cellulosulphatederivates were mixed with freeze-dried microalgae. The resulting mixture was dropped in a solution containing

Polyethyleneimine. The positively charged cellulosulphatederivate/microalgae solution precipitated immediately. A thin membrane surrounds the resulting hollow spheres. After additional treatment, the encapsulated microalgae possess good mechanical and chemical properties for using them as a new biosorbent in an adsorption column.

After optimizing the particle-size electron microscope, pictures of the biosorbents were taken to locate the heavy metals and examine the structure of the hollow spheres, e.g. the thickness of the membrane and the pore size inside the particles.

Kinetic experiments were carried out to determine the mass transport resistance as a fundamental requirement for the mathematical description and the scaleup of the process.

The metal uptake of the biosorbent and the matrix system was quantitatively evaluated using the heavy metals lead, cadmium, nickel, and zinc. The experimental results are in a good correspondence with the Langmuir-isotherm-model.

Batch experiments were made to determine the selectivity of heavy metal uptake. Depending on the encapsulated microalgae and cellulosederivate, the selectivity in heavy metal uptake is changing.

Experiments in an adsorption column were made with synthetic and real wastewater, caused by the accumulator industry, contaminated with lead and zinc. The results show that the biosorbent is suitable for using it in an adsorption column.

The desorption of the adsorbed heavy metals is established by a reduction of the pH value. Therefore, a reversible loading/unloading of the adsorbed heavy metal, using HCl or citric acid for the desorption process, is possible.

Key words: microalgae, heavy metals, immobilization, biosorption



CHEMICAL CHARACTERIZATION OF THE BIOSORPTION OF HEAVY METALS

¹Dipl.-Leb.-Chem. S. Klimmek and

²Prof. Dr. rer. nat. H.-J. Stan, ^{1,2}Technical University Berlin, Institute of Food Chemistry, Gustav-Meyer-Allee 25, D-13355 Berlin, Germany; ¹Phone: ++49-30314727782, ¹E-mail: Klimmek@lb.tu-berlin.de; ²Phone: ++49-30314727702, ²E-mail: stan@lb.tu-berlin.de.

The ability of microorganisms to enrich heavy metals from aqueous solution has been known for some decades. The enrichment of the metals occurs actively only with living cells (bioaccumulation) or passively at the surface of both living and dead cells (biosorption). The biosorption is a fast and reversible reaction of the heavy metals with the microorganism's biomass and is therefore of particular economic interest.

A project of the cooperative research program Sfb 193 financed by German Research Society, which deals with the biological treatment of industrial and commercial wastewater, is to investigate the biosorption of the industrially relevant heavy metals lead, cadmium, nickel, and zinc by algae. The results are taken as basis for an application-oriented method for the purification of wastewater as developed by Wilke, Bunke, and Buchholz, TU Berlin.

Twenty-five algae species were investigated for their ability to bind the four metals in a screening method. Quantitative evaluation of the screening results identified the most suitable algae for this application. *Chlorella salina* (Chlorophyceae) and *Lyngbya taylorii* (Cyanophyceae) proved to be the most efficient algae under investigation. Further characterization of the biosorption was carried out on the two most efficient species. The sorption isotherms of the four metals by *L. taylorii* showed, for example, maximum capacities of 1.4 mmol lead, 0.44 mmol cadmium, 0.65 mmol nickel, and 0.59 mmol zinc per gram of dry biomass

according to the Langmuir Adsorption Model. With respect to the selectivity of the biosorption, *C. salina* and *L. taylorii* showed a preference for the uptake of lead over cadmium, nickel, and zinc in a four-metal solution at the same molar concentration. In a three-metal system of cadmium, nickel, and zinc with *L. taylorii*, zinc was bound preferentially over cadmium and nickel. The capacity for nickel was the lowest. The optimum pH of sorption for *L. taylorii* was observed between pH 3 and pH 7. All metals can be quantitatively desorbed at pH 1, e.g. with 0.1 M hydrochloric acid. *L. taylorii* has been used successfully in a technical process for the purification of wastewater in the cooperation project (Wilke et al., this conference).

The cell wall of an alga consists of a variety of polysaccharides, some of which contain anionic carboxyl, sulphate, or phosphate groups. These are considered as binding sites of the metals. The surface of algae were characterized by elemental analysis and esterification of carboxyl groups and spectroscopic methods including FT-IR, scanning electron microscopy, and X-ray microanalysis. Esterification of carboxyl groups present in the cell walls resulted in a decrease in metal binding. These findings suggest that carboxyl groups are important in metal ion adsorption to these materials. Scanning electron microscopy in combination with X-ray microanalysis confirmed that the binding sites for the four metals are on the surface of the algae. X-ray microanalysis of the surface of *L. taylorii* also demonstrated the presence of high calcium content. Further sorption experiments on *L. taylorii* showed that the calcium is displaced by the metals during biosorption similar to an ion exchange process.

Capacity and selectivity of the binding of metals were studied by introduction of additional functional groups into the cell wall polysaccharides. Phosphorylation of *L. taylorii* has been the most successful method at the moment. The phosphate content of the algae could be increased from 0.6 mmol to 4.4

mmol phosphorus per gram biomass. The modified *L. taylorii* shows very good biosorption properties. *L. taylorii* showed maximum capacities of 3.22 mmol lead, 2.52 mmol cadmium, 2.91 mmol nickel, and 2.70 mmol zinc per gram of dry biomass. The desorption of the metals from phosphorylated biomass is in turn more difficult in comparison with the untreated *L. taylorii*. Tests showed that the metals can be desorbed with 3 M hydrochloric acid.

Biosorption by algae thus demonstrated itself to be an useful alternative to conventional systems for the removal of toxic metals from wastewater.

Key words: biosorption, algae, cadmium, lead, nickel, zinc



MECHANISMS OF AU(III) BINDING AND BIOREDUCTION BY ALFALFA BIOMASS

¹G. Gamez, ¹K. Dokken, ¹I. Herrera, ¹J.G. Parsons, ¹K.J. Tiemann, ²M.J. Yacaman, and ³J.L. Gardea-Torresdey, ^{1,3}Department of Chemistry and Environmental Sciences, University of Texas at El Paso, El Paso, TX 79968; ²Instituto Nacional de Investigaciones Nucleares, Mexico; ³Phone: (915) 747-5359, ³E-mail: jgardea@utep.edu.

Current precious metal recovery technologies that use harsh chemicals may represent a threat to the environment and public health. Thus, there is a necessity to develop environmentally friendly systems to retrieve precious metals. In previous experiments, dead alfalfa biomass has shown to be efficient for gold(III) recovery. Gold(III) binding to alfalfa biomass is rapid, pH independent, and increases with time and temperature. Furthermore, with X-ray absorption spectroscopy, alfalfa was found to reduce gold(III) to gold(0) and produces nanoparticles. Transmission electron micrographs showed

nanoparticles of several shapes and sizes. The reduction process was also found to be pH, time, and temperature dependent. In order to resolve the mechanism of both binding and reduction of gold(III) by alfalfa biomass, further experiments were performed. The effect of chemical modification of the alfalfa biomass on gold(III) binding and reduction was determined. Also, further X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy studies were performed to assess the oxidation state and nearest neighbor of the bound gold as a function of time. The results indicate that gold(III) goes to gold(I) and then to gold(0). Also, EXAFS shows that binding may occur via a nitrogen or oxygen ligand. Results of these experiments will be presented.

Key words: XANES, EXAFS, alfalfa, gold, phytofiltration, metal binding, chemical modification

Program Three Tuesday, May 23, 2000 Air Emissions Management



PHOTO-TREATMENT OF PERCHLOROETHENE IN SOIL VAPOR AT THE HARRISON ROAD LANDFILL, TUCSON, ARIZONA

¹Brian Barbaris, ²Eric Betterton, ³Robert Arnold, ³Wendell Ela, ³Laura Berry, ³Daniel Samorano, ³Karen Kerr, and ³Xiumin Ju, ^{1,2}Department of Atmospheric Sciences, The University of Arizona, Tucson, AZ 85721; ¹Phone: (520) 621-6832, ¹E-mail: barbaris@atmo.arizona.edu; ³Department of Chemical and Environmental Engineering, The University of Arizona, Tucson, AZ 85721; ³Phone: (520) 621-6044.

Perchloroethene (PCE) was scrubbed from contaminated landfill soil vapor by

contact with a 2-propanol/acetone solution (9:1 v/v) and then destroyed by exposure to sunlight in a photoreactor. The treatment system (scrubber and photoreactor) was deployed at the Harrison Road Landfill where soil vapor is being extracted and treated by the city of Tucson using a conventional granulated carbon absorption system. The 120-acre landfill is now closed and capped, but soil vapor containing 100-200 mg/L PCE (and other chlorinated organics) was readily obtained by diverting a small flow of soil vapor to the experimental treatment system. Exhaust gases were returned to the city's system ahead of the carbon absorption units.

In the experimental system, contaminated soil vapor is pumped at a rate of 1L/min. into the bottom of a 60 cm x 5 cm countercurrent column packed with ½" ceramic Berl saddles. PCE was stripped by dissolution in the 2-propanol/acetone mixture that flowed downward through the scrubber. Field data indicate that the scrubbing efficiency was approximately 90 percent. A number of other halogenated compounds, probably including TCE, Freon-11, and Freon-12, were also detected in the solvent.

The 2-propanol/acetone solvent, containing the scrubbed PCE, was pumped to the photoreactor, a series of four 1.2-m quartz or glass tubes (2.5cm diameter), where the PCE was destroyed by solar-promoted photolysis (Betterton et al., *Environ. Sci. Technol.*, accepted Jan. 2000). The photoreactor was designed for a theoretical detention time of one hour at a solvent flow rate of 50 mL/min. and a PCE destruction efficiency of >90 percent. The "spent" isopropanol/acetone solvent was then returned to the scrubber to close the loop.

Two types of field experiments have been conducted to date. In the first quasi-batch mode, the solvent was preloaded with PCE throughout the night and then exposed to sunlight while being recirculated in the photoreactor during the day (without further contact with the sol vapor). In the second,

continuous mode, both the scrubber and the photoreactor were operated simultaneously for extended periods of time. The effectiveness of the photoreactor was determined by comparing liquid-phase concentrations of PCE and other targets in the reactor influent and effluent. PCE concentrations are lowered by 90 percent or more in a matter of hours. Results also indicate that the reaction is inhibited by oxygen in the soil vapor (currently 10 percent due to the injection of air by city contractors). However, we were able to eliminate (photoreduce) interfering oxygen and also the PCE by increasing the number of photoreactor tubes.

We are in the process of identifying reaction intermediates detected by gas chromatography and also the final products of reaction. From the limited data to date, it is evident that scrubber design for any reasonable degree of contaminant transfer is feasible simply by increasing the gas/liquid contact time. The rate of photolysis could probably be increased by a factor of ten simply by adding parabolic reflectors to the system, thereby boosting treatment times to twelve minutes or less.

Key words: reductive dehalogenation, soil vapor, perchloroethene



EVALUATION OF COMBUSTION PROCESSES FOR PRODUCTION OF FEEDSTOCK CHEMICALS FROM AMMONIUM SULFATE AND AMMONIUM BISULFATE

¹Yvonne Liske, ¹Shubhen Kapila, ²Virgil Flanigan, ³Paul Nam, and ⁴Steve Lorbert, ¹Department of Chemistry, University of Missouri, Rolla, MO 65409; ²Department of Mechanical Engineering, University of Missouri, Rolla, MO 65409; ³Center for Environmental Science and Technology, University of Missouri, Rolla, MO 65409; ⁴Novus International L St. Louis. MO; ¹Phone: (563) 341-6187, ¹E-mail: kapilas@umr.edu; ²Phone: (573) 341-6606, ²E-mail: flanigan@umr.edu; ³Phone: (573) 341-6162, ³E-mail: nam@umr.edu; ⁴E-mail: sjlorb@novusint.com.

Several million tons of these chemicals are produced as by-products during a number of commercially important chemical manufacturing processes. At present, a large portion of these salts are disposed in deep wells at considerable cost to the chemical industry. These costs can be reduced or eliminated through the development of resource recovery technologies. Combustion-based technologies hold considerable potential in this area. The combustion of ammonium bisulfate and ammonium sulfate solutions was studied under various atmospheres in a combustion chamber designed in-house to recover the sulfur value. It was determined that varied sulfur species, such as sulfur dioxide (SO_2), hydrogen sulfide (H_2S), and carbonyl sulfide (COS) can be obtained quantitatively by manipulating the combustion stoichiometry in a single or two-stage burner configuration. Under near stoichiometric conditions, >95% of the sulfur value was recovered as SO_2 . However, traces (230 - 350 ppm) of nitrogen oxides were also obtained under these conditions. The reduced sulfur species H_2S and COS accounted for >95% of the total sulfur during sub-stoichiometric combustion. These species were readily

oxidized in a two-stage combustor to yield a NO_x free SO_2 stream. Two-stage combustion was achieved by installing a restrictor in the chamber, thus creating two stages. The combustor volume between the burner and the restrictor (the first stage) was maintained under reductive conditions and secondary air was added directly above the restrictor to create an oxidative atmosphere for the second stage. To enhance the versatility of the process catalytic conversion of H_2S and COS to methyl mercaptan, (CH_3SH) is being evaluated.

Key words: ammonium sulfate, ammonium bisulfate, combustion



IMPLICATIONS OF REDUCED SULFUR LEVELS IN FUELS

¹Kevin Brown and ²R.E. Babcock, ¹Sinclair Oil Corporation, Salt Lake City, UT; ²University of Arkansas, 3202 Bell Engineering Center, Fayetteville, AR 72701; Phone: (501) 575-4951, E-mail: reb@engr.uark.edu.

In May 1999, EPA published its proposal to reduce emissions from light-duty vehicles and light-duty trucks. The proposal, known as "Tier 2 Proposal," is to be phased in beginning 2004 and would also significantly reduce sulfur content in gasoline. Sulfur in gasoline reduces the effectiveness of a vehicle's emission control system.

The proposed sulfur levels in gasoline would require refiners to meet an average of 30 ppm by 2004, down from the current average of more than 300 ppm. The maximum amount of sulfur in gasoline for purposes of averaging would be capped at 80 ppm after a three-year phase-in. Small refiners would have an additional four years to comply.

EPA has designed its proposal in an attempt to provide flexibility for both the auto industry and the oil industry. One such flexibility allows for a market-based credit trading and banking system for both industries to

reward those who lead the way in reducing pollution. This paper discusses various process options available to refiners and the expected impact of each option.

Program Three
Tuesday, May 23, 2000
Fate and Transport



**THE IMPACT OF BIO-
DEGRADATION OF DEIC-
ING CHEMICALS IN
SAND COLUMNS ON THE
CONDUCTIVITY AND
DISPERSIVITY OF THE
POROUS MEDIA**

¹Angela Bielefeldt, ²Tissa Illangasekare, and
¹Rosanna LaPlante, ¹University of Colorado,
Campus Box 428, Boulder, CO 80309; ²Colo-
rado School of Mines, Dept. Env. Science &
Engrg., Golden, CO 80401-1887; ¹Phone:
(303) 492-8433, ¹Fax: (303) 492-6644;
²Phone: (303) 384-2126.

Deicing fluids applied to aircraft are becoming a concern as a source of environmental contamination. The mixture most commonly used as aircraft deicing fluid (ADF) is approximately 88% propylene glycol (PG), 2.5% surfactants and corrosion inhibitors, and water. PG may therefore be released into the environment at very high concentrations (on the order of 1,000 to 100,000 mg/L). PG is readily degradable by common soil bacteria, but if this glycol enters streams, dissolved oxygen could be completely removed thereby impacting aquatic life.

Studies are ongoing to determine what impacts bacterial degradation of PG and ADF have on the hydrologic characteristics of porous media. This is relevant in both natural soil where the deicers may be released and engineered biofilters used to treat the releases, such as those used at Norway's new interna-

tional airport. Experiments were conducted in packed columns (7 cm dia. x 15 cm tall) of sand that were pre-seeded with PG-degrading bacteria that were enriched from soil. In studies with unsaturated sand, the amount of PCJ removed increased with spilled concentration (from 1000 to 300,000 mg/L), but decreased as multiple pore volumes of PG or deicer were spilled.

In saturated column tests, aqueous solutions of ADF or pure PG were circulated through the columns using a peristaltic pump at a set flow rate. Changes in the hydraulic conductivity of the sand were measured over time, as calculated from the headloss across the sand at a measured flow rate. The breakthrough of slug injections of bromide were used to calculate the dispersivity. Effluent PG, chemical oxygen demand (COD) as a bulk carbon measurement, ammonia nitrogen, 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 with depth in the column.

Over the range of average loading conditions tested of 43 to 32,000 mg PG/d, there were faster declines in hydraulic conductivity with higher loading up until an inhibition threshold was reached at around 536 mg PG/d loading. At high loadings, the ADF mixture appeared somewhat more inhibitory than PG alone. The flow rate of water during the tests was also important, with higher flow rates resulting in less biomass accumulation and associated hydraulic conductivity decline. With the same average daily PG loading, hydraulic conductivity declined faster with a continuous inflow of the same concentration as compared to spikes of PG every 2 days. However, the final steady-state hydraulic conductivity was lower with the intermittent PG spikes. This may be due to a higher endogenous decay rate of the biomass in the continually loaded system versus the intermittently loaded system. Further investigation of this effect is underway. In all experiments it

was noted that the dispersivity, as calculated from bromide breakthrough curves, initially increased with biogrowth but later decreased as biofilms became more developed.

Using measured inlet and effluent PG data immediately before columns were sacrificed and biomass concentrations on the sand enabled the calculation of first-order PG biodegradation rates in the columns. These rates ranged from 0.6 to 1×10^{-5} L/mg bio-min. These rates are significantly slower than rates measured in batch tests with the suspended culture; pseudo first-order degradation rates averaged 1.4×10^{-4} L/mg bio-min. The rate difference is likely due to a combination of mass transfer through the biofilms and oxygen limitation.

Understanding the effects of bacterial growth in sand on the hydrodynamic properties of the media and the net biokinetics of the system will aid in predicting the fate of deicing compounds in the natural environment and engineered treatment biofilters. The potential for inhibition of bacterial activity at high concentrations is significant, as dilution may be required before bacteria can optimally degrade the contaminants.

Key words: biofilms, porous media, deicing fluid



EXPERIMENTAL INVESTIGATION AND MULTI-COMPONENT MODELING OF URANIUM TRANSPORT IN THE PRESENCE OF CITRIC ACID AND UNDER VARIABLE CONDITIONS

¹Cetin Kantar and ²Bruce Honeyman, ^{1,2}Colorado School of Mines, Environmental Science and Engineering Division, Golden, CO 80401; ¹Phone number: (303) 273 3420; ¹E-mail: ckantar@mines.edu; ²E-mail: bhoneyma@mines.edu.

The transport of contaminants in saturated porous media is governed by element speciation and the processes that act to trans-

port those species. Dissolved organic matter constitutes an important radionuclide-complexing ligand pool in most aquatic systems. In this study, the effects of citric acid (as a natural organic matter surrogate) on the transport of U(VI) in a saturated porous media were investigated with a series of batch and column experiments under variable system chemical conditions. Solutions containing U(VI) and citrate were introduced to the columns packed with quartz sand with an average particle size of 300 μ m. Our experimental results show that U(VI) transport was enhanced in the presence of citric acid, depending on system conditions such as pH and U(VI)/citric acid ratio. The U(VI) transport simulations were obtained using RATEQ (developed by Curtis and Rubin), a reactive transport code which incorporates a diffuse, double-layer surface-complexation model (SCM) with transport equations. The asymmetrical breakthrough curves were an indication of heterogeneous sorbent surface sites and/or a kinetically controlled adsorption/desorption surface reactions. Our transport simulations invoking kinetically controlled surface reactions successfully predicted this asymmetrical behavior. The coupled SCM/transport model improved our ability to accurately simulate the effects of uranium/citrate complexes on U(VI) transport relative to the use of distribution coefficients (K_d values) to quantify actinide/sorbent partitioning. Experimental results demonstrate that organic acid ligands may significantly enhance metal-ion transport through porous media.

Key words: uranium, citric acid, surface complexation, transport modeling



EVALUATION OF ATRAZINE BINDING TO SURFACE SOILS

¹Heather Lesan and ²Alok Bhandari, Department of Civil Engineering, Kansas State University, Manhattan, KS 66506-2905; ¹Phone: (785) 532-7717; ¹E-mail: hmlesan@ksu.edu; ²E-mail: bhandari@ksu.edu.

Triazine herbicides and their derivatives are major contaminants of surface water in the midwestern United States. Every spring 150 million pounds of triazine herbicides are applied to corn and grain sorghum fields in this region. Atrazine, (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is the most frequently applied chemical and is used extensively as a pre-emergent broad-leaf herbicide. Although atrazine and its partial degradation products are relatively mobile in soil, once applied they can associate with a variety of soil components including soil organic matter, soil solution, or the surfaces of suspended particulate matter such as colloids and humic or fulvic acids. Associations between organic matter and pesticides can result in either immobilization or enhanced transport of the contaminant, depending on the nature of the interaction. Our study focused on evaluating the nature of association of atrazine with two Kansas surface soils. The soils chosen were characterized as silty loams and belonged to the Woodson series. One soil was obtained from an agricultural field (3.4% organic matter) while the other was collected from an adjacent forested area (6.2% organic matter). U-ring-¹⁴C-labeled atrazine was used to improve detection limits and better track the distribution of the herbicide among various soil components. Bottle-point adsorption experiments with constant soil dosage were conducted for a period of 7 days followed by sequential extraction (desorption) with synthetic "surface water." The strongly adsorbed atrazine fraction was removed by multiple extractions with ethyl acetate. Next, the soil was extracted with

alkali under a nitrogen atmosphere. The organic matter removed by this method was fractionated into humic and fulvic acid components, and the atrazine associated with each component was determined. Finally, the herbicide remaining on the alkali-extracted soil was quantified by combusting the soil at 925°C and counting the ¹⁴CO₂ on a liquid scintillation counter. The effect of the presence of the soil enzyme, horseradish peroxidase, on the nature and extent of binding was also evaluated.

Key words: soil, pesticide, binding, atrazine, isotherms

Program Three Tuesday, May 23, 2000 Zero-Valent Metals



CONTAMINANT REMEDIATION BY IRON METAL: SHIFTING KINETIC REGIMES

¹Michelle Scherer, Jennifer Ginner, Pedro Alvarez, and Kathy Johnson, Department of Civil and Environmental Engineering, University of Iowa, 4016 Seamans Center, Iowa City, IA 52242; ¹Phone: (319) 335-5654, ¹E-mail: michelle-scherer@uiowa.edu.

Zero-valent metals such as iron, tin, and zinc, are moderately strong reducing agents that are capable of reducing many common environmental contaminants. Of these metals, granular iron metal has received a great deal of attention because of the pioneering work of Gillham and O'Hannesin. Early studies of reduction by iron metal focused primarily on chlorinated aliphatics (RC1), and, only recently, has the reduction of other compounds such as metals, nitrate, munition wastes, and pesticides received significant attention.

Despite the uncertainty regarding the identity of the actual reductant (i.e., Fe⁰, surface-bound Fe(II), or H₂) in iron-metal systems, it is clear that the transformation

process is a surface reaction which requires close contact of the reactive medium and the contaminant. Surface redox reactions are comprised of a series of physical and chemical processes including: (i) mass transport of the dissolved contaminant from a well-mixed bulk solution to the surface (ii) sorption of the contaminant to the surface (e.g., precursor complex formation or surface complex formation), (iii) transfer of electrons (ET) from the surface to the contaminant, and (iv) desorption of the contaminant from the surface. Any one of these four steps can limit the rate of contaminant reduction by Fe^0 .

To better explore the influence of each of these steps on rates of contaminant reduction by Fe^0 , we have used an electrochemical cell with an oxide-free Fe^0 rotating disk electrode (Fe^0 RDE). Earlier experiments conducted with the Fe^0 RDE clearly showed a negligible effect of mass transport on the overall reduction rate of carbon tetrachloride (CCl_4). Over the range of conditions of interest in environmental applications, however, both steps could influence the reaction rate, so it is not surprising that some evidence for mass transport effects has been reported in batch and column experiments.

A similar set of experiments with the Fe^0 RDE have been conducted with a series of nitrogen compounds, including nitrobenzene, nitrate, and nitrite. Results obtained with the Fe^0 RDE indicate a case of intermediate kinetics for these contaminants, where depending on the conditions of the environmental applications, either mass transport or reaction at the surface limits the overall rate of transformation. The implications of shifting between different kinetic regimes on the design and implementation of Fe^0 PRBs will be discussed.

Key words: nitrate, nitrite, nitroaromatics, permeable reactive barriers



DISSIMILATORY IRON-REDUCING BACTERIA CAN INFLUENCE THE REDUCTION OF CARBON TETRACHLORIDE BY IRON METAL

¹Robin Gerlach, ¹Al Cunningham, and ²Frank Caccavo Jr., ¹Center for Biofilm Engineering, Montana State University, 366 EPS Building, Bozeman, MT 59717-3980; ²Department of Microbiology, University of New Hampshire, Rubman Hall, Durham, NH 02824; ¹Phone: (406) 994-4770; ²Phone: (603) 862-2443.

Little is known about the long-term performance of zero-valent iron (Fe^0) subsurface barriers. Exposure to groundwater and contaminants induces corrosion processes that can passivate the Fe^0 surface and decrease barrier reaction rates. We present evidence that dissimilatory iron-reducing bacteria (DIRB) can stimulate the rate of carbon tetrachloride (CT) transformation in such cases. The DIRB, *Shewanella alga* BrY, adhered to Fe -surfaces that showed little or no capacity to transform CT. The addition of BrY to systems with decreased CT transformation rates resulted in increased ferrous iron concentrations and increased CT transformation to chloroform. The results suggest that DIRB can have an influence on the long-term performance of Fe^0 barriers for the remediation of chlorinated aliphatics.

Key words: zero-valent iron, iron-reducing bacteria, carbon tetrachloride, subsurface barrier



NITRATE REMOVAL USING WASTED INDUS- TRIAL IRON POWDER

¹Yong Huang and ²Tian Zhang, ^{1,2}Department of Civil Engineering, 205 PKI, University of Nebraska-Lincoln at Omaha Campus, Omaha, NE 68182-0178; ¹Phone: (402) 554-3565, ¹E-mail: yh_huang@hotmail.com; ²Phone: (402) 554-3784, ²E-mail: tzhang@unomaha.edu.

Batch experiments were conducted to investigate the mechanisms of nitrate reduction in an iron/water/nitrate system. Ten (10) ml serum bottles with rubber stoppers were used as reactors. Oxygen was excluded by using N₂ gas to purge the reactors. In each batch test, dozens of bottles were prepared. The tests were run under different initial conditions. The initial pH of each batch reactor was adjusted by adding HCl or NaOH. The batch reactors were put in a 1 ft. by 1.5 ft. box rotating at 30 rpm to provide complete mixing and reduce mass transfer resistance. At each predetermined time interval one reactor was sacrificed for analyzing pH, ORP, NO₃⁻, NO₂⁻, Fe²⁺, and Fe³⁺. The impacts of pH, iron (with or without magnetite coating), dissolved Fe²⁺, and magnetite powder on nitrate removal were studied.

The results indicate that two different mechanisms may be involved in nitrate removal. At low pH (2 to 4), Fe⁰ corrosion is necessary for nitrate reduction. In this case, Fe⁰ is the electron donor, and Fe²⁺ is the reaction product; NO₃⁻ acts as the electron acceptor and is reduced to NH₄⁺ (or N₂). Another mechanism is that, at pH 5 to 8, both dissolved Fe²⁺ and iron oxide (in a form of magnetite coated on the surface of granular iron) play a major role in nitrate degradation. In this process a black precipitate, presumably magnetite, was formed during nitrate reduction. The process shows a tendency of self-acceleration as the black precipitate is formed. It seems that the oxide film acts as a coordinating surface for the adsorption of Fe²⁺ and occurrence of electron transfer. The second

mechanism seems to indicate that regeneration of reactive sites, often a rate-limiting factor, may not be needed, and therefore, makes it very promising for wasted industrial Fe⁰ powder to be used for field-scale remediation of nitrate-contaminated groundwater. The results also indicate that, unlike the oxide coated on the granular iron surface, commercially available magnetite powder together with dissolved Fe²⁺ do not work for nitrate reduction. Therefore, special structures may be required for smooth electron transfer.

Key words: nitrate reduction, zero-valent iron, coordinating surface, pH, magnetite

Program One Wednesday, May 24, 2000 Phytoremediation--Exudates and Metals



INFLUENCE OF PLANT ROOT EXUDATES ON MICROBIAL POPULA- TIONS

Ken Yoshitomi and Jodi Shann, Department of Biological Sciences, University of Cincinnati, 614 Rieveschl, P.O. Box 210006, Cincinnati, OH 45221-0006; Phone: (513) 556-9765, E-mail: yoshitkj@email.uc.edu.

Phytoremediation has been investigated as a cost-effective 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 basic mechanisms contributing to this phenomena. In this study, the role of root exudates was explored. Specifically, the influence extracted plant exudates have on soil microorganisms.

Corn (*Zea mays L.*) was grown in a hydroponic apparatus designed to simulate soil while maintaining aseptic conditions. Soluble root exudates were allowed to flush through the system and over soil columns. Microbial

characterization of the soil columns was assessed by plate counts, microbial lipid analysis of biomass and activity, and their ability to mineralize a radiolabeled PAH, pyrene. Community shifts in their carbon source utilization profile were determined by Biolog™ GN analysis.

Results from the exudate amendment studies indicated that long-term application of exudates to bulk soil was able to enhance the microbial populations' potential to mineralize ¹⁴C-pyrene. However, stimulation of biomass and activity was minimal, suggesting that mere numbers or activity was not responsible for the increased mineralization. Multivariate analysis of Biolog™ GN plates revealed functional shifts in microbial communities between treatments. This data suggests exudate pressures may change the functional aspect of the community structure, favoring degrading populations of bacteria.

Current studies are further investigating the root exudate phenomena by addressing the influence of extracted root exudates on two different degrading genera of bacteria, a gram negative and a gram positive. Typically associated with different portions of the soil (rhizosphere vs. bulk soil), their responses to plant root exudates will help elucidate the role these exudates play for different types of bacteria. These studies will give a clearer understanding of the potential mechanisms controlling rhizosphere degradation.

Key words: *Zea mays*, root exudates, ¹⁴C-pyrene



LEAD HYPERACCUMULATION BY *SESBANIA DRUMMONDII*

¹Robert Barlow, ¹Natalie Bryant, ¹John Andersland, and ²Shivendra Sahi, ^{1,2}Department of Biology, Western Kentucky University, 1 Big Red Way, Bowling Green, KY 42101; Phone: ¹(270) 745-6012, ¹E-mail: Barlorl@wku.edu; ²E-mail: shiv.shai@wku.edu.

Sesbania drummondii is a leguminous plant commonly found in the southeastern United States. Our studies have shown that seedlings of *Sesbania drummondii* can hyperaccumulate lead (Pb) in a controlled hydroponic environment. The addition of a chelating compound (EDTA) further increases the amount of Pb that a seedling can accumulate. Pb-treated roots were analyzed with scanning and transmission electron microscopes equipped with energy dispersive X-ray spectrometers. Pb deposits were observed in concentric rings around the stele, on subepidermal cortical cells, and on the surface of the epidermis. The lead appeared to be localized within and on the cell wall. Phosphorus was present wherever lead was detected, suggesting that the lead precipitated as a lead phosphate. The data gathered suggests that it would be feasible to examine the Pb accumulating capabilities of *Sesbania drummondii* in a soil environment.

Key words: phytoremediation, lead, hyperaccumulation, *Sesbania*, and EDTA



CORROBORATION OF COPPER AND CHROMIUM UPTAKE BY CREOSOTE BUSH USING HYDROPONICS: SPECTROSCOPIC STUDIES

¹S. Arteaga, ¹R.R. Chianelli, ²J.L. Gardea-Torresdey, ³W.P. Mackay, and ⁴N.E. Pingitore, ^{1,2}*Departments of Chemistry and Environmental Science and Engineering, University of Texas at El Paso, El Paso, TX 79968; ³Department of Biology, University of Texas at El Paso, El Paso, TX 79968; ⁴Department of Geological Sciences, University of Texas at El Paso, El Paso, TX 79968; ²Phone: (915) 747-5359, ²E-mail: jgardea@utep.edu.*

Phytoremediation has developed as a potential remediation solution for contaminated sites. Also, phytoremediation takes advantage of the fact that plants may extract and concentrate particular elements from the environment. Creosote bush, or *Larrea tridentata*, is a common desert shrub of the Southwest, covering roughly 20 million acres from western Texas to California. This plant is found growing naturally in heavy-metal contaminated soils in the El Paso area. Previous investigations had found that this plant is able to accumulate and concentrate high amounts of copper and other metals from soils in its tissues. For this reason, this plant is considered to be a "hyperaccumulator." Creosote bush seedlings were exposed to two different concentrations of copper sulfate (63.5 ppm and 635 ppm) during 48 hours using hydroponics. Another set of plants were exposed to $K_2Cr_2O_7$ (520 ppm Cr^{+6}) and $Cr(NO_3)_3$ (520 ppm Cr^{+3}) for the same period of time. The roots, stems, and leaves of the plants were analyzed by atomic absorption spectroscopy giving positive copper and chromium uptake results. The different parts of the plants were analyzed using X-ray absorption spectroscopy. Also, the copper and chromium laden plant's tissues were analyzed with X-ray microfluorescence. Results of our experiments will be presented. We are currently performing experiments for the uptake of Cr^{+6} and Cr^{+3} by

living creosote bush seedlings. The results of those experiments will also be presented.

Key words: phytoremediation, soil contamination, creosote bush, XAS, XRMF

Program One Wednesday, May 24, 2000 Phytoremediation--Metals and Deicers



STUDY OF METAL UPTAKE AND PLANT GROWTH ON LIVE ALFALFA PLANTS GROWN IN SOLID MEDIA

¹J.R. Peralta, ¹K.J. Tiemann, ¹S. Arteaga, ¹E. Rascon, ¹J.G. Parsons, ¹E. Gomez, and ²J.L. Gardea-Torresdey, ^{1,2}*Department of Chemistry and Environmental Science and Engineering, University of Texas at El Paso, El Paso, TX 79968; ²Phone: (915) 747-5359, ²E-mail: jgardea@utep.edu.*

Heavy metals contamination is a troublesome environmental problem in many industrial countries, and phytoremediation technologies are promising solutions to clean a variety of pollutants. Preliminary studies have shown that live alfalfa plants (*Medicago sativa*) can survive in heavy metal-contaminated soils. Therefore, we decided to study the metal uptake abilities of live alfalfa plants using solid media. The objective of this study was to determine the effects of Cd(II), Cr(III), Cu(II), Ni(II), and Zn(II) on seed germination and plant growth in alfalfa. The heavy metal concentrations in the growth media varied from 0, 10, 20, and 40 ppm for each metal ion studied. Following two weeks of growth, germination rate, root, and shoot length were recorded along with the metal content. Results of these experiments indicate that Cd(II) concentrations reduced the shoot growth by 54%, 70%, and 100%, respectively. The results for the other metal ions studied also reduced growth respective to the increasing

metal content by the following amounts: Cr(III) 31%, 54%, and 93%; Cu(II) 12%, 37%, and 67%; Ni(II) 17%, 30%, and 63%. However, the presence of Zn(II) enhanced the growth of plants and it overpassed the control length by 4% with the doses of 10 and 20 ppm. The doses of 20 and 40 ppm of Cd(II), Cr(III), and Cu(II) affected the germination rate by more than 40%. These results indicate the feasibility of using live alfalfa plants in the remediation of moderately, heavy-metal contaminated soils.

Key words: phytoremediation, alfalfa, Medicago sativa, solid media



ENHANCED PHYTOREMEDIATION EFFICIENCY THROUGH PLANT BIOTECHNOLOGY

¹Elizabeth Pilon-Smits, ²Yong Liang Zhu, ³Kerry Hale, ³Marinus Pilon, and ⁴Norman Terry, ^{1,3}Department of Biology, Colorado State University, A/Z Building, Fort Collins, CO 80523; ^{2,4}Department of Plant and Microbial Biology, University of California at Berkeley, 111 Koshland Hall, Berkeley, CA 94720; ¹Phone: (970) 491-4991, ¹E-mail: epsmits@lamar.colostate.edu; ⁴E-mail: nterry@nature.berkeley.edu.

Phytoremediation, i.e. the use of plants for environmental cleanup, offers an attractive and cost-effective approach to remediate metal-polluted soils and waters. The goal of these studies is to use genetic engineering to increase metal tolerance and accumulation in plants, so as to create better plants for metal phytoremediation. In one of our studies, we have overproduced the metal-binding peptides glutathione and phytochelatins. Glutathione plays several important roles in the defense of plants against environmental stresses, and is the precursor for phytochelatins (PCs): heavy metal-binding peptides involved in metal tolerance and sequestration. Glutathione is synthesized in two enzymatic reactions, cata-

lyzed by glutamyl-cysteine synthetase (ECS), and glutathione synthetase (GS), respectively. To obtain plants with superior metal accumulation and tolerance, we overexpressed the *E. coli* ECS and GS enzymes in *Brassica juncea* (Indian mustard), a particularly suitable plant species for heavy metal remediation. The transgenic ECS and GS plants contained higher levels of glutathione and phytochelatins than the wildtype plants. The ECS and GS plants accumulated up to 3-fold more cadmium in their shoots than wildtype plants, and also showed enhanced cadmium tolerance. In another study, we overexpressed the key enzyme of the sulfate assimilation pathway, i.e. ATP sulfurylase (APS). The resulting APS plants accumulated significantly (up to 3-fold) more selenium, molybdenum, and sulfur than wildtype plants. We conclude that plant genetic engineering is a promising strategy for the production of plants with superior phytoremediation capacity. These transgenic plants are presently analyzed with respect to their tolerance and accumulation of other metals, and used in phytoremediation studies of metal-polluted mine drainage in Leadville.

Key words: phytoremediation, metals, selenium, phytochelatins



PHYTOREMEDIATION OF AIRCRAFT DEICER AND ANTIFREEZE FORMULATIONS

¹Sigifredo Castro, ²Lawrence Davis, and ¹Larry Erickson, ¹Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506; ²Department of Biochemistry, Kansas State University, Manhattan, KS 66506; ¹Phone: (785) 532-5584, ¹E-mail: scd5973@ksu.edu; ²Phone: (785) 532-6121.

Aircraft deicer fluids (ADF) and anti-freeze solutions are mainly constituted by either propylene or ethylene glycol and additives such as benzotriazole methyl substitution isomers (tolyltriazoles). The glycols are

present in concentrations that vary from 20 to 95 % and the triazoles at levels up to 1 g/L. The ADFs are used and discharged to the environment in large quantities, constituting a terrestrial and aquatic environmental risk. Although the *in situ* biodegradation of glycols has been achieved under controlled conditions, the breakdown products, (bio)degradation potential, and mode of toxicity of the triazoles remain uncertain. Triazoles are identified as possible carcinogens and inducers of toxic responses in aquatic flora and fauna. It is known that an enzyme able to degrade triazole is the lignin peroxidase, expressed by white-rot fungus, *Phanerochaete chrysosporium*. The enzyme is also the catalyst in the lignification process in higher plants, a fact that allowed us to propose a plant-based remediation process to economically detoxify the triazoles in the ADF. We found a threshold for toxicity of triazoles to common grass used at airports, and to sunflower, of about 0.1 mg/mL. Different methods to extract the triazoles from the treated plants were explored and it was not possible to recover them, indicating that the triazoles are being incorporated covalently to the plant structure. However, the presence of glycols in the ADF mixture generates an obstacle for the plant to immobilize the triazoles since during the biodegradation of the glycols, nutrient competition, nutrient deficiencies, and/or anaerobic conditions affect the normal development of plants. We are investigating ways to promote the biodegradation of both contaminants by modifying culture conditions and to determine the metabolic fate of the triazole.

Key words: deicer, glycol, triazole, biodegradation, phytoremediation

Program One Wednesday, May 24, 2000 Phytoremediation--Explosives and MTBE



PHYTOPHOTOLYSIS: A NEW MECHANISM FOR PLANT-BASED REMEDICATION OF RDX CONTAMINATION

¹Craig Just and ²Jerald Schnoor, ^{1,2}The University of Iowa, Department of Civil and Environmental Engineering, Iowa City, IA 52242; ¹Phone: (319) 335-5051, ¹E-mail: craig-just@uiowa.edu; ²Phone: (319) 335-5647, ²E-mail: gerald-schnoor@uiowa.edu.

The EPA describes phytoremediation as the direct use of living green plants for *in situ* risk reduction for contaminated soil, sludges, sediments, and groundwater, through contaminant removal, degradation, or containment. Phytoremediation has been utilized at many hazardous waste sites where more traditional remediation technologies are cost prohibitive. Uptake of explosive compounds, such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), by plants has been shown to occur at some U.S. Army installations including the Iowa Army Ammunition Plant (IAAP). An engineered wetlands system has been installed at IAAP to remediate contaminated soil and groundwater near Brush Creek. Research into the fate of RDX in wetland plants has been initiated to help determine what constitutes "success" in this application of phytoremediation.

Regulators have been inclined to declare a remediation strategy successful when the final concentration of the priority contaminant, in this case RDX, falls below a risk-based action level in the soil or water. For phytoremediation of RDX, this criterion may be inadequate due to the possibility of accumulation of RDX and/or RDX metabolites in plant tissues. Many plants, including poplar trees, reed canary grass, parrot feather, and

water plantain, have been shown to readily uptake and translocate RDX. Surveys by the University of Iowa at the IAAP showed RDX concentrations ranging from 0.5 to 2.9 mg/kg in plants growing in contaminated soil. Reed canary grass at the site showed the highest levels of RDX compared to other plant types. Reed canary grass has the highest water transpiration rate of the species sampled, which could explain the elevated RDX levels. It's also possible that reed canary grass accumulates more RDX than other plant species. Studies in our laboratory with ^{14}C -RDX and reed canary grass have provided evidence supporting the formation of formaldehyde within the plants with subsequent loss of the atmosphere. The proposed mechanism of transformation, termed "phytphotolysis," involves the translocation of contaminants to the leaves of plants with subsequent photolysis due to light exposure. This new phytoremediation mechanism could prove useful for treatment of photoactive compounds in shallow groundwater that might otherwise not be exposed to sunlight.

Key words: phytphotolysis, RDX, wetlands, IAAP, formaldehyde



BIOTRANSFORMATION OF 2,4,6-TNT IN PHYTOREMEDIATION SYSTEMS: CONJUGATION AND OXIDATION

¹R. Bhadra, ²R.J. Spanggord, ³J.V. Shanks, and ⁴J.B. Hughes, ¹Dept. of Chemical & Bioresource Engineering, Colorado State University, Ft. Collins, CO;

²Biopharmaceutical Development Division, SRI International, Menlo Park, CA; ³Dept. of Environmental Science & Engineering, Rice University, Houston, TX; ⁴Dept. of Chemical Engineering, Iowa State University, Ames, IA; ¹Phone: (970) 491-2227, ²E-mail: rajivb@lamar.colostate.edu.

The cleanup of explosives-contaminated soil and water at numerous defense-sector

facilities continues to be a serious challenge due to the recalcitrance of explosives in the environment. The primary culprit is the nitroaromatic compound 2,4,6-trinitrotoluene (TNT) and related synthesis by-products. Phytoremediation or plant-driven bioremediation is gaining prominence as a viable, low-cost option for the amelioration of TNT-contaminated media. This paper presents studies that elucidate pathways of biotransformation of TNT in plants, other than and beyond initial reduction of TNT, namely conjugation and oxidation of TNT and metabolites. These aspects of nitroaromatic metabolism in phytoremediation systems have remained largely uninvestigated, but constitute significant metabolic fate as evidenced by our findings.

Our previous studies with the aquatic species (*Myriophyllum aquaticum*) and axenic root cultures (of the terrestrial plant, *Catharanthus roseus*) have shown the significant activity of the reductive pathways, leading to the formation of 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene. Beyond the initial reduction of TNT, our present studies with axenic roots of *C. roseus* show that biotransformation of reduced TNT derivatives occurs by plant-specific conjugation processes, where a plant-associated carbon skeleton is added to the aryl-amino group. Conjugated derivatives of both 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene have been isolated from the biomass and aqueous phase, and characterized by HPLC-UV, ^1H - and ^{13}C -NMR spectroscopy, and mass spectroscopy. The conjugated derivatives of TNT represent significant metabolic fate in plants and conform to models of xenobiotic metabolism in plants.

Since reduction products and their conjugates do not completely account for TNT disappearance from the contaminated phase, TNT metabolism in plants was also investigated for possible oxidative transformation. These studies were conducted with the aquatic plant *M. aquaticum*. TNT-metabolites were isolated from the aqueous matrix, providing

conclusive evidence for oxidation of the ring-substituted methyl-group and aromatic hydroxylation. These compounds include 2-amino-4,6-dinitrobenzoic acid; 2,4-dinitro-6-hydroxy-benzyl alcohol; 2-N-acetoxyamino-4,6-dinitrobenzaldehyde; and 2,4-dinitro-6-hydroxytoluene. It is possible that oxidative transformation(s) preceded nitro-reduction since studies on exposure of *M. aquaticum* to either 2-amino-4,6-dinitrotoluene or 4-amino-2,6-dinitrotoluene did not yield any of the oxidized products identified. The accumulation of oxidized products was significant: 2-amino-4,6-dinitrobenzoic acid, 4.4%; 2,4-dinitro-6-hydroxy-benzyl alcohol, 8.1%; 2-N-acetoxyamino-4,6-dinitrobenzaldehyde, 7.8%; and, 2,4-dinitro-6-hydroxytoluene, 15.6%. These studies, and their implications of the findings to the environmental fate and phytoremediation applications for explosives, will be discussed.

Key words: explosives, phytoremediation, metabolism, fate, wetlands



PHYTOREMEDIATION OF METHYL-TERT- BUTYL-ETHER (MTBE)

¹Ellen Rubin and ²Anu Ramaswami, ^{1,2}Department of Civil Engineering, University of Colorado-Denver, Campus Box 113, PO Box 173364, Denver, CO 80217; ¹Phone: (303) 556-4734, ¹E-mail: Rubin.ellen@epa.gov; ²E-mail: aramaswa@carbon.cudenver.edu.

Methyl-tertiary-butyl-ether (MTBE) is used as a gasoline additive in EPA's oxyfuels program. MTBE in fuel can help control air pollution, but it is a potential water and groundwater pollutant. MTBE has been found widespread across the nation in municipal supply wells, irrigation wells, and groundwater monitoring wells.

MTBE is very water-soluble and does not sorb much to soil; it is also essentially non-biodegradable and non-reactive in water. Therefore, once MTBE gets into water, an

MTBE plume develops rapidly that is difficult to remediate by conventional methods. Phytoremediation is an innovative technology that utilizes plant systems to remediate hazardous waste sites. Phytoremediation is an efficient mechanism of contaminant removal for compounds whose octanol-water partition coefficient, $\log K_{o/w}$, is between 1 and 3. Since the $\log K_{o/w}$ for MTBE is 1.24, which is in the range that is readily transpired in plants and trees, phytoremediation may be a feasible remedial technique for subsurface MTBE plumes. Plants and trees may transpire many volatile-organic compounds (VOCs) into the air. While MTBE does not degrade in soil, atmospheric MTBE reacts with hydroxyl radicals in air, yielding a half-life in the order of days. Thus, transpiration of MTBE from the subsurface to air via plants can offer a low-cost method for destruction of the pollutant to benign products. Currently, there is no data available for removal of MTBE from water due to plant transpiration.

The objective of this project is to examine the potential for phytoremediation of MTBE-contaminated waters using poplar trees. Poplar trees (*populus deltoids x nigra*) were selected for this project because they are hardy, rapid-growing phreatophytes. A closed-chamber system was developed to quantify MTBE movement through the poplar tree's roots, shoots, leaves, and finally to the air. Experimental data showed the following:

- ◆ 69-80% reduction in MTBE mass.
- ◆ 46-56% reduction in MTBE concentration.
- ◆ MTBE was extracted from plant roots and shoots at a concentration of 5-10 ppb, indicating MTBE movement through the plant.

These results indicate that MTBE was readily taken up by hybrid poplar saplings in the laboratory. Ongoing experiments are evaluating MTBE phytoremediation in larger-scale soil-water systems.

Key words: phytoremediation, MTBE

Program One
Wednesday, May 24, 2000
Phytoremediation--Sediments and Sludges



VEGETATED TREATMENT OF VEHICLE WASH SEDIMENTS: DESIGN OF A MULTI-MEDIA AID DECISION SUPPORT SYSTEM

¹Suzette Burckhard, ²Kipp Thompson, ²Vernon Schaefer, ³Peter Kulakow, ⁴Blase Leven, and ⁵A. Paul Schwab, ^{1,2}Civil and Environmental Engineering Department, Box 2219, South Dakota State University, Brookings, SD 57007; ³Department of Agronomy, 2004 Throckmorton Plant Science Center, Kansas State University, Manhattan, KS 66506; ⁴Great Plains/Rocky Mountain HSRC, 101 Ward Hall, Kansas State University, Manhattan, KS 66506; ⁵Department of Agronomy, Purdue University, West Lafayette, IN 47907-1284; ¹Phone: (605) 688-5316, ¹E-mail: suzette_burckhard@sdstate.edu; ³Phone: (785) 532-7239, ³E-mail: kulakow@ksu.edu; ⁴Phone: (785) 532-0780, ⁴E-mail: baleven@ksu.edu; ⁵Phone: (965) 496-3602, ⁵E-mail: paul_schwab@hotmail.com.

The design of a vegetated treatment system requires a vast amount of knowledge regarding plants, climate, soils, contaminants, and their interactions. Most practicing environmental professionals do not have this background. As a method to bridge the gap of knowledge needed in designing a vegetated treatment option, a series of decision support tools were designed. The first tool was an introductory pamphlet of information regarding vegetated treatment options. The second tool was a decision support tree to help environmental professionals choose vegetation types for a particular site. The third tool is a

graphical user interface decision support system that will allow the environmental professional to calculate specific parameters, such as time of treatment, regarding the site. The last tool is a manual detailing answers to various questions regarding vegetated treatment options. In this presentation, a multimedia decision support system, combining these tools, will be shown. A short introduction to the problem and the need for this solution will be followed by a demonstration on the use of the product for a particular case study. Additional information regarding product development will be covered as needed during the presentation.

Key words: phytoremediation, petroleum hydrocarbons, contaminated soil, vegetation



VEGETATED TREATMENT OF VEHICLE WASH SEDIMENTS: A FIELD DEMONSTRATION

¹R. Kathikeyan, ¹K.R. Mankin, ²Peter Kulakow, ²G. Pierzynski, ³Blase Leven, and ³Larry Erickson, ¹Department of Biological and Agricultural Engineering, Seaton Hall, Kansas State University, Manhattan, KS 66505; ²Department of Agronomy, 2004 Throckmorton Plant Science Center, Kansas State University, Manhattan, KS 66506-5501; ³Great Plains/Rocky Mountain HSRC, 101 Ward Hall, Kansas State University, Manhattan, KS 66506; ¹Phone: (785) 532-2923, ¹E-mail: karthi@ksu.edu; ²Phone: (785) 532-7239, ²E-mail: kulakow@ksu.edu; ³Phone: (785) 532-6519, ³E-mail: baleven@ksu.edu.

Army training reservations contain vehicle wash facilities where combat and other equipment are washed after field maneuvers. During this process, sediments containing significant concentrations of petroleum hydrocarbons accumulate in concrete sedimentation basins. Conventional treatment methods to decontaminate these sediments include landfill

disposal or land application. However, vegetative remediation systems may offer a cost-effective alternative. A phytoremediation design that reduces petroleum hydrocarbons to acceptable levels and is simple to implement and maintain was developed for the Central Vehicle Wash Facility (CVWF), Fort Riley, Kansas. This paper presents a brief outline of site characterization, vegetation treatment system design, and complete results for a two-year study.

Key words: phytoremediation, petroleum hydrocarbons, contaminated soil, vegetation



EXPERIMENTAL AND MODELING STUDIES ON JET FUEL MOVEMENT IN VEGETATED SOIL COLUMNS

¹R. Karthikeyan, ²Lawrence Davis, ³Larry Erickson, and ⁴K.R. Mankin, ^{1,4}Department of Biological and Agricultural Engineering, 147 Seaton Hall, Kansas State University, Manhattan, KS 66506; ¹Phone: (785) 532-2923; ¹Phone: (785) 532-2911; ²Department of Biochemistry, Kansas State University, Manhattan, KS 66506; ²Phone: (785) 532-6124; ³Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506. ³Phone: (785) 532-4313; ⁴Department of Biological and Agricultural Engineering, Kansas State University, Manhattan, KS 66506; ⁴Phone: (785) 532-2911.

Jet fuels are supplied in several different grades to the U.S. Army. The U.S. Army switched from using JP-4 to using JP-8; the fate of JP-8 is not yet known in soil systems. A preliminary experiment was conducted for six months to study the fate of JP-8 in vegetated soil chambers and columns. The results suggested that biodegradation is also a major fate of JP-8 in vegetated columns. Another study is underway to assess the influence of plant-induced upward water movement on JP-8 transport and biodegradation in soils. Six soil columns, three of which are planted with

6-8 alfalfa plants and three of which are unplanted, are used to study the fate of JP-8. A constant groundwater table is maintained at 10 cm from the bottom of the column, and a 10 cm contaminated layer is placed on top of the groundwater table. The rest of the column is filled with clean soil. This paper will present the experimental and modeling results of the study.



THE ROLE OF VEGETATION IN THE PHYTOREMEDIATION AND ECOLOGICAL RECOVERY OF HAZARDOUS WASTE SITES

¹Paul Olson and ²John Fletcher, ¹Biology Department, Colorado State University, E414 A/Z Building, Ft. Collins, CO 80523; ²Department of Botany and Microbiology, University of Oklahoma, 770 Van Vleet Oval, Norman, OK 73019; ¹Phone: (970) 491-3320, ¹E-mail: peolson@lamar.colostate.edu; ²Phone: (405) 325-3174, ²E-mail: jfletcher@ou.edu.

Examination of volunteer vegetation growing in industrial sludge contaminated with polycyclic aromatic hydrocarbons (PAHs) has been used as a means of identifying particular plant species whose roots foster soil restoration and the degradation of organic contaminants. Aerial photographs taken over the last 25 years have been used to characterize plant invasion and plant succession that has resulted in the development of a diverse and healthy community of plants (51 species from 22 families) currently growing at this contaminated site. Differences between the plant community composition at the contaminated sludge basin and a non-contaminated site suggested that a select group of plants have favorable characters that the presence of plant roots growing in the contaminated sludge corresponded with a visual soil restoration and dissipation of recalcitrant PAHs. The distribution and depth of plant roots from tolerant vegetation growing at this former sludge basin were species and age dependent. In general,

tree and shrub roots penetrated the sludge to a greater extent (~90 cm), compared to grasses (~50 cm) and forbs (~60 cm) at this site. However, PAH levels were significantly lower within the root zone (10-25% the concentration present beneath the root zone) regardless of the vegetation compared to the non-rooted sludge. Thus tolerant vegetation invaded and colonized a former sludge basin, and through extensive root growth, fostered the natural attenuation and ecological recovery. The results from this study support the concept that an established plant community with associated microorganisms provides an ecologically stable, low cost, sustained bioremediation system for long-term treatment of sludge basins.

Key words: phytoremediation, polycyclic aromatic hydrocarbons (PAHs), bioremediation, plant invasion and succession, ecological recovery

Program Two
Wednesday, May 24, 2000
Bioavailability and Risk



**SOXHLET AND MICRO-
WAVE EXTRACTION IN
DETERMINING THE
BIOACCESSIBILITY OF
PESTICIDES FROM SOIL
AND MODEL SOLIDS**

¹Barbara Kramer and ²P. Barry Ryan, ¹Department of Chemistry, Emory University, Atlanta, GA 30322; ²Rollins School of Public Health, Emory University, Atlanta, GA 30322; ¹Phone: (404) 727-9259, ¹E-mail: bkram01@emory.edu; ²Phone: (404) 727-3826, ²E-mail: bryan@sph.emory.edu.

The inadvertent ingestion of contaminated soil can be an important source of pesticide exposure, especially in young children. The actual level of a pesticide that is available for absorption into a biological

system may be much lower than the overall contamination level due to the interaction of each chemical with the solid matrix. This bioaccessibility is dependent on characteristics of the chemical species as well as the soil type and residence time of the compound in the soil. In an effort to improve understanding of this phenomenon, we report a comparison of the recoveries of pesticides spiked into three model solids, as well as soil using different analytical extraction techniques, microwave-assisted extraction (MAE), and Soxhlet extraction. The efficiencies of these techniques are further compared to the results of a physiologically based extraction test (PBET) that estimates the bioaccessibility of each compound to examine the potential use of each extraction technique in bioavailability studies.

Key words: bioaccessibility, pesticides, soil, extraction



**FLUORIDE OCCURRENCE
IN TAP WATERS AT "LOS
ALTOS DE JALISCO" IN
THE CENTRAL MEXICO
REGION**

¹R. Hurtado and ²J.L. Gardea-Torresdey, ^{1,2}Department of Chemistry and Environmental Science and Engineering, University of Texas at El Paso, El Paso, TX 79968; ²Phone: (915) 747-5359, ²E-mail: jgardea@utep.edu.

Fluoride content in tap water presents public health risks, mainly when the contents are over the regulation limits. The toxic effects of fluorides include enzyme damage, which results in a wide variety of chronic diseases. There are numerous scientific studies linking fluoride to increased risk of hip fracture, cancer, genetic damage, bone pathology, premature aging, and dental *Fluorosis*, among other health risks. In Mexico, the maximum allowable level of fluoride in drinking water is 1.5 mg/L. The objective of this study was to determine the fluoride content in drinking water from more than 20 sites located in "Los Altos de Jalisco" in the Central Region of

Mexico. Water samples were obtained from wells and surface reservoirs following proper sampling procedures. The samples were analyzed electrochemically, using the approved US EPA ion-selective method (Method 340.2). "Los Altos de Jalisco" is located in the neovolcanic belt of the Central Mexico Region where most of the waters have a natural content of fluoride. Based on the results of this study, the content of fluoride in some cities such as Mezticacan (7.5 mg/L), Encarnacion de Diaz (4.3 mg/L), Lagos de Moreno (4.8 mg/L), Temacapulin (11.4 mg/L), and Tepatitlan (6.8 mg/L) represents a serious health risk and should be of major concern. This presentation will discuss the geochemistry of the waters and will present some methods or suggestions for the defluoridation of the water of each locality.

Key words: fluoride, fluorosis, defluoridation, public health, ion-selective



ESTIMATING RESIDENTIAL INDOOR AIR IMPACTS DUE TO GROUNDWATER CONTAMINATION

*David Kurz, EnviroGroup Limited, 7208 S. Tucson Way, Suite 125, Englewood, CO;
Phone: (303) 790-1340, E-mail:
dkurz@envirogroup.com.*

This paper presents information on the reliability of making risk-based corrective action (RBCA) decisions using ASTM methods for groundwater remediation and indoor air mitigation in residences located over a shallow groundwater plume contaminated with chlorinated compounds, based on the predicted concentrations of the compounds in indoor air.

Indoor air quality (IAQ) testing results for 153 residential homes in 1998 at a site in Denver, Colorado, were evaluated in this study. The homes overlie groundwater with 1,1 DCE concentrations ranging up to approximately 1,000 $\mu\text{g/L}$, resulting from the degradation of both 1,1,1 TCA and TCE.

Concentrations of 1,1 DCE in indoor air ranged up to 91 $\mu\text{g/m}^3$ in residences located over the plume and were generally below detection in homes beyond the detectable groundwater plume. Variance of results from house to house is significant (plus or minus an order of magnitude in some cases), due to site-specific geological, building, and ventilation factors.

One method that could have been used to decide whether indoor air mitigation systems or groundwater remediation were necessary was the Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites (ASTM E1739-95). Indoor air concentrations were calculated considering the 1,1 DCE concentration in groundwater, the depth to groundwater, and effective diffusion coefficients for the progressive movement of 1,1 DCE from the groundwater surface to the capillary fringe to the vadose zone through foundation/slab cracks into the residential structure at each location.

The probability of false negatives (i.e., homes above the action level being predicted to be below the action level) was evaluated for the homes in this study using the actual IAQ test results for 1,1 DCE. The overall false negative rate was approximately 10%. However, this rate was not consistent across the range of 1,1 DCE concentrations in the groundwater plume. The rate of the false negative decisions appeared to be correlated to the concentrations of 1,1 DCE in the groundwater. IAQ testing demonstrated that the estimates yielded false negative rates varying from 5%, in homes above groundwater with 1,1 DCE concentrations below 10 $\mu\text{g/L}$, to over 50%, in homes above groundwater with 1,1 DCE concentrations of 50 $\mu\text{g/L}$. At 1,1 DCE concentrations greater than 100 $\mu\text{g/L}$ in groundwater, there would have been no false negative decisions, but the false positive rate was approximately 15%. Based on the results of this evaluation, indoor air quality (IAQ) testing should be used, rather than RBCA predictive modeling, to establish the extent of impacts and determine the need for mitigation.

Key words: risk, residential, decisions, chlorinated, groundwater

Program Two
Wednesday, May 24, 2000
NAPLs



**LNAPL DISSOLUTION IN
AQUEOUS LIQUID:
LABORATORY COLUMN
EVALUATION AND NU-
MERICAL SIMULATION**

^{1,2}Dongping Dai, ¹Tissa Illangasekare, and
^{2,3}John Ewing, ¹Environmental Science and
Engineering Division, Colorado School of
Mines, Coolbaugh Hall, 14th and Illinois St.,
Golden, CO 80401; ²Duke Engineering &
Services, 9111 Research Blvd Austin, TX
78758; ¹Phone: (303) 384-2126, ¹E-mail:
tillanga@mines.edu; ²Phone: (303) 384-
2237, ²E-mail: ddai@mines.edu; ³Phone:
(512) 425-2065, ³E-mail:
jeewing@dukeengineering.com.

Understanding of the fate and transport of nonaqueous-phase liquid (NAPL) and dissolved NAPL constituents, such as BTEX, is important in design and implementation of NAPL-contaminated site cleanup. This laboratory column study is designed to better understand dissolution of BTEX from the LNAPL at low saturation into water at one-dimension, and scale up to the larger scale with numerical simulation.

Soil cores and LNAPL from an LNAPL-contaminated site were used in the column test. Segments of the core were packed into columns in eight, 3-inch sections, each column section facility with ports for both sampling and monometer. This design made possible evaluating dissolution at a range of sample lengths during one column test. The residual LNAPL saturations of the columns were estimated with a partitioning tracer technique at the beginning of the dissolution process for

each column section, as well as the entire column.

From the scan of the dissolved hydrocarbons, primarily BTEX over time, the relationship between NAPL saturation, aqueous-phase velocity, length-of-dissolution path, and dissolution rate were determined. This correlation provides critical input for a numerical model (UTCHEM) to simulate the dissolution in one dimension, and coupled with scale relationships developed numerically, the mass transfer correlation of large systems are predicated.

Key words: dissolution, saturation, transport, dimension, simulation



**A PROTOCOL FOR
MULTI-PHASE NUMERICAL
MODEL VALIDATION**

¹Tarek Saba and ²Tissa Illangasekare, ^{1,2}Division of Environmental Science and Civil Engineering, Colorado School of Mines, Golden, CO 80401-1887; ¹Phone: (303) 273-3483, ¹E-mail: saba@bechtel.colorado.edu; ²Phone: (303) 384-2126, ²E-mail: tillanga@mines.edu.

The lack of understanding of the complex behavior of nonaqueous-phase liquids (NAPLs) in heterogeneous systems has resulted in improper model conceptualization and validation. The primary goal of a project currently in progress is to develop a protocol for validation of multi-phase flow models. Data that focuses on the influence of heterogeneity on the behavior of NAPLs in the subsurface will be compiled. This data on NAPL subsurface entrapment and dissolution will be placed in a data bank. Candidate numerical models that simulate NAPL behavior in the subsurface, including FEHM, TOUGH2, and UTCHEM, will all be studied and used in this research.

This paper presents results from a preliminary investigation where simulations are performed on dissolution of entrapped NAPLs.

Results show the sensitivity of different models to input parameters and the resulting effects on the model predictions. These results will be used to develop guidelines on tolerances in input data errors and the resulting model outputs. Future studies will demonstrate a systematic approach to define which physical and chemical parameters are important in model applications involving regulations and design. The findings of this work will help researchers in the identification of the critical parameters in subsurface NAPL investigations and will aid in improving technologies and characterization methods to obtain these parameters in the field.

Key words: multi-phase, NAPL, dissolution, numerical, models



A MULTI-SCALE LABORATORY ASSESSMENT OF CLEANUP ENDPOINT FOR A NAPL-CONTAMINATED SITE

¹Frank Barranco Jr., ²Tarek Saba, ³Dongping Dai, ⁴Tissa Illangasekare, ⁵Denton Mauldin, ⁶Ken Vogler, and ⁷Mike Klein, ^{1,2,3,4} Environmental Science and Engineering Division, Colorado School of Mines, Coolbaugh Hall, 14th and Illinois St., Golden, CO 80401; ^{5,6,7}Safety-Kleen Consulting, 5665 Flatiron Parkway, Boulder, CO 80301; Phone: (303) 938-5500; ⁵E-mail: Dmauldin@Safety-Kleen.com; ¹Phone: (303) 384-3427, ¹E-mail: fbarranc.@mines.edu; ²E-mail: tsaba@mines.edu; ³E-mail: ddai@mines.edu; ⁴E-mail: tillanga@mines.edu; ⁶E-mail: Kvogler@Safety-Kleen.com; ⁷E-mail: Mklein@Safety-Kleen.com.

Pore-scale, meso-scale, and pilot-scale studies have been conducted in the laboratory to assess the performance of several subsurface restoration technologies for their potential to meet groundwater beneficial use requirements outlined in a Record of Decision for a petroleum-contaminated site. Pilot studies at the field scale were deemed infeasible due to

the inability to fully characterize subsurface heterogeneities and the resulting distribution of light nonaqueous-phase liquid (LNAPL). Remedial Action Objectives in the interim locality of the site were geared toward restoring groundwater to domestic and industrial nonconsumptive use, and protecting current and future users from pumping well impacts caused by diesel fuel in the form of LNAPL and/or hydrocarbon sheen. Because compliance with beneficial-use criteria required an understanding of the conditions influencing mobilization and entrapment of nonaqueous-phase hydrocarbons, controlled laboratory studies have been performed to determine LNAPL residual saturation resulting in no free hydrocarbon mobilization from representative soil samples. Measured residual saturation was utilized, subsequently, as an “endpoint hydrocarbon saturation” for evaluating whether specified restoration technologies sufficiently reduced LNAPL saturation to endpoint levels. Because of the high degree of spatial variability of soil characteristics in the subsurface at the study site, it was expected that end-point conditions, as defined by residual LNAPL saturation, would also vary spatially at the field scale. In order to incorporate this variability, the laboratory experiments (to determine residual LNAPL saturation and to assess the performance of several subsurface restoration technologies) were conducted within intermediate-scale experimental cells. Production of free product and/or aqueous sheen from an array of sampling ports was spatially and temporally correlated to LNAPL saturation within the cells to assess endpoint compliance for the technologies evaluated. This information is beneficial for use with future field-pilot studies and determining the feasibility and performance of applicable restoration technologies.

Key words: NAPL, technology assessment, remediation, endpoints

Program Two
Wednesday, May 24, 2000
Metals Remediation



KINETICS OF CHROMATE REDUCTION BY CARBONATE GREEN RUST

¹Aaron Williams and ²Michelle Scherer,
^{1,2}Department of Civil & Environmental
Engineering, University of Iowa, 4016
Seamans Center, Iowa City, IA 52242;
Phone: (319) 335-5654, ¹E-mail:
aaron@zeus.ia.net; ²E-mail: michelle-
scherer@uiowa.edu.

Recently, interest in abiotic redox reactions at iron oxide-water interfaces has increased significantly because of their importance in natural attenuation processes and engineered remediation technologies. Specifically, transformation of contaminants by green rusts has emerged as a possible transformation pathway in both anoxic environmental systems (i.e., soils, sediments, and aquifers) and remediation technologies based on reduction by iron metal. Green rust minerals are mixed-valent iron hydroxides composed of positively charged octahedral sheets with interlayers containing anions such as chloride, sulfate, and carbonate. The significance of transformation by green rusts in these systems, however, is still unclear. The identification of green rust minerals in both systems has been limited due to their rapid oxidation when removed from reductomorphic or anoxic environments. Although synthesized green rusts have been shown to reduce some hazardous chemicals (e.g., nitrite, selenium, and carbon tetrachloride), the mechanisms and kinetics of these reactions are not well known.

To this end, we are investigating the reduction of chromate by carbonate green rust. Carbonate green rust is synthesized in an anaerobic glove box, freeze dried, and characterized by x-ray diffraction (XRD) and

Mössbauer Spectroscopy to verify its structure and composition. Preliminary experiments reveal chromate removal rates that are both rapid (half-lives less than ten minutes) and directly proportional to the concentration of green rust. The strong influence of green rust concentration on chromate disappearance confirms that the transformation is surface-mediated. Investigation into the role of adsorption and ion exchange of chromate with green rust interlayer anions has revealed that these processes appear to be limited or not occurring due to the rapid reduction of chromate by either structural or surface bound Fe(II) on the green rust. Further work is underway to identify the properties and structure of the Cr(III) precipitate; previous research suggests this is a Fe,Cr(OH)₃ oxide. Additional research is underway to evaluate the effect of pH, mixing intensity, and initial chromate concentration.

Key words: green rust, chromate, abiotic reduction, reduced-iron minerals



REMOVAL AND RECOVERY OF CR(III) AND CR(VI) WITH ALFALFA BIOMASS

¹K. Dokken, ¹K.J. Tiemann, ¹G. Gamez, ¹J.G. Parsons, ¹I. Herrera, ²J.L. Gardea-Torresdey, and ³N.E. Pingitore, ¹Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968; ²Department of Environmental Science and Engineering, University of Texas at El Paso, El Paso, TX 79968; and ³Department of Geological Sciences, University of Texas at El Paso, El Paso, TX 79968; ²Phone: (915) 747-5359, ²E-mail: jgardea@utep.edu.

Contamination of ground and surface waters by trivalent and hexavalent chromium has become a great health risk to the public due to increased industrial activity over recent years. Current technologies used to remediate chromium contamination pose a threat to the environment and are costly. A more environmentally friendly and cost-effective alternative

utilizes plant or bacterial matter as biosorbents for chromium remediation. Alfalfa is a possible biosorbent because of its affinity for trivalent and hexavalent chromium under single-metal and mixed-metal conditions. In addition, we have found that alfalfa reduces hexavalent chromium to trivalent chromium which was characterized through x-ray absorption near-edge structure (XANES) spectroscopy and extended x-ray absorption fine-structure (EXAFS) spectroscopy. However, a problem commonly encountered in ion exchange resins, as well as biosorbents like alfalfa, is the recovery of chromium after adsorption. Some stripping agents provide low recoveries while others damage the biosorbent which, in each case, affects recyclability of the biosorbent. In this study we investigated the use of a wide array of stripping agents such as dilute acids and bases under batch experimental conditions. Also, flow studies using silica-immobilized biomass were used to further investigate the ability of various stripping agents to recover hexavalent and trivalent chromium. The results of these experiments will be presented.

Key words: XANES, EXAFS, alfalfa, chromium, recovery, metal binding, stripping agents



FORMATION AND STABILITY OF SUBSTITUTED PYROMORPHITES: A MOLECULAR MODELING APPROACH

¹Abhijit Shevade and ²Shaoyi Jiang, ¹Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506; ²Department of Chemical Engineering, University of Washington, Seattle, WA 98195; ¹Phone: (785) 532-4322, ¹E-mail: ajs1513@ksu.edu; ²Phone: (206) 616-6509, ²E-mail: sjiang@u.washington.edu.

Soils contaminated with Pb pose significant risk to humans as well as terrestrial and aquatic ecosystems. The formation of pyromorphites is an attractive alternative to immo-

bilized lead, but their formation and stability is affected by possible substitutions (partial or total) by cations e.g., Cd²⁺, Zn²⁺, etc. for Pb²⁺ or anions, e.g., OH⁻, Br⁻ etc. for Cl⁻ in the soil. We report a molecular modeling approach based on *ab initio* quantum mechanics principles to investigate the stability and formation of substituted pyromorphites by competing cation and anions. The stability of these metal phosphates is investigated based on the binding energy and by calculating the Gibbs free energy for these complex periodic crystals using molecular simulation tools. Geochemical calculations are also performed using MINTEQA2 to investigate the speciation and solubilities of various substituted pyromorphites under specified conditions similar to those in experiments. The impact of the present work will provide a fundamental understanding of the interactions of metals with a phosphorous (P) source and address important questions such as how metals compete for P in soils.

Key words: pyromorphite, substitution, stability, formation, molecular modeling

Program Two
Wednesday, May 24, 2000
Mine Waste Remediation and
Drainage Treatment



**THE RELEVANCE OF
REDOX TO REMEDIATION**

*Andy Davis, Geomega, 2995 Baseline Road,
Suite 202, Boulder, CO 80303; Phone: (303)
938-8115, E-mail: adavis@geomega.com.*

Redox conditions represent an important control on the speciation of metals including As (III/V), Cr (III/VI), Sb (III/V), and Se (IV/VI) chemistry. Although the measurement and environmental geochemistry of these constituents is well understood, application of this knowledge in setting regulatory standards for soils, groundwater, surface waters, and sediments is rare. Hence, bulk chemistry is usually considered in setting standards rather than evaluating the ameliorating effect of metal valence on toxicity and mobility. Given the escalating costs of environmental restitution, it is critical that reasonable options, including the influence of valence, be considered in setting realistic, risk-based cleanup goals.

This paper provides examples of the value of understanding redox conditions and species in the environment. For example, the mitigating influence of precipitation reactions in sediments is demonstrated through sulfides precipitation and encapsulation of metals in a biologically active system in Richmond, California. Arsenic is less bioavailable in the As(III) form in mine wastes due to sparing dissolution of these less soluble forms in the short GI tract residence times. In addition, novel approaches to constrain metal solubility by modifying the valence state are realistic goals. For example, the solubility of Cr(III) in acid groundwaters can be reduced by careful pH control while remediation of acid pit lakes can be affected by modification of the pH with concomitant precipitation of amorphous ferric

hydroxide as the Fe(II)/Fe(III) ratios change, and sequestration of previously soluble ions.



**DETERMINING HISTORI-
CAL MINING IMPACTS IN
THE ROBINSON DIS-
TRICT, ELY, NEVADA**

*¹Andy Davis, G.G. Fennemore, and J.A.
Anderson, Geomega, 2995 Baseline Road,
Suite 202, Boulder, CO 80303; ¹Phone: (303)
938-8115, E-mail: adavis@geomega.com.*

Field data were collected and incorporated within a coupled transport model to understand the incremental impact of historic waste rock dumps and their associated seeps on groundwater at the Robinson Mining District. The rate of pyrite oxidation in waste rock dumps was predicted using the WROC-2D code calibrated to measured oxygen and temperature profiles collected from waste rock dumps across the site.

The resulting seepage pond chemistry was used as input to HYDRUS 2D to estimate infiltration, coupled with PHREEQC to simulate solute reactive transport to the water table. This flux was used as a source term in a steady state, MODFLOW model using MT3D96 and PHREEQC to determine COC concentrations at downgradient locations. A series of six 3650-day stress periods (60 years from 1940 to 2000) was run to simulate transport from the identified historical source areas during leaching and draindown of the waste rock dumps.

Site topography, dump surface configuration, and anthropogenic leaching played an integral role in determining the propensity for leachate to emanate from the base of waste rock dumps. All dumps generating acid seeps coincided with historic operations that promoted percolation of ambient precipitation and/or sulfuric acid amendments through the waste rock. Sumps that collected storm water runoff formed in the historic drainages upslope from these waste rock dumps.

Because of the complex structural geology and metamorphism in the Robinson Dis-

strict and the depths to the regional aquifer, there have been no impacts from historic mine operations to the deep carbonate aquifers within the Robinson Mining District. Laterally, groundwater flow from the mine area into the adjoining hydrogeologic provinces is minimal due to numerous hydraulically impeding faults and low conductivity rocks.

Solute groundwater transport simulations demonstrated that even sparingly reactive solutes, such as sulfate, have not migrated more than 1600 feet laterally from the Intera Pond area, nor deeper than 5,400 feet amsl within the area of investigation. Thus, anthropogenic surface sources have not contributed to degradation of deeper potable waters beneath the mine site.



SUBSURFACE FLOW TREATMENT SYSTEM FOR MINE DRAINAGE

^{1,3}T.M. Harris, ²V. Orrostietai, ²W.A. Roschet, and ³G. Rodolph, ¹Departments of Chemistry and Biochemistry, University of Tulsa, Tulsa, OK 74104; ²Biological Sciences, University of Tulsa, Tulsa, OK 74104; ³Chemical Engineering, University of Tulsa, Tulsa, OK 74104; ¹Phone: (918) 631-3090, ¹E-mail: thomas-harris@utulsa.edu.

Mine drainage occurs when mines become flooded with groundwater and the water comes in contact with sulfide minerals (e.g. pyrite, FeS₂). The sulfur in these minerals is oxidized to sulfate ion, resulting in solubilization of the metals (primarily iron) and acidification of the water. Several groups have had some success treating mine drainage with subsurface flow (SSF) passive treatment systems. In these systems, sulfate-reducing bacteria (SRB) convert the sulfate ion to sulfide, which in turn precipitates the metals and/or scavenges hydrogen ion. A new SSF treatment system design featuring horizontal flow has been developed in the present study. This system features a gravel layer, for en-

hanced fluid flow, overlain by a thick layer of organic matter, which provides a suitable environment for the SRB. The performance advantages of this design demonstrated in laboratory experiments will be presented. In addition, experiments with this system have indicated that the SRB are not the only type of microorganism that must be considered in SSF treatment systems; fermentative heterotrophs must be present and active in order to convert biomass into the simple organic substrates utilized by the SRB.

Key words: mine drainage, sulfate-reducing bacteria, subsurface flow, passive treatment system, constructed wetland



SILICA MICRO ENCAPSU- LATION: ARD TREAT- MENT AND BEYOND

Paul Mitchell and Amy Anderson, Klean Earth Environmental Company, 19023 36th Ave. W., Suite E, Lynnwood, WA 98036; Phone: (425) 778-7165, Email: keeco@nwlinc.com.

Klean Earth Environmental Company developed the silica micro encapsulation (SME) technology to treat metals in water and soil. Unlike conventional neutralization/precipitation methods, SME encapsulates the contaminants in a permanent silica matrix resistant to degradation under even extreme environmental conditions. Encapsulated metals are effectively immobilized, minimizing the potential for environmental contamination and impacts on human or ecosystem health. SME is a very robust technology and has cost-effectively treated heavy metals (such as chromium, copper, lead, mercury, and zinc), metalloids (such as arsenic), and radionuclides (such as uranium). It can be applied to surface and groundwaters, wastewaters, sediments, sludges, soils, mine tailings, and other complex media. In addition to the control of metals, SME chemicals have been shown to reduce dissolved solids (such as sulfates) and to

degrade or destroy hydrocarbons (such as gasoline and fuel oil) and other organic chemicals through a high-energy oxidation process. The most common SME application to date has been in the treatment of acid rock drainage (ARD) from abandoned and operational mining and quarrying sites. A wide range of pilot- and field-scale projects, alongside commercial contracts, have demonstrated that it provides better, faster, and cheaper treatment than liming and other conventional methods. However, over the past year SME has been applied to a much wider range of metal contamination issues. This paper briefly describes the theory and practice of the SME technology and its applications and then focuses on recent ARD and non-ARD applications, including:

- ◆ Treatment of metal plating and other industrial wastewaters
- ◆ Treatment of storm water
- ◆ Treatment of landfill leachate
- ◆ Polishing of municipal and industrial water supplies
- ◆ Recovery of resources from metals-rich waters
- ◆ Onsite remediation of contaminated soil
- ◆ Stabilization of sediments
- ◆ Stabilization of industrial and municipal sludges
- ◆ Silica coating to prevent or control future acid generation
- ◆ Combined-metals encapsulation and hydrocarbon oxidation

Key words: metals, silica, encapsulation, stabilization, treatment

Program Three Wednesday, May 24, 2000 Containment



BIOCLOGGING OF CLAY LINERS

Lakshmi Reddi, and Hugo Davalos, Department of Civil Engineering, Kansas State University, Manhattan, KS 66506; Phone: (785) 532-1586, Fax: (785) 532-7717, E-mail: [reddi@ksu.edu](mailto:redi@ksu.edu).

It is common practice to use compacted clays as liners for waste containment facilities such as animal waste lagoons. The integrity of such waste containment systems depends to a large extent on mass transport and transfer characteristics of the clay liners. In this paper, results from an experimental study are reported addressing the permeability changes of compacted clay samples permeated with cattle waste and influents containing known bacterial cultures. The experiments were conducted using Plexiglas columns similar to compaction permeameters. Pore-size distributions of the samples were determined using mercury porosimetry before and after permeation with influents. In an attempt to explain the time-dependent changes in the permeability as a result of bioclogging, the pore-size distributions were used in the Kozeny hydraulic radius model and the permeabilities were estimated. In spite of the large-pore development in permeated samples (perhaps due to cracking of the samples), the permeabilities at the end of 3-month long permeation were about the same as or lower than the initial permeabilities. A comparison of the experimental observations with estimates using the hydraulic radius model reveals that gas accumulation in the large pores could be the likely reason (and not the biomass growth) for the time-dependent reductions in permeability. It was concluded that permeability reductions as a result of

bioclogging may not occur during the time it takes for breakthrough of certain important contaminants in the influent. Thus it may not be a conservative design approach to account for bioclogging reductions in the designed permeabilities of clay liners.

Key words: bioclogging, compacted clay liners, permeability, animal waste lagoons



EFFECTS OF SUBSTRATE CONCENTRATION ON PERMEABILITY REDUCTION AND TCE DEGRADATION IN A MULTI-SPECIES BIOFILM

¹John Komlos, ¹Al Cunningham, and ²Robert Sharp, ¹Center for Biofilm Engineering, Montana State University, 366 EPS Building, Bozeman, MT 59717-3980; ²Environmental Engineering Department, Leo Hall, Manhattan College, Riverdale, NY 10471; ¹Phone: (406) 994-4770; ²Phone: (718) 862-7169.

Recalcitrant compounds, such as trichloroethylene (TCE), show little natural attenuation. The development of a biologically produced subsurface barrier capable of degrading TCE while reducing its migration could result in a significant advancement in bioaugmentation technology. *Burkholderia cepacia* PR1-pTOM31c has the ability to aerobically degrade TCE but is unable to form a biofilm capable of significantly reducing porous media permeability. This research examined the effects of combining *B. cepacia* with *Klebsiella oxytoca*, a thick biofilm-producing bacteria, in order to create a reactive/reduced-permeability biobarrier.

The research indicated that species growth rate was not an adequate predictor of which microorganism would out-compete the other in a biofilm. Rather, substrate concentration was a dominant variable in controlling the population distribution of the two organisms. At high substrate concentrations, *K. oxytoca* was the dominant organism in a dual-species biofilm. At lower substrate concentrations,

there was a shift in the population distribution with *B. cepacia* being the dominant microorganism. Varying substrate concentration enabled us to manipulate the population distribution in this dual-species biofilm. This concept was expanded to a constant head, porous media reactor. The results from the porous media reactor showed a similar shift in population with change in substrate concentration. *K. oxytoca* provided similar permeability reduction at high and low substrate concentrations. *B. cepacia* achieved greater population density, and higher TCE-degrading potential, at the lower substrate level. Thus, similar reduction in hydraulic conductivity coupled with a significantly higher TCE-degrading potential at the lower substrate level was observed.

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



MODELING OF SUBSURFACE BIOBARRIER FORMATION

¹Benito Chen and ²Hristo Kojouharov, ¹Department of Mathematics, University of Wyoming; ²Department of Mathematics, Arizona State University; ¹Phone: (307) 766-4221, ¹E-mail: bchen@uwyo.edu; ²Phone: (480) 965-3745, ²E-mail: hristo@math.la.asu.edu.

Biofilm-forming microbes can form biobarriers to inhibit contaminant migration in groundwater. Also subsurface biofilms have the potential for biotransformation of organic contaminants to less harmful forms, thereby providing an *in situ* method for treatment of contaminated groundwater supplies. We present a mathematical and numerical model to describe the population distribution, growth, and movement of bacteria in porous media. The model is based on the convection-dispersion equation with nonlinear reaction terms.

Accurate numerical simulations are crucial to the development of contaminant remediation strategies. We use the nonstandard numerical approach that is based on nonlocal treatment of nonlinear reactions and modified characteristic derivatives. It leads to significant, qualitative improvements in the behavior of the numerical solution. Numerical results for a simple biobarrier formation model are presented to demonstrate the performance of the proposed new method. We will show comparisons with experimental results obtained from the Montana State's Center for Biofilm Engineering.

Key words: biobarriers, models, biofilms, simulations

Program Three Wednesday, May 24, 2000 Remediation I



SUPERCRITICAL FLUID TECHNOLOGY FOR REMEDICATION OF PCB/ PAH- CONTAMINATED SOILS/ SEDIMENTS

¹L.L. Tavlarides, W. Zhou, and G. Anitescu, Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, NY; ¹Phone: (315) 443-1883, ¹E-mail: ltavlar@sy.edu.

A two-stage technology employing green solvents such as supercritical CO₂ (SC-CO₂) and supercritical water (SCW) for the extraction and destruction of polychlorinated biphenyls (PCBs)/polynuclear aromatic hydrocarbons (PAHs) from contaminated soils/sediments is proposed. Results of our laboratory and bench-scale investigations indicate that SC-CO₂ modified with 5% methanol is an effective solvent and conditions have been defined to achieve sub 5 ppm in 45-60 minutes for 99.8% removal. Comprehensive data on

PCB/PAH solubilities in SC-CO₂/MeOH, partition equilibria and desorption provide a solid basis to develop models regarding the extraction of these pollutants from solid matrices. Further, the supercritical water oxidation (SCWO) stage, coupled to the extraction process with three possible configurations, would provide clean effluent materials. The ultimate products of the proposed technology are mainly clean soil/sediments and inorganic species such as H₂O, CO₂ and small amounts of chlorides. Our SCWO studies indicate that 5245 ppm Aroclor 1248 in methanol-simulated soil extract solutions can be oxidized to 99.95% conversion in less than one minute at 550°C. An economic analysis based on a conceptual design of the process indicates that the expected costs of \$198-318 m³ of soil processed is economically competitive.

Key words: PCB, remediation, supercritical extraction/oxidation



COMBINED FENTON'S OXIDATION AND BIO- DEGRADATION FOR THE TREATMENT OF PCP- CONTAMINATED WATER

¹Julio Zimbron and ²Kenneth Reardon, ^{1,2}Department of Chemical and Bioresource Engineering, Colorado State University, Fort Collins, CO 80523-1370; ¹Phone: (970) 491-1123, E-mail: jzimbron@lamar.colostate.edu; ²Phone: (970) 491-6505, ²E-mail: reardon@engr.colostate.edu.

Chlorinated compounds, often found in industrial wastes such as wood treating and paper pulp manufacturing waste, are a common source of water contamination. These compounds are intrinsically recalcitrant to biodegradation, resulting in limited applications of biodegradation to water contaminated from this type of waste. A promising solution to this problem is the combination of chemical oxidation with biological degradation.

Combinations of chemical and biological degradation processes can be more effective and cost-efficient than either chemical or

biological treatment alone for the treatment of groundwater, process wastewater, and drinking water. The goals of this research are (1) to develop a mathematical model for the combination of chemical oxidation using Fenton's reagent (hydrogen peroxide and ferrous ion) and biological degradation of chlorinated phenols, and (2) to use the model to optimize operating conditions and reactor configurations for the combined system.

This presentation includes new data on the mechanisms and rates of Fenton's reaction for PCP in water, as well as new data on the biodegradation rates of chemically oxidized intermediates. The Fenton's degradation rate of PCP was determined by the competitive kinetics method, and compared with the Fenton's degradation rates for other chlorophenols by means of Hammett's equation, a group contribution method. It was found that these degradation rates were inversely proportional to the degree of chlorination of the phenolic ring.

A model aqueous waste consisting of PCP has been treated with a sequential combination of Fenton's reagent (for chemical oxidation) and a packed-bed bioreactor inoculated with activated sludge from a municipal wastewater treatment plant. The PCP concentrations in the feed to the chemical reactor, the effluent of the chemical reactor, and the effluent of the bioreactor were determined. In addition, the amount of protein in the effluent from the bioreactor was measured to estimate the extent of biodegradation of the waste. At a residence time of 1.5 hr in the Fenton's reactor, operating at molar dosage ratios of H_2O_2 /PCP of 3.0 and 7.7, 42% and 63% of the PCP present in the feed was degraded, respectively. PCP was not biodegraded in the following biodegradation stage at a residence time of 5.5 hr. However, the extent of biodegradation achieved by the microbial population on the Fenton's pretreated, PCP-contaminated water was proportional to the extent of the previous Fenton's degradation of PCP.

Key words: mineralization, mixture-based model, advanced oxidation process, biodegradation



PREDICTING GROUNDWATER CIRCULATION WELL PERFORMANCE

¹Jason Hellman, and ²Andrew Curtis Elmore,
¹URS Greiner Woodward Clyde, 101 South
 108th Avenue, Omaha, NE 68154; ²URS
 Greiner Woodward Clyde, 10975 El Monte,
 Suite 100, Overland Park, KS 66211; ¹Phone:
 (402) 334-8181, ¹E-mail:
 jason_hellman@urscorp.com; ²Phone: (913)
 334-1154, ²E-mail:
 curt_elmore@urscorp.com.

Groundwater circulation well (GCW) techniques are an innovative remedial technology that may effectively remediate contaminated groundwater in areas where more traditional technologies are unfavorable. Traditional pump and treat systems may be problematic where concentrated hot spots of contamination are present, where aquifer drawdown due to remedial activities is unacceptable, where surface discharge of treated groundwater is unwanted, or where property acquisition is challenging. The vertical component of groundwater flow induced by GCW systems presents a new challenge to practitioners evaluating the potential performance of GCW systems. Modifications were made to two familiar pump and treat analysis tools, capture-zone type curves and MODFLOW numerical groundwater flow modeling, to predict site-specific effectiveness of GCW technologies. These techniques were used to predict the GCW treatment area dimensions. This included the capture zone, recharge zone, and circulation cell diameter. Additionally, GCW design parameters, including GCW spacing, screen length, screen placement, and circulation flowrate, were determined. The state of the practice is to use these predictive tools to design an instrumentation scheme that

can effectively evaluate the performance of GCW systems during full-scale pilot testing.

Key words: groundwater circulation well (GCW), capture zone, recharge zone, circulation cell, MODFLOW

Program Three Wednesday, May 24, 2000 Remediation II



ENHANCED *IN SITU* BIOREMEDIATION OF CHLORINATED SOL- VENTS WITH THE BIOLUXING SYSTEM

¹Theodore Meiggs, ¹C. Alvin Yorke, ¹Jeffrey Fleischman, and ²William Mahaffey, ¹Foremost Solutions, Inc. 350 Indiana Street, Suite 415, Golden, CO 80401; ²Pelorus EnBiotech Corporation, 3528 Evergreen Pkwy, Evergreen, CO 80439; ¹Phone: (303) 271-9114, ¹E-mail: formost@earthlink.net; ²Phone: (303) 670-2875, ²E-mail: mahaffwr@worldnet.att.net.

BioLuxing is a remediation technology that utilizes jetting and hydraulic fracturing techniques to create large porous networks within contaminated soil or groundwater zones. These subsurface networks can be installed at great depths and in a variety of soil types. They make effective distribution systems for the repeated delivery of contaminate-degrading bacteria, nutrients, and electron acceptors or electron donors to stimulate biodegradation processes in the contaminated zones. This paper will discuss the application of this technology for enhanced bioremediation of chlorinated solvents in both aerobic and anaerobic environments.

Key words: chlorinated solvents, BioLuxing, hydraulic fracturing



AIR-SPARGING REMEDICATION: A STUDY ON HETEROGENEITY AND AIR-MOBILITY REDUCTION

¹Shoeleh Di Julio and ²Andrew Drucker, ¹California State University, Northridge, Northridge, CA 91330; ¹Phone: (818) 667-2496, ¹E-mail: sdijulio@ecs.csun.edu; ²Phone: (805) 982-4847, ²E-mail: adrucke@nfesc.navy.mil.

Contaminated groundwater is a widespread problem often requiring innovative technology to remediate. The use of one such technology, *in situ* air-sparging (Johnson, et. al., 93, Ahfield et. al., and 1994, Hinchey, 1994), has lead to an increased interest in understanding the mass transfer process. The purpose of this paper is to present the laboratory results of air-sparging models. Initial tests used very fine porous media (glass beads packed column) to represent relatively homogeneous soil samples. Subsequent testing employed budded core samples taken from a site of interest to represent more realistic, heterogeneous samples. 1,1,1 Trichloroethane (TCA) was used as the dissolved contaminant to represent BTE/gasoline contamination; however, results obtained here can be applied to any NAPI-dissolved phase. A technique to improve the contaminant removal based on foam injection is presented. The laboratory results are compared with the numerical model prediction of an advection-diffusion, air-sparge simulation model based on the mathematical model developed by Wilson, et al. (1994). Sensitivity analysis of the numerical model provides the range of some key parameters used to screen/evaluate air sparging as the remediation method for a given contaminated site of interest. The numerical model developed here simulates air flow as it travels through a saturated soil column contaminated with dissolved volatile organic compounds (VOCs). Eventual scaleup of the model to an actual site application can be justified by the favorable results presented in this paper.

Key words: remediation, air sparging, NAPL, foam



MONITORED NATURAL ATTENUATION OF CHLO- RINATED COMPOUNDS

Timothy Cox, Rocky Mountain Consultants, Inc., 825 Delaware Ave, Suite 500, Longmont, CO 80501; Phone: (303) 665-6283, E-mail: tcox@long.rmcco.com.

Natural attenuation was evaluated as a possible corrective action for a plume of volatile organic compounds (VOCs) migrating from a closed landfill in Littleton, Colorado. In January 1995, a corrective action was implemented at the request of the state to prevent the further migration of VOCs, which included installation of a groundwater interceptor trench and collection sump (recovery system) immediately downgradient of the landfill boundary. Performance monitoring of the recovery system has been conducted since 1995, and decreasing concentrations of parent concentrations and production of daughter products were observed, suggesting that natural attenuation processes were occurring. A supplemental evaluation was conducted in January 1999 to determine if the groundwater system was capable of naturally attenuating VOCs, such that the recovery system could be shut down. The evaluation was conducted using technical guidelines for demonstrating natural attenuation of chlorinated solvents prepared by the U.S. Air Force Center for Environmental Excellence. The guidelines call for evidence of 1) reduction in contaminant concentrations, 2) loss of contaminant mass, and 3) geochemical data supporting biodegradation. A decrease in contaminant concentrations had already been demonstrated from the four years of monitoring data; however, collection of additional geochemical data and assessment of the reduction of contaminant mass were required. The first component of the supplemental evaluation included collec-

tion of site-specific geochemical data from monitoring wells, including measurements of dissolved oxygen, reduction/oxidation potential (redox), nitrate, iron (II), sulfate, and sulfite. Some of the compounds may serve as electron donors or acceptors, and depending on their concentrations, may either facilitate or impede reductive dechlorination. Dissolved oxygen and redox were measured to determine if the groundwater system was reducing, thereby favoring reductive dechlorination. Additionally, end-member compounds were analyzed including ethane, ethene, methane, and chlorethane, where the presence of these compounds would support complete reductive dechlorination. The second component of the evaluation was to calculate the reduction of mass. The calculation was made by comparing isocontour maps of VOC concentrations measured prior to start-up of the recovery system to recent concentrations measured in January 1999. A particular concern at the site was the rising groundwater levels due to increased water use of residential development within the watershed. Therefore, the effect of rising water levels had to be considered to identify if the mass reduction was simply due to dilution or due to actual biodegradation processes. Results of the evaluation demonstrated that the groundwater system was under reducing conditions and geochemical conditions support reductive dechlorination. End-member compounds were detected which further demonstrated that dechlorination was occurring. Also, the mass of VOCs had been reduced even after accounting for dilution. Results of the evaluation were presented to state regulators together with a plan for future monitoring to assure that natural attenuation is occurring. The recovery system was shut down in June 1999 and subsequent monitoring has shown that VOC concentrations continue to decrease.

Key words: attenuation, groundwater, VOCs, monitoring

Program Three
Wednesday, May 24, 2000
Nanotechnology Applications



**NANOCRYSTALLINE
ADSORBENTS OF ACID
GASES**

¹Gavin Medine and ²Kenneth Klabunde, ^{1,2}111 Willard Hall, Kansas State University, Manhattan, KS 66506; ¹Phone: (785) 532-6829, ¹E-mail: aberdeen@ksu.edu; ²Phone: (785) 532-6849, ²E-mail: kenjk@ksu.edu.

The intrinsic differences between nanocrystalline MgO (AP-MgO), microcrystalline MgO (CP-MgO), and commercial MgO (CP-MgO) in relation to morphology, reactivity, and active sites were studied. Morphologically the nanoparticles (AP-MgO) are unique and very different from the conventional samples (CP-MgO, CM-MgO).

Nanocrystalline MgO possesses more defects, edge and corner sites, higher surface area, and higher index surfaces. Sulfur dioxide was used as an absorbate due to its variety of possible bonding geometries and for more practical reasons for its involvement in producing acid rain.

Key words: nanocrystalline, sulfur dioxide, MgO



**NANOSCALE METAL
OXIDES USED AS
DEHYDROHALOGENATION
CATALYSTS**

¹Ryan Richards, ²Ilya Mishakov, ³Vladimir Chesnokov, ⁴Alexander Volodin, and ⁵Kenneth Klabunde, ^{1,5}Department of Chemistry, Willard Hall, Kansas State University, Manhattan, KS 66502; ^{2,3,4}Boreskov Institute of Catalysis, Prospekt Lavrentieva 5, Novosibirsk 630090, Russia; ¹Phone: (785) 532-6849, ¹E-mail: ryanr@ksu.edu; ²E-mail: ilshik@mail.ru; ⁴E-mail: volodin@catalysis.nsk.su; ⁵E-mail: kenjk@ksu.edu.

The unique properties and chemistry of metal oxide nanoparticles including characterization of Lewis acid and base sites using electron paramagnetic resonance (EPR), structures using transmission electron microscopy (TEM), and catalytic properties have been investigated. These metal oxide nanoparticles have been found to demonstrate high activity and selectivity for the dehydrochlorination of 1-chlorobutane. The selectivity towards dehydrochlorination to butylene is much higher for autoclave prepared (AP) MgO and CaO catalysts than Al₂O₃. This catalytic activity has been found to increase upon conversion of the metal oxide catalyst to chloride. Experiments have been expanded in scope to investigate compressed metal oxide samples, 1-bromobutane catalytic dehydrohalogenation, and surface area and pore structure analysis, as well as mechanistic studies.

Key words: nanoparticles, dehydrohalogenation, catalysis, metal oxide



BIOCIDAL CAPABILITIES OF NANOPARTICLES

¹John Klabunde, ¹George Marchin, and ²Kenneth Klabunde, ¹Departments of Chemistry and Biology, Kansas State University, Manhattan, KS 66506; ²111 Willard Hall, Kansas State University, Manhattan, KS 66506; ¹Phone: (785) 532-6829 or (785) 532-6635, ¹E-mail: jsk6388@ksu.edu or amarchin@ksu.edu; ²Phone: (785) 532-6849.

The biocidal capabilities of autoclaved-prepared halogenated metal oxide nanoparticles were studied. Chlorinated MgO (AP-MgO-Cl₂), brominated MgO (AP-MgO-Br₂), iodinated MgO (AP-MgO-I₂), chlorinated CaO (AP-CaO-Cl₂), brominated CaO (AP-CaO-Br₂), and iodinated CaO (AP-CaO-I₂) were allowed to contact *Bacillus cereus* spores. Times of exposure were varied. The results showed that the spores were disinfected, and the efficiency of this process depended on halogen loading and time of contact. Electron microscope pictures showed that the spores were cleaved open. These and related results will be discussed.

Key words: nanoparticles, biocidal, halogenated, conventionally prepared, autoclaved prepared, magnesium oxide, calcium oxide, metal oxide



NANOSTRUCTURED METAL OXIDES AS CATALYSTS FOR ENVIRONMENTALLY BENIGN CHEMICAL PROCESSES

¹Ravichandra Mulukutla and ²Kenneth Klabunde, ^{1,2}Department of Chemistry, Kansas State University, Manhattan, KS 66506-3701; ¹Phone: (785) 532-6829, ¹E-mail: ravi@ksu.edu; ²Phone: (785) 532-6849, ²E-mail: kenjk@ksu.edu.

There has been a growing concern to develop environmentally viable chemical processes by finding alternatives for the toxic

lewis acid catalysts such as AlCl₃, ZnCl₂, and BF₃ which are being applied in Friedal-Crafts alkylation reactions. Similarly there has been an interest for developing newer and more selective ways for chlorination of hydrocarbons which is presently done at high temperatures or photocatalytic methods, or by employing HCl/ZnCl₂ as reagents. Nanostructured MgO and CaO prepared by an aerogel method are highly reactive having 4-7 nm crystalline size with high surface area. Nanocrystalline MgO, when exposed to Cl₂ gas at atmospheric pressure and room temperature, formed an extremely reactive MgO-Cl₂ adduct and has been used as a catalyst in the chlorination of hydrocarbons. The chlorination of hydrocarbons was performed in a specially designed pulse reactor to handle the corrosive Cl₂ gas, and this method overcomes the difficulties in the high-temperature/photocatalytic pathways and in the use of HCl/ ZnCl₂ reagents. The results report an unique application of nanocrystalline metal oxides as catalysts in chemical processes to find remedies for environmental problems.

Key words: nanostructure, catalyst, chlorination, selectivity, magnesium oxide

Program One
Thursday, May 25, 2000
Oilfield Production Remediation I



**A NATIONWIDE FIELD
TEST OF
PHYTOREMEDIATION
FOR PETROLEUM CON-
TAMINATED SOILS**

¹Peter Kulakow and ²Larry Erickson, ¹Department of Agronomy, 2004 Throckmorton Plant Sciences Center, Kansas State University, Manhattan, KS 66506; ²Center for Hazardous Substance Research, 101 Ward Hall, Kansas State University, Manhattan, KS 66506; ¹Phone: (785) 532-7239, ¹E-mail: kulakow@ksu.edu; ²Phone: (785) 532-4313, ²E-mail: lerick@ksu.edu.

The EPA-sponsored Research Development Technology Forum (RTDF) for Phytoremediation, Total Petroleum Hydrocarbon (TPH) Subgroup has developed a protocol for a nationwide field test of phytoremediation of petroleum hydrocarbon-contaminated soils. Currently 11 sites are entered in the trial. The experimental protocol specifies three vegetation treatments including a standard grass/legume mixture planted at all locations, a locally determined vegetation treatment usually including native species or trees, and an unvegetated control. Soils are to be sampled annually at two depths with the analysis of soil samples performed at common laboratories. Petroleum hydrocarbon analysis includes determination of total petroleum hydrocarbons by GC/FID, estimation of polycyclic aromatic hydrocarbons, and estimation of biomarkers for use in normalization of the data. Petroleum hydrocarbon composition also will be assessed using the TPH Criteria Working Group method to fractionate hydrocarbons into 13 aliphatic and aromatic fractions. The status of the field sites will be summarized along with a summary of the experimental protocol and some of the issues addressed in early phases of the trial.

Key words: phytoremediation, petroleum hydrocarbons, contaminated soil, vegetation



**PHYTOREMEDIATION OF
PETROLEUM-CONTAMI-
NATED SOIL**

¹G.J. Thoma, ¹T.J. Gentry, ¹L.J. Krutz, ¹D.C. Wolf, ¹C.A. Beyrouthy, and ²C.M. Reynolds, ¹University of Arkansas, Plant Science 115, Fayetteville, AR 72701; ²USACRREL, Hanover, NH; ¹Phone: (501) 575-5739, ¹E-mail: dwolf@comp.uark.edu.

Traditional techniques of remediating petroleum-contaminated soil can be expensive and labor intensive. Phytoremediation is an economical alternative technology that could be used at many drilling rig sites. The goal of phytoremediation is to enhance the biodegradation rate and to lower the contaminant concentration to an acceptable level. Research on phytoremediation is needed to define appropriate plants to establish at the sites, the fertility levels to optimize plant growth and petroleum degradation, and the benefits of adding soil amendments. A greenhouse experiment was conducted to evaluate germination and growth of bermuda grass, rye grass, fescue, crabgrass, and alfalfa in a crude oil-contaminated soil. In addition to an unamended control, broiler litter, inorganic fertilizer, paper mill sludge, and sawdust amendments were studied. Analysis of plant and amendment effects on phytoremediation will increase our understanding of the remediation processes in oil-contaminated soils.

Key words: petroleum-contaminated soil, phytoremediation, contaminant concentrations



BIOSURFACTANT-PRODUCING BACTERIA FOUND IN CONTAMINATED AND NON-CONTAMINATED SOILS

¹Eleanor Jennings and ²Ralph Tanner, ^{1,2}Department of Botany and Microbiology, University of Oklahoma, 770 Van Vleet Oval, Norman, OK 73019; ¹Phone: (405) 325-1647; ¹E-mail: ejennings@ou.edu; ²E-mail: rtanner@ou.edu.

Microbially produced surfactants have been studied for use in the bioremediation of hydrocarbons and microbially enhanced oil recovery (MEOR). However, most of these studies involved only a small number of bacteria isolated in a laboratory and then taken back to an environment. Here, we examined soils from two different hydrocarbon-impacted sites—one in northeastern Oklahoma and the other near Ft. Lupton, Colorado. Uncontaminated soils from both of these sites were examined also. Biosurfactant-producing bacteria were found in numbers ranging from 10^2 to 10^4 , and neither site showed any significant difference between their uncontaminated and contaminated soils. Aerobic heterotrophs were also enumerated and again no significant difference was determined between soil conditions on either site. Identification of isolated bacterial colonies showed that *Pseudomonas* and *Bacillus* species were the primary biosurfactant-producing bacteria in these soils. Future work suggested by these results includes an examination of additional hydrocarbon-contaminated sites as well as artificial contamination of the soil to see if the established trend continues.

Key words: biosurfactant, *Bacillus*, *Pseudomonas*



LEAD HYPERACCUMULATION BY *SESBANIA DRUMMONDII*

¹Robert Barlow, ¹Natalie Bryant, ¹John Andersland, and ²Shivendra Sahi, Department of Biology, Western Kentucky University, 1 Big Red Way, Bowling Green, KY, 42101; ¹Phone: (270) 745-6012, ¹E-mail: Barlorl@wku.edu; ²E-mail: shiv.shai@wku.edu.

Sesbania drummondii is a leguminous plant commonly found in the southeastern United States. Our studies have shown that seedlings of *Sesbania drummondii* can hyperaccumulate lead (Pb) in a controlled hydroponic environment. The addition of a chelating compound (EDTA) further increases the amount of Pb that a seedling can accumulate. Pb-treated roots were analyzed with scanning and transmission electron microscopes equipped with energy dispersive X-ray spectrometers. Pb deposits were observed in concentric rings around the stele, on subepidermal cortical cells, and on the surface of the epidermis. The lead appeared to be localized within and on the cell wall. Phosphorus was present wherever lead was detected, suggesting that the lead precipitated as a lead phosphate. The data gathered suggests that it would be feasible to examine the Pb-accumulating capabilities of *Sesbania drummondii* in a soil environment.

Key words: phytoremediation, lead, hyperaccumulation, *Sesbania*, EDTA

Program One
Thursday, May 25, 2000
Oilfield Production Remediation II



**REMEDICATION OF
OILFIELD BRINE-IM-
PACTED SOIL WITH
SUBSURFACE DRAINAGE**

^{1,2}Thomas Harris, ¹C. Dewan, ³K. Sullivent,
²R. Yates, ³J.B. Tapp, and ²Kerry Sublette,
¹Departments of Chemistry and Biochemistry,
University of Tulsa, Tulsa, OK 74104;
²Chemical Engineering, University of Tulsa,
Tulsa, OK 74104; ³Geosciences, University of
Tulsa, Tulsa, OK 74104; ¹Phone: (918) 631-
3090, ¹E-mail: thomas-harris@utulsa.edu.

The contamination of soil and water resources with the brine that is typically co-produced with petroleum is arguably the most serious environmental problem associated with the exploration and production of petroleum. Soil that is contaminated with salt cannot sustain vegetation, and is thus susceptible to erosion. The consequent runoff of both topsoil and salt will also have an adverse effect on downstream water resources. Subsurface drainage, coupled with deep-well injection of the collected leachate, is capable of decontaminating brine-impacted soil while limiting secondary contamination of nearby surface waters and freshwater aquifers. This technology is being demonstrated on a recent two-acre brine spill in the Tallgrass Prairie Preserve, Osage County Oklahoma. Results of the chemical analysis of the leachate and soil samples collected over a two-year period will be presented. The latter will be correlated with the extensive revegetation that has occurred through two growing seasons.

Key words: petroleum production, brine, brine-impacted soil, salinity, erosion, subsurface drainage



**PLANTING CROPS ON
LAND SPREAD WITH
TANK BOTTOMS: A
POSSIBLE DISPOSAL
SOLUTION FOR
OILFIELDS**

¹Lorna Bradbury and ²Sandra Mark, ¹University of Regina, Regina Saskatchewan, P.O. Box 1040, Williston, ND 58802; ²Petroleum Technology Transfer Council, Golden, Colorado, Colorado School of Mines, PTTC/Geology Department, 1500 Illinois Street, Golden, CO 80401; ¹Phone: (701) 774-1319, ¹E-mail: gbradbur@dia.net; ²Phone: (303) 273-3107, ²E-mail: smark.95@alum.mines.edu.

Tank bottoms from a Williston Basin oilfield were applied to test plots in which crops were subsequently planted. Naturally occurring microbes reduced the 6% total petroleum hydrocarbon (TPH) concentration to 3.8% in a few months (a 37% reduction), but reduced it no further, possibly due to an insufficient amount of nitrogen or water or both. For the first three years of the study, the 6% TPH test plot did not grow crops. It was apparent that the high (6%) application rate of this high-paraffin oil seriously restricted the infiltration of water into the soil; this is considered to be the primary cause of crop failure, rather than toxicity of the tank bottoms. After manure was applied in the fall of the third year following the tank bottoms application, crops were successfully grown for the next two seasons. In the fifth year, when the manure had degraded, crop growth was again very poor.

The second phase of the project studied the addition of straw and large amounts of nitrogen and phosphate fertilizer to new test plots. A 0.6% TPH concentration was applied to two test plots that had been previously planted to spring wheat. Because there had been no rain, the crop was poor, and there was concern that the application of oil plus tilling would kill the crop. When it did rain later in the summer, the seed left in the ground germinated and successfully produced a crop. The

addition of straw did not increase the chances of crop growth; rather, it reduced the yield of the crop significantly, even with a higher rate of fertilizer application. The original 0.6% TPH concentration was reduced to 0.14% in one year, a 77% reduction, suggesting that lower application rates may remediate faster, in addition to allowing crops to grow.

This study suggests that application of low concentrations of tank bottoms on agricultural land may be possible, but additional research is needed to discover how to control the hydrophobic effects of this disposal method. The addition of manure (rather than straw) to land spread with tank bottoms appears to be favorable to plant growth by increasing water infiltration and retention.

Key words: tank bottoms, oilfield waste disposal, bioremediation, landfarming, hydrophobic soils



CLOSURE OF AN EXPLORATION AND PRODUCTION WASTE DISPOSAL FACILITY

¹Patrick Flynn, ²David Boyce, and ³Thomas Murphy, ¹HS Resources, Inc., 1999 Broadway, Suite 3600, Denver, CO 80202; ¹Phone: (303) 296-3600; ²BP Amoco; ³LT Environmental, Inc., 4400 W 46th Ave., Denver, CO 80212; ³Phone: (303) 433-9788, ³E-mail: tmm@ltenv.com.

Site Background

The Weld County Waste Disposal, Inc. (WCWD) site was a 40-acre commercial waste disposal facility originally permitted to receive oil field brines and other petroleum-related liquid waste derived from oil and gas exploration and production (E&P) activities. The facility was built in the late 1970s and was permanently closed in May 1995. Prior to closure, liquids received were off-loaded into a concrete receiving sump and transported via aboveground pipe to a clay-lined impoundment (Pond C) where liquid hydrocarbons were separated from the produced water (brine) and

recycled. The water was transferred to a second clay-lined impoundment (Pond D) where enhanced evaporation occurred as the primary water disposal method.

The work was conducted in fulfillment of the requirements of a U.S. Environmental Protection Agency (EPA) RCRA 7003 Administrative Order (Orders) received by the owner and the two largest local producers who had previously used the facility. EPA developed the orders in response to environmental concerns as a result of the operational practices.

The structures containing the waste products at the time of closure consisted of the concrete receiving sump, eight ASTs, two impoundments, and a sludge drying bed. Since August 1995, remedial measures were initiated to eliminate the waste present. These measures included the following:

- ◆ Removal of over 647,000 bbls (~27,000,000 gallons) of water through the operation of an enhanced evaporation system. A residual 15,000 bbls of heavy brine was injected into a permitted Class I well;
- ◆ Removal of 4,300 bbls (180,000 gals) of nonhazardous hydrocarbon liquids and 20 yd³ of BS&W solids from the ASTs and receiving sump. The waste was disposed of at a commercial biobed operation; and
- ◆ A sludge landfarming program of an estimated 20,000 yd³ of sludge with elevated hydrocarbon and salts.

Sludge Landfarm Program

The objectives of the program were to:

- ◆ Eliminate the potential for wildlife to be exposed to the sludge;
- ◆ Reduce the accumulation of free water in the pond from precipitation;
- ◆ Provide easy access to the pond for subsurface characterization activities;
- ◆ Reduce the potential for vertical migration of organic and inorganic compounds;
- ◆ Provide oxygen, nutrients, and proper substrate (wood chips and manure) to

initiate in-place biodegradation of the hydrocarbons; and

- ◆ Reduce the oily matrix to allow for more precise chemical characterization of the sludge.

Establishment of Cleanup Objectives

To accomplish the on-site landfarming project, chemical-specific cleanup objectives were established through the risk assessment process that protects potential human receptors. The primary contaminants of concern—benzene, polynuclear aromatic hydrocarbons (PAHs), and arsenic—were evaluated. The objective was to establish what the maximum concentration of these compounds could be after the sludge treatment so as not to pose a threat based on potential future land use scenarios. This process was concurrent with the implementation of the landfarming program.

The cleanup goals established were derived from risk-based concentrations (RBCs), background values, and soil-to-groundwater transfer concentrations using the SESOIL/AT123D fate and transport models. Cleanup goals based primarily on the more conservative RBCs were established for benzene (0.65 mg/kg) and the PAHs (chemical specific). Background values were used to establish an arsenic cleanup goal of 22 mg/kg.

Implementation of Landfarming Program

The initial mixing of bulking material and nutrients was conducted in May 1997 in Pond C and in March 1998 in Pond D. An estimated 4,125 yd³ of wood chips and 1,000 yd³ of cow manure were added, increasing the sludge volume by 25%. After conducting baseline analyses, the initial nutrient addition consisted of six tons of urea and one ton of monoammonium phosphate. Tilling of the amended sludge occurred on average three times per month from June 1997 through September 1998. A second nutrient application occurred in June 1998 with 3.8 tons of

urea and 0.65 tons of monoammonium phosphate added.

Performance Results

Periodic performance monitoring of the amended sludge occurred. By September 1998, the benzene concentration in the sludge was non-detect at reporting limits below the cleanup goal of 0.65 mg/kg. The observed benzene reduction since the inception of the aggressive tilling program is 99%. This is accompanied by an overall reduction in total hydrocarbons (TRPH) concentration of 84%. Although reporting limits of two PAHs exceeded the established RBC cleanup goals, mitigation was achieved through the use of the SESOIL/AT123D models and closure design criteria (i.e. soil cover). The models demonstrated that as a result of biodegradation in the groundwater, the potential pathway was not completed. Arsenic concentrations did not exceed the established background values for the area.

Site Closure

Permanent closure was achieved through the elimination of the waste products and removal of the remaining structures. The ASTs were dismantled and removed from the site. The concrete sump was rubbleized and buried on site. Pond C containing the remediated sludge from both ponds was backfilled with berm material, a soil cover with drainage controls constructed, and the site revegetated. Final EPA approval is imminent and post-closure monitoring occurring to document the success of the closure activities.

Key words: waste disposal, EPA, landfarming, fate and transport models, sludge

Program Two
Thursday, May 25, 2000
Mine Pits and Pit Lakes I



**PIT LAKES--PAST,
PRESENT, AND FUTURE**

*Andy Davis, Geomega, 2995 Baseline Road,
Suite 202, Boulder, CO 80303; Phone: (303)
938-8115, E-mail : adavis@geomega.com.*

Concern over pit lake chemistry is a recent phenomenon, initiated by the realization that the Berkeley Pit Lake would contain a large reservoir of acidic, metal-rich surface water. However, over the past 10 years there has been a rapid metamorphosis in pit lake issues, the focus of this paper, including predictive analysis, model verification, ecological risk, closure, and the eventual use of the water in pit lake storage in the 21st century.

Current predictive efforts have resulted in a general recognition that Carlin-type deposits will have adequate neutralizing capacity to preclude the formation of acidic pit lakes, while those hosted in metamorphic terrain are likely to generate acidity with associated poor water quality. Analog laboratory pit lakes are a useful screening tool because no pit lakes investigated prior to refilling have yet formed to test model results.

It is likely that beneficial use issues will become important due to the huge volume of water in storage in pit lakes, the increasing requirements for water, and the generally good water quality in many pit lakes. Other issues include the technical efficacy of pit backfilling during active mining, pit lake closure with respect to the ultimate equilibrium chemistry, and the value of undertaking uncertain modeling exercises. For example, a screening level analysis of water quantity and water quality issues may suffice, with the funds for a comprehensive study better utilized for activities that directly benefit the community. Finally, it

is likely that more regulatory agencies will become involved in pit lakes in the U.S. and that scrutiny abroad will intensify as environmental regulations become more stringent.



**A BIOLOGICAL SURVEY
OF THE BERKELEY PIT**

*Grant Mitman, Biology Department, Montana
Tech of the University of Montana, Butte, MT
59701; Phone: (406) 496-4617, E-mail:
gmitman@mtech.edu.*

The Berkeley Pit Lake System is estimated to contain more than 30 billion gallons of acidic, metal-laden water. Current investigations examine how the naturally occurring organisms in the Berkeley Pit Lake System might be stimulated by nutrient additions to begin a self-purification process for aqueous environments impacted by acid mine drainage. The combined physiological processes have been observed to bioremediate aquatic mine waste environments. Consequently, if a mine waste site like the Berkeley Pit Lake System is properly nitrified with nitrogen, phosphorous, or potassium (e.g. manure or sewage as inexpensive sources), this nitrification may cause a successional cascade of increased diversity and biomass that is coupled with an increase in pH. A pH increase, in turn, may lead to a natural restoration process. Thus, if systems are to function correctly and to recover from pollution-induced perturbations, fundamental information both on the autotrophic and heterotrophic components of the microbial community is essential. Defining the baseline community structure is the first step toward understanding the interactions of the different groups of extremeophiles and toward assessing any improvement in biodiversity within the biotic community.

*Key words: acid mine drainage, Berkeley Pit
Lake System, nitrification*



CURRENT SEASONAL LIMNOLOGY OF THE BERKELEY PIT LAKE

*Jim Jonas, 9852 Independence Street,
Westminster, CO 80021; Phone: (303) 421-
7527, E-mail: jpjonas@aol.com.*

The Berkeley Pit Lake was sampled during two seasons, fall 1997 and spring 1998, from the surface to the bottom. Various parameters were measured to determine what effect the seasons had on the water chemistry. It appears that a seasonal turnover did occur between the fall and the spring sampling; however, the depth of mixing due to turnover could not be established. Trends were observed which suggested the microbial activity was altering the iron speciation at depth, and subsequently masking the extent of mixing. Various trace metals were removed from the surface water by either co-precipitation with schwertmannite or adsorption. Optical microscopy, scanning electron microscopy, and geochemical modeling were performed to determine the composition of the precipitates formed in the surface water. This work is being performed under the Mine Waste Technology Program, funded by the U.S. Environmental Protection Agency (EPA) and jointly administered by the EPA and the U.S. Department of Energy, Contract Number DE-AC22-96EW96405.



DETERMINATION AND CHARACTERIZATION OF ORGANIC CARBON IN THE WATER AND SEDI- MENT OF THE BERKE- LEY PIT LAKE, BUTTE MONTANA

*¹Douglas Cameron and Margery Willett,
Chemistry and Geochemistry Department,
Montana Tech of the University of Montana,
1300 West Park Street, Butte, MT 59701;
¹Phone: (406) 496-4247, ¹E-mail:
dcameron@mtech.edu.*

Past work has focused on the inorganic chemistry of the Berkeley Pit Lake; however,

recent work has shown that the water in this pit lake also contains organic carbon at a level comparable to the infiltrating groundwater (2-3 ppm). Depth profiles of the organic carbon were obtained during the fall of 1997 and the spring of 1998. The results from these previous studies will be compared to those obtained from a fall 1999 sampling. The organic carbon profile, from the previous studies, shows some correlation with the iron concentration and the iron (II)/iron (III) ratios in the pit lake. The possible effect of organic carbon on the iron chemistry in the pit lake will be discussed. Preliminary analyses have indicated that the organic carbon content in sediments from the Berkeley Pit Lake are 100 times greater than that found in the overlying water. The presence of this much organic carbon could have a significant impact on the redox potential of the sediment and hence mineral formation. Organic carbon depth profiles from two cores will be presented and a comparison will be made with iron and sulfur speciation in the sediment cores. The analysis of organic carbon by nondispersive infrared absorption spectroscopy in acid mine drainage waters is complicated by the high concentration of sulfate and apparently the oxidation state of iron. The reason for this sulfate interference will be shown and methods to correct for this interference will be discussed.

Key words: organic carbon, pit lake, redox potential

Program Two
Thursday, May 25, 2000
Mine Pits and Pit Lakes II



**ALGAL
BIOREMEDIATION OF
THE BERKELEY PIT
LAKE**

Grant Mitman, Department of Biological Sciences, Montana Tech of the University of MT, 1300 West Park Street, Butte, Montana 59701; Phone: (406) 496-4617, E-mail: gmitman@mtech.edu.

Ongoing research is unraveling the intricacies of the microbial ecology of the Berkeley Pit Lake System, with ever increasing information becoming available regarding the diversity of algae, protists, fungi, and bacteria that inhabit this mine waste site. Defining the baseline community structure has been the first step not only toward understanding the interactions of the different groups of organisms, and also toward assessing any improvement in biodiversity within the biotic community. Now that this first step has begun, some of these extremophiles, specifically algae, that have been isolated from the Berkeley Pit Lake System are being used as a potential solution for bioremediation. The specific objectives of this research are fivefold: 1) To evaluate the bioremediative potential of our four most rapidly growing species: (*Chromulina freiburgensis* Dofl., *Chlorella ellipsoidea* Gerneck, *Chlorella vulgaris* Beyerinck and *Chlamydomonas acidophilla* Negoro) in Berkeley Pit Lake System water with the additions of NaNO_3 and NaPO_4 by using an experimental matrix. This matrix will be used to estimate the minimum nutrient concentrations that would be necessary to achieve the maximum growth of algae and maximum bioremediation of the Berkeley Pit Lake System. 2) To determine which combination of nutrients will stimulate growth of the best bioremediator of our four isolated species in

natural Berkeley Pit Lake System waters. In other words, what nutrient combination will give the best bioremediator a competitive edge over the other species. If time permits, different species may be grown in combination to determine if there are synergistic effects (protocooperation) between species. 3) To determine a temperature profile for these four species in order to determine their optimal growth temperature in Berkeley Pit Lake System water. 4) To continue to isolate organisms from the Berkeley Pit Lake System and determine their bioremediative potential. 5) Monitor algal and bacterial counts from a profile of Pit Lake System waters. The results to date will be presented for this conference.



**AN INVESTIGATION INTO
THE EFFECTS OF OR-
GANIC AMENDMENTS
ON BERKELEY PIT LAKE
WATER QUALITY UNDER
VARIOUS ENVIRONMEN-
TAL CONDITIONS**

¹Douglas Cameron and Margery Willett, Chemistry and Geochemistry Department, Montana Tech of the University of Montana, Butte, MT 59701; ¹Phone: (406) 496-4247, ¹E-mail: dcameron@mtech.edu.

Wetland studies to ameliorate acid mine drainage have shown 10-80% metal removal by sorption to insoluble or slightly soluble organic matter. These works have also demonstrated decreases in the aqueous Eh values resulting from organic oxidation, increases in pH due to chemical reaction of the organic matter, and the organic matter acting as a carbon source for sulfate-reducing bacteria (SRB). We have recently started investigation of the effects added organic amendments have on the water quality of the Berkeley Pit Lake. The added organic carbon comes from sewage sludge, local grass clippings, local foliage, and sawdust. The sawdust, foliage, and grass represent precursors to natural humic material and are often deposited in the local landfill. The sewage sludge is a readily available and

economic source of carbon. Each organic amendment is mixed separately with the water in a 10% mass ratio, and the mixture is stirred continuously. The experimental matrix is such that a replicate of each mixture is exposed to the following conditions: sunlight and air, sunlight and no oxygen, oxygen and no sunlight, or no oxygen and no sunlight. Small fractions of the mixture will be removed as a function of time and then filtered and analyzed to monitor the amount of dissolved metal ions, anions, and organic carbon. The pH of the mixture will be monitored frequently, and the gases and volatile organic matter emitted from the mixture will be collected and analyzed periodically. We will be reporting the results from these experiments.



MWTP-BERKELEY PIT LAKE RESEARCH

¹Karl Burgher and Steve Anderson, *Montana Tech of The University of Montana, 1300 West Park Street, Butte, MT 59701*; ¹Phone: (406) 496-4410, ¹E-mail: kburgher@mtech.edu.

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 Pit Lake 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.

Program Three Thursday, May 25, 2000 Multi-Stakeholder Decision Making I



CLEANUP AT THE RAMP SITE IN DENVER, COLO- RADO

¹Erna Waterman and ²Keith Anderson, ¹Environmental Engineer/Project Manager US EPA, Region VIII, 999 18th Street, Suite 500, Denver, CO 80202-2466; ²Environmental Chemical Corporation; ¹Phone: (303) 312-6762.

RAMP, a privately owned and operated consolidation and storage facility located in Denver, Colorado, was abandoned in 1994. RAMP processed low-level radioactive wastes and “mixed” wastes (wastes containing a mixture of both radioactive waste and hazardous waste). The mixed waste that RAMP received contained solvents such as trichloroethane, tetrachloroethylene, methylene chloride, acetone, ethyl benzene, toluene, and methanol. The U.S. Environmental Protection Agency responded to an emergency request from the state of Colorado in August 1994. When EPA initiated the cleanup of the site, they identified approximately 5,500 drums of unprocessed waste that needed removal. In addition to the technical difficulties in the removal process, the site location required diligent effort in the public participation process due to the Environmental Justice “EJ” issues. The EPA addressed the removal action

at the site through consolidation of similar waste streams, applying aggressive and creative characterization techniques, on-site stabilization, and numerous off-site treatment technologies. The EPA completed the removal action in 1999 and the site will not be placed on the National Priorities List (NPL).



APPORTIONING SLUDGE VOLUMES DISPOSED IN A LANDFILL

¹Andy Davis, P. DeCurnou, S. Helgen, and J. van Middlesworth, Geomega, 2995 Baseline Road, Suite 202, Boulder, CO 80303; ¹Phone: (303) 938-8115; ¹E-mail: andy@geomega.com.

Sludges from a galvanizing operation and a tile manufacturer were sent to a Texas landfill over a 17-year period. Closure was complicated by the estimated \$14m cost, so a two-part solution was proposed. First a cheaper, less complicated (yet effective) closure plan received regulatory approval while cost allocation proceeded in parallel. The closure plan was modified (with regulatory approval) to avoid sludge stabilization because the caustic soda and lime added to both sludges resulted in immobilization of lead and zinc (the compounds of concern). In addition, the siliceous nature of the material rendered further compaction prior to closure unnecessary. Waste apportionment used the end member materials to identify the mineralogic and chemical signatures of each that were used to develop a three-component (Pb/Zn/Fe) mixing model. The proportions of the two wastes in 201 samples of mixed sludge in the landfill were computed, the spatial distribution kriged, and the results summed to apportionment waste volumes between the two entities. The parties were able to settle when the landfill closure costs were reduced to ~\$4m and the mixing model showed that 93% of the waste was from the tile manufacturer and 7% from the galvanizing operation.



A TRIBAL PERSPECTIVE ON FEDERAL DEPARTMENTS' AND AGENCIES' ENVIRONMENTAL JUSTICE POLICY AND PROCEDURES: CASE STUDIES FROM THE DEPARTMENT OF ENERGY

Jessica Alcorn, Council of Energy Resource Tribes, Department of Energy-Headquarters, Office of Intergovernmental and Public Accountability, EM 11, Office of Environmental Management, 1000 Independence Ave. SW, Rm. Lh-087, Washington, D.C. 20585; Phone: (202) 586-0798, E-mail: Jessica.Alcorn@em.doe.gov.

The environmental justice movement had its beginnings in the growing perception that environmental benefits and burdens have been inequitably distributed--that the poor, the disenfranchised, and minority communities are the unwilling hosts to a disproportionate number of waste management and disposal facilities and other environmentally undesirable developments. President Clinton, in response, committed federal departments and agencies to develop and implement environmental justice strategies to address "disproportionately high and adverse human health or environmental effects of [their] programs, policies, and activities on minority populations and low-income populations in the United States" when he signed Executive Order 12898 in February 1994. However, casting environmental justice in distributive justice terms has not proven very effective in addressing the community empowerment prong of the environmental justice movement's goals. The distributive justice paradigm leads federal agencies to adopt a two-step approach to environmental justice: agencies first determine whether their activities will have impacts on "environmental justice communities" and second, determine whether such impacts on such communities are disproportionately high.

American Indian tribes have a growing concern about the interpretation federal departments and agencies have taken for envi-

ronmental justice in relation to tribes. Executive Order 12898 and the subsequent Council of Environmental Quality environmental justice guidance have defined tribes as “Native American communities” to be included as a minority group. This definition does not recognize tribes’ sovereign nation-state status, nor identifies the federal trust responsibility to tribes. The author suggests that environmental injustice is not fundamentally about distributions of benefits and burdens or the definition of minority communities and disproportionate impacts, but is, instead, about the inability of community institutions to participate in the broad range of decisions that determine if, where, when, and under what conditions undesirable land uses and development will be approved. The author maintains that the final report of the U.S. Environmental Protection’s Federal Facilities Environmental Restoration Dialogue Committee suggest that more than procedural justice or participation in decision making is required. This paper sets out a capacity-building model of environmental justice based on the recommendation of the FFERDC report and the approach taken by the Department of Energy to implement its Indian Policy.

Key words: environmental justice, American Indian tribes, DOE

Program Three **Thursday, May 25, 2000** **Multi-Stakeholder Decision** **Making II**



COMMUNITY SKEPTICISM NEEDED IN SUCCESS FORMULA

Stuart Hill, Community Involvement Coordinator (P-19J), U. S. Environmental Protection Agency, 77 West Jackson Boulevard, Chicago, IL 60604; Phone: (312) 886-0689; E-mail: hill.stuart@epamail.epa.gov.

A healthy dose of skepticism is one of the many legacies left for a community in an environmental melodrama that became a movie script.

That skepticism lay dormant, like the DDT in the river which bisected the Michigan town of St. Louis, until the Environmental Protection Agency announced plans to change its remedial plans from natural attenuation to dredging. Latent emotions exploded from the community which feared the return of television cameras, which watched its principle employer disappear overnight decades before, and which was excluded from decisions influencing its future.

Armed with a healthy respect for the skepticism the community so openly expressed, the U.S. EPA encouraged its critics through the use of several proven tools in its Community Involvement process at Superfund sites. To date, the results are favorable and range from doubt to enthusiasm—expressed in taking brownfield initiatives. Other, more subtle, changes have occurred in the community with Superfund activities serving as the catalyst. These include a community riverbank cleanup and a fishing derby, now annual events, in a body of water ignored by residents for the contamination it contained.

In only two short years since Region 5 began remediation of the Pine River in central Michigan, the town has made a remarkable

transition from the quaint, unassuming small town depicted in the 1981 movie “Bitter Harvest,” starring Ron Howard. Once the center of a crisis calling for the slaughter of dairy herds—the mid-1970’s event which made the city synonymous with chemical contamination—the town now views its brownfields as development opportunities. Yet, the skeptics remain and they are still encouraged.

The long-standing EPA tool of a Community Advisory Group (CAG) was first developed to address doubts. The Community Advisory Group quickly became one of the more active and aggressive in Region 5 with close to 40 people attending monthly meetings. When the meetings became so heavily indoctrinated with technical matters that non-technical members lost interest, a Technical Advisory Group (TAG) was formed. The two groups became the general and the specific doubters, respectively.

Community involvement methods were devised to address the issues of both groups. But what about others? How about business and youth interests? How could they be served? Simple answers provided in a brief oral presentation.



COMMUNITY RELATIONS ISSUES RELATED TO RESIDENTIAL SITE IN- VESTIGATIONS AND CLEANUPS

¹Lisa Sigler, and ²David Folkes, ¹Sigler Communications, Inc, 1324 S. University Blvd, Denver, CO 80210; ²EnviroGroup Limited, 7208 S. Tucson Way, Suite 125, Englewood, CO 80112; ¹Phone: (303) 778-8355, ¹E-mail: lisa@siglerinc.com; ²Phone: (303) 790-1340, ²E-mail: dfolkes@envirogroup.com.

Communication with and involvement of the public are critical aspects of any environmental investigation or cleanup. Experience at two of the highest profile residential remediation sites in Denver, Colorado (one involving soil cleanup at over 500 homes and

the other involving indoor air testing at over 150 homes), demonstrate that community relations issues are even more important, and challenging when the investigation and cleanup occur at residential properties. Community issues at sites involving remediation in homes and yards are different than those at a removed plant site or manufacturing facility. Community opinion and emotions can influence regulator’s decisions on remediation, monitoring, and long-term site use. The invasive nature of these cleanups requires access to be arranged with each property owner. Homeowners have more of a personal investment and say in the cleanup activities at their homes or yards. As a result, extensive communications, sensitivity, and flexibility are the critical elements to establishing and maintaining a positive relationship with the homeowner.

In working on these sites, Sigler Communication, Inc., a communications/community relations consulting firm, and EnviroGroup, Ltd., an environmental consulting firm, worked closely together to:

- ◆ Develop strategies that would gain community cooperation for the remediation projects;
- ◆ Obtain community input to ensure residents needs were being met; and,
- ◆ Keep residents constantly informed to help alleviate problems encountered during cleanup and monitoring and keep projects on schedule.

Comprehensive, proactive communications and community outreach programs were developed at both sites that include the following activities:

- ◆ Conducting community opinion research to determine concerns and identify the best ways to communicate.
- ◆ Implementing a comprehensive outreach program that includes the same staff members setting up

appointments and making in-home visits for monitoring. Staff members develop a personal relationship with homeowners to ease apprehension about “outsiders” in the home and gain more cooperation. Keeping a personal information notebook (e.g., pets and upcoming vacations) allows staff members to establish a person dialogue with the homeowners.

- ◆ Establishing a close working relationship with regulators to ensure consistent information is being delivered to the public.
- ◆ Hosting public information open houses that allow the public to ask questions and learn about next steps from the technical team.
- ◆ Distributing written materials, videos, and newsletters regularly to update homeowners on project status.
- ◆ Developing an information source in the community staffed by a community member that houses cleanup photos and information.
- ◆ Establishing a telephone hotline updated monthly that homeowners can call for updates on the project.
- ◆ Making technical staff available to meet one-on-one with homeowners.
- ◆ Tracking real estate transactions in the neighborhood to answer the homeowners’ questions about real estate values.

Key words: community, involvement, communications, residential

Posters

Analytical Methods



MEASURING MASS DEPLETION BY DISSOLUTION OF ENTRAPPED NONAQUEOUS-PHASE LIQUIDS IN FRACTURED MEDIA WITH X-RAYS

¹Joseph McGahee and ²Tissa Illangasekare,
¹Colorado School of Mines, 1012 14th Street,
 Golden, CO 80401; ¹Phone: (303) 384-2237,
¹E-mail: jmcgahee@mines.edu; ²AMAX
 Professor, Division of Environmental Science
 and Engineering, Colorado School of Mines,
 1012 14th Street, Golden, CO 80401; ²Phone:
 (303) 384-212, ²E-mail: tillanga@mines.edu.

Nonaqueous-phase liquids (NAPLs) pose a potential risk to humans when released into the environment. Once a NAPL is released into the environment, it could have the ability to contaminate the groundwater and nearby bodies of water. With this in mind, the dissolution of NAPLs needs to be better understood in order to adequately predict the impact of these contaminants in the subsurface, as well as for determining the best remediation process for removing the NAPL.

The ability to detect spatial differences and to monitor changes in the various phases within a porous medium is vital to enhancing the information extracted from multi-phase flow and transport experiments. Radiation attenuation techniques have been productively used in multi-phase research at Colorado School of Mines and elsewhere with the use of radioisotopes (gamma rays). X-ray generators can theoretically offer advantages as a radiation source in the nondestructive measurement of phase fractions in porous media as compared with radioisotopes emitting photons of similar energy. This is true because x-ray generators can produce a photon flux two to three orders of magnitude greater than radioisotopes, thus allowing the time necessary to take a measurement to be reduced. Also, photon energies can be optimized to yield the

best measurement precision for a given experiment by choosing the voltage setting on the x-ray generator and by filtering the emitted radiation spectrum with filters. X-ray generators have been shown to have enough flexibility in photon-energy settings to allow accurate and precise measurements, and sufficient photon flux and detector throughput to perform these measurements in short durations.

Currently, gamma rays are being used in the laboratory at Colorado School of Mines to measure the location and dissolution of NAPLs in porous media. With the use of x-rays, better resolution and accuracy will be obtained in measurements compared to the use of gamma rays. Once the x-ray generator is assembled, experiments will be performed to measure the dissolution of NAPLs in fractured media, as well as various other experiments. This x-ray system will also be used in conjunction with the gamma system in order to better understand and determine the behavior of NAPLs in porous media.

Key words: fracture, x-rays, dissolution, NAPL, radioisotopes



COMPARATIVE ANALYSIS OF RESPIROMETRY AND DIESEL DEGRADATION

¹Cynthia Davis, ²Tissa Illangasekare, ²Frank Barranco Jr., ³Denton Mauldin, and ⁴Ken Vogler, ^{1,2}Environmental Science and Engineering Division, Coolbaugh Hall, 14th and Illinois St., Colorado School of Mines, Golden, CO 8040; ^{3,4}Safety-Kleen Consulting, 5665 Flatiron Parkway, Boulder, CO 80301; ¹Phone: (303) 384-2237, ¹E-mail: cadavis@mines.edu; ³Phone: (303) 938-5500, ³E-mail: Dmauldin@Safety-Kleen.com, ⁴Email: Kvogler@Safety-Kleen.com.

Respirometry is one method available to monitor biodegradation kinetics of hydrocarbon contaminants that degrade aerobically in

soil media. Few field or laboratory studies, however, have validated respirometry information with confirmatory analysis of actual hydrocarbon degradation in soil. The goal of this study was to comparatively evaluate (within controlled lab- and pilot-scale conditions) biodegradation rates obtained from respirometry versus rates obtained from actual hydrocarbon depletion in soil. Initial experiments have been performed in small-scale laboratory bioreactors to determine diesel-degradation rates through oxygen-consumption data collected over a period of time. Results show that oxygen depletion occurred simultaneously with carbon dioxide production, indicating that aerobic mineralization of an aged diesel occurred. Analysis of initial and final hydrocarbon mass within the bioreactors indicated that estimates of diesel depletion based on respirometry were reasonably accurate. Evaluation of the data, assuming first-order kinetics, led to calculated degradation rates ranging from 0.5-5.2mg/kg/day, values that are within published ranges for diesel fuel. Pilot-scale studies are currently underway to assess respirometry results versus actual hydrocarbon depletion within simulated bioventing systems comprised of 3 in. diameter columns that are up to 5 ft. in length. Respirometric testing is being performed on the gas-phase generated at the top of the column, while *in situ* measurements are being performed spatially within the soil to determine hydrocarbon depletion. In this way, the validity of respirometric data to quantify hydrocarbon degradation is being evaluated.

Key words: remediation, degradation, respirometry, bioventing, diesel



DEVELOPMENT OF A BIOSENSOR FOR ATRA- ZINE

¹Neema Das and ²Kenneth Reardon, ^{1,2}Department of Chemical and Bioresource Engineering, Colorado State University, Ft. Collins, CO 80523-1370; ¹Phone: (970) 491-1137, ¹E-mail: neema@lamar.colostate.edu; ²Phone: (970) 491-6505, ²E-mail: reardon@engr.colostate.edu.

Atrazine is one of the most commonly used herbicides. It affects metabolic processes within weeds, resulting in chlorosis and eventual death. It is moderately persistent in soil ($t_{1/2}$ =4-57 weeks) and does not sorb strongly to the soil matrix. These properties have led to groundwater contamination following over-application and spills of atrazine. Hence, continuous monitoring of the atrazine concentration in groundwater is desirable.

The aim of this study is to design a biosensor that will measure atrazine concentration in groundwater. This biosensor is based on measurement of pH change, which is proportional to the concentration of atrazine. The tip of the biosensor is coated with two layers. The first layer contains a pH-sensitive fluorescent dye and the second layer contains bacteria (*Pseudomonas* sp. ADP or *Clavibacter michiganese* sp. ATZ1) immobilized in an alginate medium. These microorganisms use atrazine as a substrate and produce HCl. The production of acid lowers the pH and this change is detected by the first layer.

The biosensor made from *Clavibacter* has shown high specificity for atrazine in comparison to other commonly found groundwater contaminants (toluene, ethylacetate and chlorobenzene) and naturally occurring chemicals (aminoacids). It has shown a large response for simazine (84% that of atrazine response). It has high sensitivity, with a detection limit of 1 ppb (lowest measurement taken is 60 times the background noise). The response of this biosensor is linear for atrazine concentrations

from 1 ppb to 100 ppb. It has high reproducibility at low concentrations. Most (95%) of the total signal change is observed in 10 minutes, which is one-third of the response time. It loses 45% of its activity in 6 days. The biosensor performance at various temperatures and pH is also studied. The biosensor made from *Pseudomonas* measured atrazine concentration from 25 ppb to 150 ppb. Its response became non-linear at high concentrations and it lost 72% of its activity in two days.

Key words: biosensor, immobilization

Posters

Contaminants in Porous Systems



SURFACTANT- ENHANCED DISSOLU- TION AT ELEVATED TEMPERATURES

¹Quentin Robert Moore and ²Tissa Illangasekare, ¹Colorado School of Mines, 1012 14th Street, Golden, CO 80401; ²AMAX Professor, Division of Environmental Science and Engineering, Colorado School of Mines, 1012 14th Street, Golden, CO 80401; ¹Phone: (303) 384-2237; ¹E-mail: qmoore@mines.edu; ²Phone: (303) 384-2126; ²E-mail: tillanga@mines.edu.

The release of light nonaqueous-phase liquids, or LNAPLs, by surface spills, leaking underground storage tanks, or careless disposal practices into the subsurface, has the potential to infiltrate into the groundwater and contaminate local aquifers. Due to varying pumping rates or fluctuating seasonal conditions, the height of the water table may change, thus creating a smear zone of LNAPL contamination. Large capillary forces immobilize the LNAPL in the saturated region below the capillary fringe and are stronger than the viscous and buoyancy forces combined. The LNAPL lens will therefore exist as a residual

covering a large region of soil. Current remediation technologies are limited by the strength of the capillary forces; therefore, as an adaptation of enhanced oil recovery in petroleum engineering, surfactants have received much attention in recent years as a viable means of residual LNAPL remediation. Surfactants reduce the interfacial tension between an organic and an aqueous phase and, therefore, have the ability to greatly increase the mobility of LNAPLs.

The focus of this research is to study the behavior of a surfactant to decrease the interfacial tension between an LNAPL and the aqueous phase in the saturated zone of the subsurface at elevated temperatures to increase the amount of LNAPL mass recovered. The effects of temperature on the LNAPL partitioning behavior between the adsorbed and aqueous phases and the possibilities of localized density effects are also considered. Several experiments were run with a well-defined LNAPL source at residual saturation to quantify the recovery of an LNAPL. Dissolution experiments in a 2D tank provided a means of determining whether a surfactant and an increase in temperature increase the amount of NAPL solubilized. As a baseline to compare against, a natural dissolution simulation provided a LNAPL mass recovery without the effects of an added surfactant. Experiments with a nonionic surfactant injected at room temperature directly upstream from the LNAPL contamination studied the rate limiting behavior and quantified the mass recovery of surfactant enhanced dissolution. Lastly, an experiment injecting the same surfactant at 85°C showed the effects of temperature on the relative buoyancy of the surfactant and the resulting mass recovery.

The surfactant-enhanced experiments showed a large increase in the amount of LNAPL mass recovered as compared to natural dissolution. The amount of mass recovered from the hot surfactant-enhanced dissolution, however, proved to be less than the injection of surfactant at room tempera-

ture. It is hypothesized that due to a buoyancy effect, the hot surfactant injection displaced the cooler surrounding groundwater as it rose up above the injection point. Once the hot surfactant cooled, ceasing the upward migration, much of the surfactant had risen higher than the source of LNAPL contamination and as a result bypassed the LNAPL.

Key words: LNAPL, surfactant, dissolution, residual, temperature



THE EFFECTS OF MICROBIAL GROWTH AND TRANSPORT ON SOIL CHARACTERISTICS: A ONE-DIMENSIONAL ANALYSIS

¹Rock Richard, ²Tissa Illangasekare, ³Angela Bielefeldt, and ⁴Anu Ramaswami, ^{1,2}Environmental Science and Engineering Division, Colorado School of Mines, Golden, CO 80401;

³Department of Civil Engineering, University of Colorado at Boulder; ⁴Department of Civil Engineering, University of Colorado at Denver; ¹Phone: (303) 348-2237, ¹E-mail: rrichard@mines.edu; ³Phone: (303) 492-8433, ³E-mail: angela.bielefeldt@colorado.edu; ⁴Phone: (303) 556-4734, ⁴E-mail: aramaswa@carbon.cudenver.edu.

The use of polyaromatic hydrocarbon (PAH)-degrading microorganisms to treat and contain dense nonaqueous-phase liquid (DNAPL) soil contamination is an effective and efficient solution to an often costly and labor-intensive problem. The prohibitive costs associated with traditional cleanup options such as full removal of contaminated soil or various pump-and-treat technologies create the need for such a long-term, low-cost, minimum labor solution. While the biochemical processes involved in the breakdown of DNAPL-derived contaminants by microorganisms have been well documented, information is currently lacking on the direct and indirect effects of the

growth and movement of the resultant biomass on the surrounding media.

The goal of this research is to evaluate, in one dimension, the changes in the properties of porous media associated with microbial growth and deposition as well as the subsequent shearing and redeposition caused by subsurface flow. To measure these changes, several soil column systems were constructed. A nutrient-solution mixture containing a live consortium of PAH-degrading bacteria was passed through the columns via syringe pump at rates comparable to real-world low, medium, and high groundwater flow rates (1m/yr, 10 m/yr, and 100 m/yr, respectively). The PAH-degrading bacteria consortium consisting of *Stenotrophomonas maltophilia*, *Pseudomonas fluorescens*, *Pseudomonas putida*, and *Pseudomonas stutzeri* was cultivated for over one year in a CSTR. The consortium was exposed to Naphthalene, N-Methyl Naphthalene, and Phenanthrene. These constituents were found to be most abundant, in terms of mole fractions, in common DNAPLs such as coal tar. This cultivation procedure was followed in an attempt to create a population of bacteria representative of those naturally present in the soil surrounding a common DNAPL spill.

Before the microbe solution was circulated through the columns, and at regular intervals thereafter, information was gathered to measure the hydraulic conductivity, dispersivity and porosity of the soil at various stages of bacterial residence. Microbial concentration was measured in both the influent and the effluent by means of direct counts via epifluorescent microscopy as well as a measurement of the volatile suspended solids (VSS). Biogrowth density was also measured throughout the column length to provide information about shearing and redeposition.

The results from this research will be useful in upscaling to the two-dimensional and field levels as well as in numerically modeling the effects of microbial growth and transport on porous media. This in turn could be useful

in designing the most effective biostabilization and bioremediation systems for treatment of contaminated soils.

Key words: biostabilization, bioremediation, DNAPL, PAH, column



LIGHT NONAQUEOUS-PHASE LIQUID WEATHERING AT VARIOUS FUEL RELEASE SITES

Don Kampbell, EPA/RSKERC, P.O. Box 1198, Ada, OK 74820; Phone: (580) 436-8564, Fax: (580) 436-8703, E-mail: kampbell.donald@epamail.epa.gov.

A fuel weathering study was conducted for database entries to estimate natural LNAPL weathering and source-term reduction rates for use in natural attenuation models. A range of BTEX weathering rates from mobile LNAPL plumes at eight field sites with known release dates was documented. Free-phase fuel BTEX weathering rates varied among sites and were influenced by many factors. First-order weathering rate for five JP-4 fuel sites was 16%/year. Benzene and toluene exhibited higher weathering rates than ethylbenzene and xylene, as expected, because of higher water solubility. The primary weathering mechanism of mobile LNAPL was dissolution. Meaningful determination of mobile LNAPL weathering rates for BTEX in gasoline was difficult because of the large ranges of initial BTEX values.

Key words: LNAPL, dissolution, natural attenuation



GROUNDWATER MODELING OF A PERMEABLE REACTIVE BARRIER TO ENHANCE SYSTEM PERFORMANCE

¹Kenneth Scott, and ²David Folkes,

^{1,2}EnviroGroup Limited, 7208 South Tucson Way Suite 125, Englewood, CO 80112;

^{1,2}Phone: (303) 790-1340; ¹E-mail:

kscott@envirogroup.com, ²E-mail:

dfolkes@envirogroup.com.

Experience has shown that one of the most common reasons permeable reactive barriers (PRBs) fail to meet performance criteria is inadequate understanding of the groundwater flow system. For example, contaminated water may flow around the ends of the barrier or funnelling slurry walls, under the barrier walls, or through the slurry walls. An analysis of the groundwater flow regime resulting from the installation of a PRB can lead to an effective design that significantly reduces the escape of untreated water through associated slurry walls and/or around the ends of the PRB system. A three-dimensional groundwater flow model using Modflow was developed to evaluate the effectiveness of groundwater capture and treatment resulting from the installation of a funnel-and-gate PRB. The reactive barrier was one remedy evaluated for containment of an on-site chlorinated solvent plume with concentrations of 1,1 DCE ranging up to 3,000 ug/l resulting from the degradation of 1,1,1 TCA and TCE. The plume is approximately 750 feet wide and flowed off site into a residential area. The on-site plume is of sufficient size that a linear design with one or more gates could not be constructed entirely on site and still provide for complete capture of impacted groundwater. The results of the model analysis provided for a design that incorporated several barrier and gate segments at varying orientations to groundwater flow for optimization groundwater capture. The model indicated the ideal location for gates to minimize head increases along the upgradient portion of the slurry wall, which resulted (as compared to a more sim-

plistic design) in reducing seepage of untreated groundwater through the wall and reduced flow around the end points of the barrier by 57 percent. The length and thickness of the gates were also optimized to provide sufficient resident time of groundwater in the PRB to accomplish treatment. Important design features affecting PRB performance include orientation of slurry walls to groundwater flow and contrast between slurry wall and formation permeability. Minor seepage through the slurry walls may be addressed by short extensions of the PRB to capture flow parallel to the slurry wall. The model results were also used to locate optimum sites for downgradient monitor wells to assess performance of the system.

Key words: barrier, modeling, PRB



A STUDY OF SOIL WATER-HOLDING PROPERTIES AS AFFECTED BY TPH CONTAMINATION

¹Suzette Burckhard, ²Dan Pirk, ²Vernon Schaefer, ³Peter Kulakow, and ⁴Blase Leven, ^{1,2}Civil and Environmental Engineering Department, Box 2219, South Dakota State University, Brookings, SD 57007; ¹Phone: (605) 688-5316, ¹E-mail: suzette_burckhard@sdstate.edu; ³Department of Agronomy, 2004 Throckmorton Plant Science Center, Kansas State University, Manhattan, KS 66506; ³Phone: (785) 532-7239, ³E-mail: kulakow@ksu.edu; ⁴Great Plains/Rocky Mountain HSRC, 101 Ward Hall, Kansas State University, Manhattan, KS 66506; ⁴Phone: (785) 532-0780, ⁴E-mail: baleven@ksu.edu.

The measurement of soil water content is one of the most common kinds of soil analysis performed. The potential effects of the soil water content on the behavior of soil make it an important measurement in every type of soil study. The relationship between soil water content and metric suction is known as the soil-water characteristic curve. The soil-water characteristic curve is often used for calculating unsaturated hydraulic values. The introduction of petroleum hydrocarbons into an unsaturated soil, due to a spill, alters unsaturated hydraulic properties of the soil, but current computer modeling of flow in unsaturated soil does not account for this change in unsaturated hydraulic properties. This presentation will present results from a laboratory experiment measuring the hydraulic properties of contaminated soils.

Key words: *phytoremediation, petroleum hydrocarbons, contaminated soil, vegetation*

Posters Bioremediation



BIOREMEDIATION OF MTBE IN THE RHIZOSPHERE

¹Suzanne Bonola and ²Anu Ramaswami, ^{1,2}Department of Civil Engineering, University of Colorado at Denver, Denver, CO 80217; ¹Phone: (303) 556-6726, ¹E-mail: sbonola@hotmail.com; ²Phone: (303) 556-4734, ²E-mail: aramaswa@carbon.cudenver.edu.

Accidental leaks or spills of gasoline containing the fuel oxygenate methyl-*tert*-butyl ether (MTBE) are of concern because of MTBE's high water solubility and low octanol/water partition coefficient (among other factors). Once in the groundwater, MTBE can move at virtually the same velocity as water, whereas benzene and other petroleum constituents tend to biodegrade and adsorb to soil particles. The degradation of MTBE in water can lead to the formation of *tert*-butyl alcohol, which can cause some carcinogenic activity in laboratory animals. Although MTBE is generally believed to be resistant to biodegradation, research has revealed that microbial biodegradation, particularly *in situ* in the vadose zone, may be an effective remediation option. The goal of this project is to determine the effect of grasses such as *Festuca arundinacea* (tall fescue) and *Medicago sativa* (alfalfa) on the degradation of MTBE in soil systems.

Key words: *MTBE, rhizosphere, biodegradation, phytoremediation*



NUTRIENT AND SURFACTANT ADDITIONS, PYRENE DEGRADATION, AND MYCOBACTERIA DIVERSITY IN PAH-CONTAMINATED SOIL

¹Pui-Yi Cheung and Brian Kinkle, Department of Biological Sciences, P.O. Box 210006, University of Cincinnati, Cincinnati, OH 45221-0006; ¹Phone: (513) 556-9757, ¹E-mail: cheungpi@email.uc.edu.

Polycyclic aromatic hydrocarbons (PAHs) are recalcitrant pollutants produced in fossil fuel combustion or as by-products of many industrial processes. There has been growing interest in the study of fast-growing species of mycobacteria due to their potential for PAH degradation. It has been suggested that addition of nutrients and surfactants may stimulate bioremediation of contaminated sites. However, little is known about the effects of these introduced chemicals on microbial community structure and degradative activity. In this study, we measured the mineralization of ¹⁴C-labeled pyrene in a PAH-contaminated Superfund soil with and without nutrient or surfactant amendments. Results showed that little degradation occurred in the control soil with no supplements. Higher levels of mineralization occurred when the soil was amended with nitrate, phosphate, Triton X-100, or Tergitol NP-10. Soils that received 1.5 mg/g soil of nitrate resulted in a higher level of pyrene mineralization than those that received 0.15 mg/g soil of nitrate. There was no observable difference in the level of mineralization between soils amended with phosphate at 0.15 mg/g or 1.5 mg/g soil. Triton X-100, at a concentration above its critical micelle concentration (CMC), was slightly more effective in enhancing mineralization than below the CMC. In contrast, there was no observable difference in the level of mineralization between soils amended with Tergitol NP-10 slightly below or above its CMC. Soil samples will be analyzed by PCR and temperature gradient gel electrophoresis (TGGE) to determine the relationship between the addition of nutrients and surfac-

tants, patterns of mineralization, and changes in mycobacterial community structure.

Key words: PAH, mycobacteria, surfactant, TGGE



THE EFFECTS OF ETHANOL ON BTEX NATURAL ATTENUATION (PURE CULTURE AND AQUIFER COLUMN EXPERIMENTS)

¹Marcio Luis Busi da Silva, ²Nanh Lovanh, ³Craig Hunt, and ³Pedro Alvarez, ^{1,2,3}Department of Civil and Environmental Engineering, 2130 SC, University of Iowa, Iowa City, IA 52242; ¹Phone: (319) 335-5054; ¹E-mail: msilva@engineering.uiowa.edu; ²E-mail: nanh-lovanh@uiowa.edu.

Although considerable progress has been made toward understanding hydrogeochemical factors that affect BTEX migration and biodegradation, little attention has been given to how differences in gasoline formulation affect natural attenuation processes. In this regard, the use of ethanol as a gasoline additive is increasing worldwide, both as a substitute fuel for imported oil and as an oxygenate to minimize air pollution from combustion. Yet, little is known about the effect of ethanol on biodegradation and migration of the toxic BTEX contaminants.

In this work, chemostat experiments were performed to investigate the effect of ethanol on aerobic benzene degradation, and to delineate the conditions that lead to simultaneous versus preferential biodegradation of ethanol when BTEX compounds are present. Chemostats were seeded with *Pseudomonas putida* F1 (PpF1), and fed benzene and ethanol. The influent benzene concentration was about 1 mg/L, and the dilution rate was 0.25 h⁻¹. The addition of ethanol to the influent at a concentration with equal chemical oxygen demand (COD) to the added benzene resulted in a 70% decrease in the steady-state effluent benzene concentration. This effect was representative of results with carbon-limiting conditions, and

was attributed to an ethanol-supported increase in biomass, resulting in faster benzene degradation rates. When ethanol was added to the influent at a high enough concentration that oxygen became limiting, no significant benzene degradation occurred. This suggests that simultaneous degradation is the normal mode of multiple substrate degradation when carbon is limiting, and preferential degradation would occur when carbon is not limiting.

Additional research of the effect of ethanol on BTEX bioremediation is being conducted. Aquifer columns have been constructed to study both the biotic and abiotic effects of ethanol on natural attenuation of gasoline releases. The column is of a large enough size (120 cm length by 5 cm diameter) and the hydraulic residence time is long enough (~7 days) for anaerobic zones to develop. One hypothesis for this work is that ethanol will be preferentially degraded under both aerobic and anaerobic conditions, extending the time and distance required for BTEX concentrations to be attenuated below regulatory limits. Theoretical considerations and preliminary results also indicate ethanol could increase BTEX migration velocities by decreasing sorption-related retardation during transport.

In conclusion, the use of ethanol as a gasoline oxygenate represents potential economic and air-quality benefits. Nevertheless, the inhibition of BTEX biodegradation and the possible decrease in sorption-related retardation suggests that ethanol is likely to increase BTEX plume lengths. The net effect of ethanol on natural attenuation of BTEX is likely to be system specific, depending largely on the release scenario and the assimilative capacity of the aquifer.

Key words: natural attenuation, ethanol, MTBE, BTEX



BIOLOGICAL SULFATE REDUCTION IN ALKALINE WATERS FOR THE REPROCESSING OF TRONA TAILINGS PONDS

¹Leigh Ann Boyack, ²Shelly Robertson, and ³Patrick Gilcrease, ^{1,2,3}Department of Chemical and Petroleum Engineering, University of Wyoming, P.O. Box 3295, Laramie, WY 82071-3295; ^{1,2,3}Phone: (307) 766-2500; ¹E-mail: lulu@uwyo.edu; ²E-mail: srobe@uwyo.edu; ³E-mail: gilcreas@uwyo.edu.

Sodium carbonate, commonly known as soda ash, is used in the production of glass, detergents, and other products. In the production of soda ash from trona ore, crystallizer purge streams are disposed of in large tailings ponds. The sodium carbonate levels in these ponds are quite high (8 to 14 weight percent); thus, after 50 years of operation, these ponds represent a significant potential source of sodium carbonate. Unfortunately, moderate levels of sodium sulfate (1 to 2 percent) prevent the further recovery of soda ash from these waters. In this research, a novel biological process which utilizes sulfate-reducing bacteria (SRB) was investigated.

SRBs that can survive the high pH conditions of the tailings ponds have been detected. These strict anaerobes have been tentatively identified as *Desulfovibrio* species through various staining techniques. They require organic matter for growth and use sulfate as a final electron acceptor. Soil and water samples from trona tailings ponds were set up in Winogradsky columns to enrich for SRBs. Samples collected from the Winogradsky columns and site soils were used to inoculate batch reactors (serum bottles). The batch reactors were used to optimize the organic carbon source and measure sulfate-reduction kinetics for the cultures. Reduction kinetics were also determined from chemostat data at different dilution rates. The resulting kinetic data will be used to evaluate various bioreactor designs. Support for this research was provided by OCI Wyoming.

Key words: biological sulfate reduction, sodium bicarbonate, soda ash



**AGRICULTURE-BASED
REMEDIATION PRO-
GRAM-TECHNOLOGY
DEVELOPMENT AND
TRAINING IN
BIOREMEDIATION**

¹Charles Kinoshita and ²Traci Sylva, ^{1,2}University of Hawaii at Manoa, Department of Biosystems Engineering, 3050 Maile Way, Gilmore 111, Honolulu, HI 96822; ^{1,2}Phone: (808) 956-8863; ¹E-mail: kinoshita@wiliki.eng.hawaii.edu; ²E-mail: kuromoto@hawaii.edu.

Bioremediation--the application of biological processes to address environmental problems--is among the technologies being touted to treat contaminated soils and water sources, and to process wastes. There are significant advantages to using bioremediation over other approaches. Most bioremediation processes can be performed *in situ*, which reduces cost and disruption to operations, simplifies logistics, and minimizes liability. Unlike many traditional methods that rely solely on disposal or containment, bioremediation usually aims to decompose pollutants, and therefore represents a permanent strategy, minimizing long-term liability.

Technological commercialization, moving scientific discovery to the marketplace, logically begins with an assessment of the scientific and engineering parameters of the technology and its potential application in a particular market. Widespread adoption depends on acceptance of the technology by the public and by regulators. Many technologies that are at the commercial or near-commercial stage can produce significant positive impacts in agricultural and military settings, but are not in use because specific skills are lacking or because little is known of available technologies or of providers of those technologies.

This report describes the University of Hawaii's component of the Agriculture-Based

Remediation Program (ABRP). The ABRP aims to strengthen bioremediation skills locally, nurture a bioremediation industry that can serve Hawaii and other locations in the Asia-Pacific region, and increase public awareness of agriculture-based bioremediation technologies. The present work consists of two components: (1) Technology Development and Capacity Building and (2) Information Dissemination and Outreach.

The primary objective of the first component, Technology Development and Capacity Building, is to strengthen biologically based environmental remediation skills to support the military and agricultural sectors locally and nationally, and help develop a bioremediation industry that has the capability to share technologies and services internationally. This is being achieved by assessing the appropriateness of existing bioremediation technologies and the professional pool in Hawaii and targeting efforts and resources to strengthen deficiencies. Particular emphasis is being given to ABRP-supported projects and technologies; filling critical voids in analytical and other industry-supporting capabilities; and working with the Governor's Millennium Workforce Development Initiative subgroup, which is focused on the development of an environmental workforce in Hawaii.

The primary objective of the Information Dissemination and Outreach component is to provide formal training to educators, government agencies, and the general public on advances in bioremediation and increase public awareness of the social and economic benefits of environmental restoration through agriculture-based bioremediation. These are being achieved by providing training to university and secondary-education faculty and government agencies; offering courses and hands-on training in environmental remediation to secondary-school and university students as well as post-graduate professional training; and disseminating information on bioremediation activities that are taking place under ABRP.

Key words: bioremediation, phytoremediation, environmental remediation, community outreach

Posters

Phytoremediation--Organics



METABOLISM OF TRICHLOROETHYLENE IN HYBRID POPLAR

¹Annette Dietz and ²Jerry Schnoor, ¹Department of Civil and Environmental Engineering, 122 ERF, University of Iowa, Iowa City, IA 52242; ²Department of Civil and Environmental Engineering, 116 ERF, University of Iowa, Iowa City, IA 52242; ¹Phone: (319) 335-5053, ¹E-mail: annette-dietz@uiowa.edu.

Phytoremediation efforts often use hybrid poplar trees, which may prove to be an inexpensive method of cleaning up groundwater contaminated with trichloroethylene. Hybrid poplar trees have been shown to take up and convert trichloroethylene to trichloroacetic acid, dichloroacetic acid, and trichloroethanol. These metabolites indicate that TCE may be transformed via an oxidative pathway similar to that found in mammalian systems, possibly involving a cytochrome P450-type enzyme. The subcellular microsomal fraction was isolated from hybrid poplar leaf tissues, and was tested for the ability to convert trichloroethylene to trichloroacetic acid. The effects of known inhibitors and inducers of cytochrome P450s on the formation of trichloroethylene metabolites were studied.

Key words: phytoremediation, trichloroethylene, cytochrome P450, poplar



ENHANCED PHYTOREMEDIATION OF SMEAR-ZONE SOILS THROUGH OXYGEN ADDITION

¹Jeremy Rentz and ²Jerry Schnoor, ¹Department of Civil and Environmental Engineering, 125 ERF, University of Iowa, Iowa City, IA 52242; ²Department of Civil and Environmental Engineering, 116 ERF, University of Iowa, Iowa City, IA 52242; ¹Phone: (319) 339-1005, ¹E-mail: Jeremy-rentz@uiowa.edu.

Hybrid poplar trees have been shown to clean soils and groundwater contaminated with hydrocarbons. The most successful phytoremediation projects have cleaned sites with moderate concentrations of contaminants at shallow depths. One limitation of the technology is often the presence of a "smear zone," an area of soil with elevated levels of contamination that is often anaerobic. These two characteristics serve to inhibit the roots of poplars from penetrating and cleaning the soil. It has been hypothesized that poplar trees can transport oxygen to anaerobic soils, but this characteristic has not been shown experimentally. In an effort to increase the usefulness of phytoremediation, the addition of oxygen to soils by chemical and physical means was investigated. The addition of oxygen to soils may aid in the penetration of smear-zone soil by the roots of hybrid poplar trees. Hybrid poplar (*Populus deltoides* x *nigra* DN34) cuttings were planted in eight-inch plastic tubes filled with soil from a former refinery and spill site at Heath, Ohio. The top 1.5 feet of soil in the tubes was excavated from a depth of zero to four feet at Heath, Ohio, with background levels of hydrocarbon contamination. The soil from 1.5 to 2.5 feet was excavated from Heath, Ohio, from depths of ten to fourteen feet. Six inches of gravel were added for adequate drainage. Five different experimental setups were used to evaluate various methods of oxygen transfer to roots and soils. Two methods for ORC (oxygen release compound) application and two different aeration tube configurations were tested along with one

set of tubes without oxygen addition. Growth, root density with depth, and final hydrocarbon concentration were used to evaluate the various scenarios.

Key words: phytoremediation, oxygen, poplar



PHYTOREMEDIATION OF A PETROLEUM REFIN- ERY LAND TREATMENT UNIT

Katherine Gomez and Jodi Shann, University of Cincinnati, Department of Biological Sciences, 821 A Rieveschl, P.O. Box 210006, Cincinnati, OH, 45221-0006; Phone: (513) 556-9765, E-mail: Holmeske@email.uc.edu.

Phytoremediation has shown promise in the laboratory as a remediation technique for different individual soil contaminants. Few studies, however, examine the application of phytoremediation to actual field sites, which are often contaminated with a mixture of compounds and have complicating factors associated with the specific site's history. In this study we investigated the potential for phytoremediation on a Land Treatment Unit that received petroleum refinery wastes more than 10 years ago and is currently under a RCRA closure plan. We conducted field sampling, lab analysis, and greenhouse treatability studies to determine, respectively, the vertical and horizontal distribution of contaminants on the site, their availability in soil, and site management strategies that could enhance remediation. Metal and organic analysis of soil cores sampled from across the site confirmed the presence of high concentrations of Cr, Pb, Zn, Cu, Ni, and several large ring PAHs with pyrene and chrysene predominating. The level of contamination varied with location on the site and depth in soil. The depth and the aging of the contaminants may limit their bioavailability to plants and microorganisms and the potential for remediation. Plants may be able to increase the bioavailability of aged contaminants through release of exudates, or plant root penetration. Sequential extractions

were performed before and after planting to determine the bioavailability of contaminants to plants and to see if different plant species affect the bioavailability of compounds to plant uptake or microbial degradation. Previous plantings at the site may have allowed phytoremediation to occur resulting in a distinct upper and lower soil layer. Some preliminary studies were done with plants in large clear columns with each of the layers separately and with both layers together, to determine if the layers existed because the roots could not grow deep enough to reach the lower layer or if the lower layer was more phytotoxic. Our results showed that plants were able to grow on the deeper layer, indicating that limited rooting depth may have been responsible for the observed layers. To determine if deep tilling to incorporate the two layers would allow for more phytoremediation, a treatability study was performed on different concentrations of the upper and lower soil layers with several plant species. The species used were perennial rye; a mixture of legume, rye, and fescue; lambsquarter; and timothy.

Key words: phytoremediation, petroleum hydrocarbons, bioavailability



VEGETATED TREATMENT OF VEHICLE WASH SEDIMENTS: DEVELOPMENT OF A DECISION SUPPORT TREE

¹Suzette Burckhard, ²Kipp Thompson, ²Vernon Schaefer, ³Peter Kulakow, and ⁴Blase Leven, ^{1,2}Civil and Environmental Engineering Department, Box 2219, South Dakota State University, Brookings, SD 57007; ³Department of Agronomy, 2004 Throckmorton Plant Science Center, Kansas State University, Manhattan, KS 66506; ⁴Great Plains/Rocky Mountain HSRC, 101 Ward Hall, Kansas State University, Manhattan, KS 66506; ¹Phone: (605) 688-5316, ¹E-mail: *suzette_burckhard@sdstate.edu*; ²Phone: (785) 532-7239, ³E-mail: *kulakow@ksu.edu*; ⁴Phone: (785) 532-0780, ⁴E-mail: *baleven@ksu.edu*.

There is a need for a support tree that will allow for simple design of the natural treatment of a contaminated soil using vegetation. This support tree has the potential to offer the background needed for design rather than requiring the user to possess this background. This will allow persons seeking choices regarding information on the design of a natural treatment using vegetation to approach the design and find simple and generalized solutions. The objective of this paper is to show an initial guide for a natural treatment option, decision support tree. The decision support tree will require input from the user. The input would consist of answering a few questions related to the type of contamination, soil, and climate. From this input, the decision support tree will provide a list of plants that would be suited to the site. Output from this decision tree has been designed to work with a graphical user interface to further help environmental professionals design vegetated treatment options.

Key words: phytoremediation, petroleum hydrocarbons, contaminated soil, vegetation



VEGETATED TREATMENT OF VEHICLE WASH SEDIMENTS: DESIGNING A GRAPHICAL USER INTERFACE

¹Muralidharan Narayanan, ²Jai Bharath Reddy, ³Suzette Burckhard, ⁴David Gustafson, ⁵Larry Erickson, ⁶Peter Kulakow, and ⁷Blase Leven, ^{1,2,4}Department of Computing and Information Sciences, Kansas State University, Manhattan, KS 66506; ³Department of Civil and Environmental Engineering, South Dakota State University, Brookings, SD 57007; ⁵Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506; ⁶Department of Agronomy, Kansas State University, Manhattan, KS 66506; ⁷Great Plains/Rocky Mountain Hazardous Substance Research Center, Kansas State University, Manhattan, KS 66506; ^{1,2,4}Phone: (785) 532-6350; ¹E-mail: *nmurali@ksu.edu*; ²E-mail: *jai@cis.ksu.edu*; ⁵Phone: (785) 532-4313; ⁵E-mail: *lerick@ksu.edu*; ⁷Phone: (785) 532-0780, ⁷E-mail: *baleven@ksu.edu*.

Graphical user interfaces (GUIs) help create user-friendly interactions between a model application and an inexperienced user. A GUI helps to package the various software tools that are essential for effective user interactions. The paper presents a GUI based on mathematical model used for simulating a vegetated treatment of a site contaminated with petroleum hydrocarbons. The mathematical model, described elsewhere, helps to simulate fate and transport of water and solute in the subsurface environments. The simulated results are graphically displayed as model predictions to the user in a friendly and clear manner. To successfully develop a GUI, integration of components from various platforms is essential: (1) Databases component may be used to retrieve or update information about specific soil properties, solute properties, plant properties, and climatic conditions of the site; (2) Graphical units such as graphics editor, menu bars, tool bars, and dialog boxes allow the user to generate useful site-specific data as input components to the

GUI; (3) The mathematical modeling component, developed in FORTRAN, is coupled and executed using the GUI, based on the generated input component; and (4) The output component of the GUI is used to display to the user the model predictions in a graphical format. These predictions help the user to make effective management-related decisions such as irrigation and fertilization requirements. The GUI could also include various estimates such as the desired cleanup levels, amount of time required for these cleanup levels, and cost incurred in this treatment process. This GUI would also be a useful tool for environmental professionals who are making decisions with regard to phytoremediation treatment of any contaminated site.

Key words: GUI, contaminated site, decision making



**VEGETATED TREATMENT
OF VEHICLE WASH SEDI-
MENTS: MATHEMATI-
CAL MODELING OF
GROUNDWATER AND
SOLUTE TRANSPORT**

¹Muralidharan Narayanan, ²Suzette Burckhard, ³Larry Erickson, ⁴Peter Kulakow, and ⁵Blase Leven, ¹Department of Computing and Information Sciences, Kansas State University, Manhattan, KS 66506; ²Department of Civil and Environmental Engineering, South Dakota State University, Brookings, SD 57007; ³Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506; ⁴Department of Agronomy, Kansas State University, Manhattan, KS 66506; ⁵Great Plains/Rocky Mountains Hazardous Substance Research Center, Kansas State University, Manhattan, KS 66506; ¹Phone: (785) 532-6350, ¹E-mail: nmurali@ksu.edu; ³Phone: (785) 532-4313, ³E-mail: lerick@ksu.edu; ⁵Phone: (785) 532-0780, ⁵E-mail: baleven@ksu.edu.

The transport and fate processes of water and solutes in a contaminated site with veg-

etated treatment (phytoremediation strategy) are mathematically modeled. Subsurface groundwater flow, precipitation events, and transpiring vegetation significantly influence soil-water transport. This in turn influences the transport and fate processes of contaminants in subsurface environments. The transport of soil-water is modeled in a variably saturated environment in vertical dimension and is represented as a Richards equation supported with a van Genuchten model as its constitutive relations. The fate and transport of solutes is coupled to the water transport through the Darcy water flux equation. The solute transport model considers various physicochemical phenomena such as adsorption, volatilization, gas-phase diffusion, biodegradation by soil microbes, and plant uptake as fate processes of the solutes. Vegetation may play an important role by enhancing indigenous soil microbial degradation and by also absorbing or transpiring the contaminants. Moreover, volatile contaminants could escape to the atmosphere under the influence of atmospheric conditions. This condition is treated as an open-contaminant, evaporative-flux boundary condition at the soil surface. The mathematical model is validated with experiments performed in laboratory columns. The validated model is also employed to investigate the fate and transport processes in an actual field site at Ft. Riley, Kansas. The site was contaminated with petroleum hydrocarbons. The time scales considered for the model simulation stretch over seasons of varying precipitation events. The model results help to predict the soil conditions, plant activities, and contaminant fate processes in the soil environments for the simulation period.

Key words: soil-water transport, van Genuchten model, petroleum hydrocarbons

Posters

Phytoremediation--Metals



NEW PHYTOREMEDIATION METHOD FOR TITE CLEANING OF RADIOAC- TIVE-CONTAMINATED AQUATIC SYSTEMS

*Oleksandr Mikhyeyev, Boris Sorochinsky,
Mikle Ruchko, and Alexey Prokhnevsky,
Institute of Cell Biology and Genetic Engi-
neering, National Academy of Science of
Ukraine, 148 Zabolotnogo St., Kiev-252143,
Ukraine; Phone: +380-44-263-61-67; Fax:
+380-10-50; E-mail: valmih@akcecc.kiev.ua.*

The problem of soil and water polluted with radionuclides is very important for many countries. For example, in the Ukraine more than 4.6 billion hectares of agricultural lands and woods and 2200 occupied properties with a population of about 2.4 million people have undergone radioactive pollution as a result of failure at the Chernobyl Nuclear Power Station (ChNPS) in 1986. The task of water reservoirs' deactivation from short-living radionuclides is no longer an urgent concern. Unfortunately, there is still an unsolved problem of environment cleaning from the long-living radionuclides like ^{137}Cs and ^{90}Sr . These isotopes are the main source of irradiation for the people and animals in the polluted territories. The preservation of all useful properties must be an obligatory condition for the environmental cleanup. Plant-based technologies seem to be the solution for some cleanup problems. The radionuclides' low biological availability may limit use of plant technologies for remediation of soils. However, phytotechnologies can be rather effective in aquatic systems where the radionuclides exist in the dissolved state. ^{137}Cs and ^{90}Sr isotopes are the main sources of irradiation at Chernobyl's accident territories. The laboratory investigations took place with sunflower plants, Indian mustard, and peas. The maximal

transfer factors (TF - magnitude of a ratio of specific activity of plant object to specific activity of a medium, i.e., ground or water) for ^{137}Cs are determined in roots of the mustard and were equal to 2350. The maximal TF for ^{90}Sr is equal to 374 for sunflower roots. When the plants with large biomass levels were used, the activity of ^{137}Cs was reduced from 90 Bq/L to 9 Bq/L. The efficiency of water clearing from ^{90}Sr was not so effective. The field trials were carried out at a natural pond located near Yanov village (10-km exclusion zone of ChNPS; the volume of the pond is equal to 18-20 m³). Plants were cultivated directly at the water surface by using special floated constructions. The plants have taken out from a reservoir more than 380 kBq ^{137}Cs and near 1100 kBq ^{90}Sr , respectively 74% and 14% from the initial amount of these isotopes. It is remarkable that many plants can demonstrate larger sorption ability at the conditions of aquatic culture than other water vegetation. The plant species capable of producing large biomass levels seems to be a determining factor in rhizofiltration technology. Sunflower plants and pea plants are most preferable from this point of view. The results allow a conclusion that there is a high degree of clearing of water polluted with the soluble forms of radionuclides and puts into perspective the application of this technology. Vegetative biomass with high activity must be converted to ash and the ash buried as high activity waste. It solves the problem of radioactivity and reduction of quantity for such waste. At the same time, low-radioactive phytomass may be used as raw material for the production of biogas and allocation of various vegetative products, including some secondary metabolites, cellulose, etc.

Key words: ChNPS, radionuclides, aquatic systems, phytoremediation



USING PLANT BIOTECHNOLOGY TO INCREASE THE POTENTIAL FOR PHYTOREMEDIATION OF MOLYBDENUM AND TUNGSTEN

Kerry Hale, Steven Stack, and Elizabeth Pilon-Smits, Colorado State University, Department of Biology, A/Z Building, Fort Collins, CO 80523; Phone: (970) 491-3320; E-mail: halekl@lamar.colostate.edu.

Phytoremediation, environmental cleanup using plants, offers a cost-effective and environmentally friendly alternative to conventional methods of pollutant remediation. We are exploring the potential of using *Brassica juncea* (Indian mustard) for the phytoremediation of heavy metals such as molybdenum (Mo) and tungsten (W). In our study, seedlings were treated with Mo and W to test their tolerance and accumulation capacities for these elements.

We are also interested in determining the metabolic pathways of these elements in plants. To test whether the sulfate assimilation pathway may be involved in uptake and reduction of these oxyanions, genetically engineered mustard plants overproducing the enzyme ATP sulfurylase (APS) were compared to normal (wild-type) mustard plants for tolerance and accumulation of Mo and W. Differences between APS and wild-type were found to be significant. The transgenic APS plants are able to accumulate up to 1% of their dry weight as Mo, an increase of 40% over wild-type. APS plants also show a decrease in Mo tolerance, as seen in their reduced size, when compared to wild-type. One explanation for this reduced tolerance to Mo is that ATP sulfurylase reacts with Mo to form unstable esters that result in a loss of ATP. Also interesting is the appearance of blue compounds within the epidermal/subepidermal layers of the plant tissue when the plants are exposed to high concentrations of Mo and W. It appears that *B. juncea* is converting the metal into a blue form that is accumulated in the periphery of the stem, perhaps as a tolerance mechanism. Overall, *B. juncea* appears to be a good species for the

phytoremediation of Mo, and the application of plant biotechnology may serve to increase this potential.

Key words: *phytoremediation, molybdenum, tungsten*



UPTAKE OF METALS AND PAHS BY *BRASSICA JUNCEA* AND *MEDICAGO SATIVA*

¹Anamaria Bukvic and ²Jodi Shann, ^{1,2}University of Cincinnati, Department of Biological Sciences, 614 Rieveschl Hall, P.O. Box 210006, Cincinnati, OH 45221-0006;

^{1,2}Phone: (513) 556-9700, ¹E-mail: bukvicic@email.uc.edu; ²E-mail: jodi.shann@uc.edu.

Phytoremediation is an emerging technology in which plants remove contaminants from the environment. One of the common cleanup strategies in phytoremediation is phytoextraction where plants participate in decontamination directly through the uptake of pollutants. Many contaminated sites contain complex mixtures of organic and inorganic compounds released from the same anthropogenic sources. Plant uptake mechanisms may act differently when pollutants are present as mixtures than when they occur separately. To address this situation, uptake of PAHs and metals by *Brassica juncea* (mustard) and *Medicago sativa* (alfalfa) is being investigated. To determine the potential of *B. juncea* and alfalfa for uptake of the heavy metals, Cd, Ni, and Zn, and the PAHs, pyrene and benzo[a]pyrene, plants were exposed to hydroponic solutions containing the individual contaminants or mixtures of them. In hydroponics, all factors that would normally interfere with plant uptake, such as microbial activity and adsorption to the soil particles, were eliminated, creating a sterile and homogeneous experimental environment. Uptake was determined by metal and/or PAHs loss from the hydroponic solution over time and from analysis of plant tissues. Metals and

PAHs were determined by AAS, ICP, HPLC, and GC-MS, respectively. Uptake of chosen contaminants, present individually or in the mixture, was observed by both model species. Experiments were also conducted on the uptake in *B. juncea* excised roots using ^{14}C radiolabeled pyrene and benzo[a]pyrene. Subsequent loss of the contaminants from the treatment solution was observed over time, as well as its incorporation in the root tissue.

Key words: uptake, phytoremediation, PAHs, heavy metals

Posters Remediation



PHOTOOXIDATION OF METHYL-*TERT*-BUTYL ETHER ON TITANIA USING A PLUG-FLOW REACTOR

Shaogang Chu, Chia-Swee Hong, and Rajinder Narang, Wadsworth Center, New York State Department of Health, and School of Public Health, State University of New York at Albany, NY 12201-0509; Phone: (518)473-7299, E-mail: hongc@wadsworth.org.

The gas-phase photocatalytic degradation of methyl-*tert*-butyl ether (MTBE) using TiO_2 -impregnated fiberglass mesh was investigated. The kinetics of the photocatalytic process was measured with a continuous flow of reactants through the plug-flow reactor, which was illuminated with UVA light lamp. A plot of $(V/Q)/(C_0-C)$ versus $\ln(C_0/C)/(C_0-C)$ showed a linear relationship by varying C_0 , the initial concentration of MTBE, and measuring C , the concentration of MTBE in the outlet, where V and Q represent the volume of the reactor and the flow rate through the reactor, respectively. The oxidation kinetics of MTBE followed the Langmuir-Hinshelwood model. The effect of humidity on the photocatalysis was also examined. The adsorption constant K and rate

constant k was 92.42 L/mmol and $0.07 \text{ mmol/L min}^{-1}$, respectively, under the humidity of 15% in comparison to the corresponding values of 125.84 L/mmol and $0.14 \text{ mmol/L min}^{-1}$ in dry air condition. Both adsorption constant and rate constant decreased with increasing humidity. It indicated that water produced from the reaction process is enough for the hole scavenging to form hydroxyl radicals and extra water vapor-inhibited MTBE photodegradation. The half-lives of MTBE with initial concentration of 0.14 mmol/L were 1.05 and 0.53 min for 15% humidity and dry air condition, respectively. The reaction by-products have been identified by GC/MS. Acetone and *tert*-butyl formate (TBF) were the primary intermediates. Other by-products, formaldehyde and *tert*-butyl, alcohol (TBA) were also detected. The degradation pathway of MTBE in the photocatalysis was believed to be similar to that in TiO_2 slurries. The concentration of carbon dioxide in the outlet gas was increased rapidly after the reactions were initiated. It showed that MTBE could virtually be completely mineralized after extended reaction time.

Key words: photocatalysis, MTBE, titanium dioxide, GC/MS



TREATMENT OF PETROLEUM CONTAMINATED GROUNDWATER BY ELECTROCHEMICAL PEROXIDATION

¹M. Wunderlich, J. Chiarenzelli, R. Scrudato, and L. Falanga, Environmental Research Center, SUNY Oswego, 319 Piez Hall, Oswego, NY 13126; ¹Phone: (315) 341-3639, ¹E-mail: wunderli@oswego.edu.

Electrochemical peroxidation (ECP), a proprietary process developed by SUNY at Oswego researchers, is an enhancement of Fenton's Reagent (FR) that utilizes sacrificial steel electrodes, electricity and stoichiometrically balanced applications of hydrogen peroxide. This process has been used to degrade aqueous phase organics including petroleum hydrocarbons, MTBE and

BTEX in groundwater. Bench scale FR has been conducted on petroleum contaminated groundwater taken from two recovery wells at the site of a leaking subsurface storage tank at the Onondaga Nation located near Syracuse, N.Y. FR treatment reduced benzene, MTBE, ethylbenzene, toluene and total xylenes to non-detect levels within minutes. Subsequent ECP experiments also showed the elevation of dissolved oxygen levels in anaerobic groundwaters during treatment resulting in aerobic conditions. Bench scale ECP experiments were also conducted on petroleum contaminated groundwater from the site of a previously removed subsurface gasoline storage tank in Saratoga Springs, N.Y. ECP treatment of this groundwater resulted in complete degradation of ethyl benzene, m-, o-, and p- xylene at a pH of 2 and 5. Similar experiments conducted on petroleum contaminated groundwater from the site of a subsurface gasoline release in Amsterdam, N.Y. showed complete destruction of BTEX and phenolic compounds. MTBE was reduced by 82% and 97% in duplicate experiments. ECP technology has been selected by the New York Department of Environmental Conservation (NYSDEC) to treat groundwater at the Saratoga Springs and Amsterdam sites. Pilot scale tests will be conducted involving ECP treatment of groundwater and recharge upgradient of the plume utilizing dry wells or glass filled infiltration galleries. Geochemical characterization of both groundwaters show substantial amounts of ferrous iron facilitating in-situ Fenton's Reagent reactions and oxidation. Therefore, residual peroxide will be maintained in the effluent for in-situ reactions with contaminants sorbed to sediment particles. ECP is also being considered for a pilot scale demonstration to degrade BTEX and MTBE at the Onondaga Nation site, near Syracuse, N.Y., by the NYSDEC and the United States Environmental Protection Agency.

Key words: electrochemical peroxidation, petroleum, MTBE, Fenton's Reagent



KINETICS AND PRODUCTS OF THE TiO_2 PHOTOCATALYTIC DEGRADATION OF 4,4'-DICHLOROBIPHENYL IN WATER

¹Fu Fang, ²Shaogang Chu, ³Chia-Swee Hong, and ⁴Steven Connor, ^{1,3}Department of Environmental Health and Toxicology, School of Public Health, State University of New York at Albany, NY 12201-0509; ^{2,3,4}Wadsworth Center, New York State Department of Health, Albany, NY 12201-0509; ¹Phone: (518)486-1830, ¹E-mail: fangf@wadsworth.org.

Photocatalytic processes in the presence of titanium dioxide provide an interesting route to destroy hazardous organic contaminants, such as polychlorinated biphenyls, being operational in the UV-A domain with a potential use of solar radiation. In this paper, 4,4'-dichlorobiphenyl (4,4'-DCB) was tested as a model compound at bench scale. A generator-column technique was used to prepare the PCB aqueous solution. 4,4'-DCB was irradiated in a TiO_2 aqueous suspension under UV-340. The degradation of 4,4'-DCB followed the Langmuir-Hinshelwood kinetic model at natural pH. Rate constant k was proportional to the concentration of TiO_2 up to 5 mg/L. Adsorption equilibrium constant K of 4,4'-DCB was calculated to be 3.59×10^7 L/mol and was independent of the concentration of TiO_2 . Pentafluorobenzoyl chloride (PFBC) was used as a derivatizing agent for hydroxylated PCBs. The derivatives were identified by gas chromatography-mass spectrometry (GC-MS) and quantified by using gas chromatography with an electron-capture detector (GC-ECD). The derivatization method improved the detection limits of the targeted compounds to 19.0 pg/mL for 4'-chloro-4-biphenyl-ol, and 12.6 pg/mL for 4,4'-dichloro-3-biphenyl-ol, respectively. The primary by-products included three hydroxylated PCBs, 4'-chloro-4-biphenyl-ol, 4,4'-dichloro-2-biphenyl-ol, and 4,4'-dichloro-3-biphenyl-ol. A first-order parallel/consecutive reaction model was developed based on an assumed oxidative

mechanism. Time profiles of hydroxylated PCBs based on the predicted model were in agreement with those from the experimental data. Hydroxylation was confirmed to be the major pathway in the photocatalysis. OH radicals could substitute either hydrogen or chlorine on a phenyl ring. Hydroxylation could occur at all sites of a biphenyl ring despite steric hindrance and/or resonance effects; however, the ortho position was more favorable for substitution than meta or para positions. Other important intermediates were identified as 4-chlorophenyl-ethanone, 4-chlorobenzaldehyde, and 4-chlorophenol. Neither 4-chlorobiphenyl nor biphenyl were detected, which indicated that dechlorination was a minor pathway if any. A reaction scheme involving hydroxyl radicals has been proposed.

Key words: PCB, TiO₂, photocatalysis, derivatization, pentafluorobenzoyl chloride



THE EFFECTS OF LOW-LEVEL RELATIVE HUMIDITY ON THE CARBON ADSORPTION EFFICIENCY OF A VOLATILE ORGANIC HYDROCARBON

¹Jefrey Sipple, R. Putnam, and Anu Ramaswami, 13226 E. Kansas Dr., K183, Aurora, CO 80012; ¹Phone: (303) 338-5390; ¹E-mail: Jefrey.Sipple@uchsc.edu.

The removal of volatile organic hydrocarbons (VOCs) is extremely important to the protection of human health and the environment. Carbon adsorption is one such technology which is used to remove these contaminants with greater than 99% efficiency. The removal is facilitated by Van Der Waal forces, which enhance the stability of the bonds between carbon atoms which make up the contaminant and the elemental carbon atoms comprising the carbon bed. Though this removal efficiency is slightly lower than incineration, it also has a lower overall environmental impact. However, the literature suggests

that under humid conditions (i.e. somewhere between 30 and 70% or above), solvent bonding to activated carbon is impaired, decreasing the overall carbon adsorption efficiency. Practical experiences indicate that even a one percent decrease in the overall removal efficiency by activated carbon can be significant, especially in instances that cleanup goals cannot be achieved. It is generally accepted that under humid conditions, water molecules in some way interfere with the binding sites available to the carbons of the contaminant, but what effects, if any, low relative humidity may have on carbon adsorption is unknown. In fact, all experimental models and data are currently based on the recovery of pure solvents or combinations of pure solvents, so a model incorporating the effects of any relative humidity on recovery is unavailable. The major goal of our project is to test the hypothesis that a decrease in the carbon adsorption efficiency of a pure VOC occurs under conditions of low relative humidity. If this decrease in carbon adsorption efficiency is a statistically significant one, we will propose a theoretical, mathematical model which could explain these changes.

Posters

Metals-Enhanced Remediation



ZERO-VALENT IRON FOR TREATMENT OF HIGH ARSENIC WATER

¹Santhiti Tawachsupha, ²Mehmet Isleyen, and ³Anu Ramaswami, ^{1,2,3}Department of Civil Engineering, University of Colorado, Denver, CO 80217; ¹Phone: (303) 504-4916, ¹E-mail: Santhiti@earthlink.net.

The international community is urgently seeking low-cost, point-of-use arsenic removal technologies appropriate for use in rural areas of Bangladesh and West Bengal, India, where

an estimated 76 million people are exposed to high concentrations (50 ppb to ~3,500 ppb) of arsenic in drinking water. The affected populations reside in villages with little electricity and no running water, and they rely on the drinking water pumped from borewells which has been shown to be contaminated with high levels of arsenic. Low-cost and in-home treatment technologies are required for rapid removal of arsenic from the contaminated drinking waters. This poster presents results from a screening study designed to evaluate the efficiency of zero-valent iron for arsenic removal from water stored in vessels within individual homes. Batch equilibrium experiments, with initial arsenic concentrations of 2000 ppb and 200 ppb, showed arsenic removal efficiencies of ~95% with iron in the presence of sulphate in solution. The kinetics of arsenic removal by iron was examined under various conditions. High removal efficiencies (~93%) were observed from high arsenic waters (2000 ppb) over short contact times (30-40 min) with iron, in the presence of sulphate in solution. Most rapid arsenic removal was observed in the absence of air in the system, while phosphate buffers were observed to inhibit arsenic removal by iron. Arsenic was found to be firmly bound on iron filings in the presence and absence of sulphate. The final concentrations of iron seem to be dependent on arsenic concentration in solution, and it was shown that a dose of iron concentration (2,500 mg/L) is suitable for the process to the EPA's standard for people's health.

Key words: arsenic, zero-valent iron, water treatment



REDUCTION KINETICS OF INORGANIC CONTAMINANTS BY IRON METAL

¹Michael Alowitz, ²Ryan Gettler, and ³Michelle Scherer, ^{1,2,3}Department of Civil and Environmental Engineering, University of Iowa, 4016 Seamans Center, Iowa City, IA 52242; ¹Phone: (319) 335-6164, ¹E-mail: michael-alowitz@uiowa.edu; ²Phone: (319) 335-6164, ²E-mail: ryan-gettler@uiowa.edu; ³Phone: (319) 335-5654, ³E-mail: michelle-scherer@uiowa.edu.

In recent years, research into zero-valent iron walls has yielded hundreds of papers and over 40 field installations of permeable reactive barriers (PRBs). Zero-valent iron is a strong reductant capable of degrading many oxidized compounds. Reduction of organic compounds by zero-valent iron is well studied. Observed rate constants (k_{obs}) for reduction of chlorinated aliphatic compounds by iron span more than three orders of magnitude. Normalization of observed rate data to iron surface area concentrations has decreased the variability to a single order of magnitude for most compounds. Reactivity of chlorinated aliphatic compounds with iron correlates well with measures of electron affinity such as one-electron reduction potential and the energy of the lowest unoccupied molecular orbital (E_{LUMO}).

Reduction of inorganic compounds by iron metal has not been studied as thoroughly as the degradation of organic compounds. We are exploring published kinetic data for reduction of inorganic compounds such as chromate, nitrate, and uranium in an attempt to elucidate a correlation between reported rate constants and several parameters including reaction pH, iron surface area concentration, and electron affinity. We will also examine the rates of reduction by iron from different sources.

The reactivity of iron from different sources has been reported to vary by more than would be expected by surface area differ-

ences alone. Iron commercially available in bulk often has a significant oxide layer on the particles and may contain substantial impurities such as magnesium, carbon, and sulfur. Many contaminant reduction studies have used expensive high purity iron; however, the cheaper bulk iron is used in field installations. We will examine the importance of iron source by comparing the kinetics for reduction of inorganic compounds by several different types of iron.

The results will aid in the design of iron metal permeable reactive barriers by providing a better estimate of the expected rates of reduction of inorganic compounds. Information about the reactivity of different iron types may allow for improved cost analysis and lower construction costs by promoting selection of a more effective iron.

Key words: iron, PRB, reduction, chromate, nitrate



**GEOMICROBIOLOGICAL
INTERACTIONS AMONG
IRON SULFIDE MINERALS AND
METHANOGENIC CON-
SORTIA**

¹Jerry Gander, ²Gene Parkin, and ³Michelle Scherer, ^{1,2,3}Department of Civil and Environmental Engineering, The University of Iowa, 2130 Seamans Center, Iowa City, IA 52242; ¹Phone: (319) 335-6164; ¹Email: jerry-gander@uiowa.edu; ²Phone: (319) 355-5655, ²Email: gene-parkin@uiowa.edu; ³Phone: (319) 355-5654, ³Email: michelle-scherer@uiowa.edu.

Iron sulfide minerals are common soil constituents that have been identified in a number of anaerobic aquatic systems. Iron sulfide minerals are produced primarily via anaerobic microbial activity where hydrogen sulfide produced by sulfate-reducing bacteria reacts with various iron species. The initial iron sulfide species formed is mackinawite, FeS_{1+x} . Changes in the environmental condi-

tions, including pH, temperature, and exposure to sulfate-reducing bacteria, however, will alter the iron sulfide minerals to other crystalline structures such as greigite, Fe_3S_4 , and pyrrhotite, FeS_{1+x} . Pyrite, FeS_2 , (i.e., fool's gold) is the most stable form of iron sulfide mineral, and sulfate-reducing bacteria can produce pyrite from mackinawite when elemental sulfur is present.

Iron sulfide minerals represent a potential reductant in the natural attenuation of chlorinated aliphatic hydrocarbons (CAHs) in reduced anaerobic environments, and it may have application as an additive in certain passive remediation applications using iron metal as a reductant. Iron sulfide reactions with hexachloroethane have been shown to be insensitive to many organic amendments and mild changes in ionic strength, suggesting that iron sulfide may retain its reactivity in diverse environments. In some cases, iron sulfides may prove to be more beneficial than iron metal in CAH degradation. This hypothesis is particularly promising, given that one iron sulfide form, troilite, has been shown to react much faster than iron metal in trichloroethane degradation.

Along with independent abiotic transformation processes, iron sulfide minerals could serve a purpose in CAH degradation during biological productive dechlorination processes as well. Methanogenic microbial populations need sources of both ferrous iron and sulfide to maintain normal metabolic processes. This requirement for ferrous iron and sulfide implies that iron sulfide is present in environments where methanogens thrive. Both methanogenic populations and iron sulfide minerals have been shown to reduce CAHs through independent processes. What has not been investigated is the relationship, if any, between the iron sulfide degradation reactions and the reductive dechlorination processes of methanogens.

To this end, we are investigating the role of iron sulfide minerals as a source of CAH reduction, both in the presence and absence of

methanogenic populations. This will aid in determining any relationships between iron sulfide transformation reactions and the reductive dechlorination processes of methanogens, and it could help predict which mechanism(s) dominate within these combined abiotic/biotic environments. To assess the interaction of iron sulfide minerals and methanogenic cultures, a number of laboratory techniques will be used. Preliminary laboratory work has provided a method of iron sulfide mineral synthesis that has been confirmed with X-ray powder diffraction (XRD). Formation of iron sulfide minerals has also been observed via the reduction of sulfate by iron metal. Due to the high sensitivity to oxygen of both iron sulfide minerals and methanogenic cultures, synthesis and materials preparation will be conducted in an anaerobic chamber, and all reactors will be prepared with methods that simulate anaerobic conditions. Batch and column studies will be conducted to investigate the reaction kinetics and product distribution of CAH reduction in the following systems: (1) iron sulfide + CAH contaminant, (2) methanogenic culture + CAH contaminant, and (3) iron sulfide + methanogenic culture + CAH contaminant. Conclusions drawn based on comparisons of the performance of these various experimental systems will aid in defining the roles of both iron sulfide minerals and methanogenic populations in natural attenuation of CAH contaminants. Preliminary results have shown that reduction of 1,1,1-trichloroethane by iron sulfide minerals occurs with a half-life of approximately three days. The products resulting from this reaction have not yet been identified and are currently being investigated.

Key words: chlorinated hydrocarbons, iron reactive barriers



ABIOTIC REMOVAL OF TETRACHLOROETHENE (PCE) AND TRICHLOROETHENE (TCE) WITH SAND UNDER VARIOUS CONDITIONS

Lei Wang, Maina Githinji, and Robert Segar Jr., Department of Civil and Environmental Engineering, University of Missouri-Columbia, Columbia, MO 65211; Phone: (573) 882-0075; E-mail: segarr@missouri.edu.

This study was conducted to investigate the extent of tetrachloroethene (PCE) and trichloroethene (TCE) removal imposed by five types of sand (quartz, garnet, ilmenite, hematite, and magnetite) and iron filings under various conditions. The conditions included control (medium water only), oxidative (hydrogen peroxide), aerobic (pure oxygen purged), anoxic (nitrogen purged), and anaerobic (nitrogen purged with formate as reductant) conditions. Under control condition, TCE and PCE had no significant removal. Under anaerobic, anoxic, and aerobic conditions with and without sand, 20% or less PCE and TCE removal occurred, which was mainly due to diffusion, volatilization, and errors. Most significant removal occurred when hydrogen peroxide existed, resulting in 91% of PCE and 99% of TCE being reduced during 12 hours without sand. High-iron-content sand had no significant effect because the content of iron was fully oxidized iron. However, the decomposition rate of hydrogen peroxide was increased 15 to 30 times when sand existed, which decreased PCE and TCE removal and need to add more hydrogen peroxide. Further continuous flow column studies showed that sands had no significant effect on removal of PCE and TCE. Iron filings could remove 93% of PCE and 69% of TCE under anoxic, 82% of PCE and 70% of TCE under aerobic, and 95% of PCE and 98% of TCE under oxidative conditions. A serious clogging problem occurred under pure oxygen and hydrogen peroxide conditions with the iron filings.

Key words: tetrachloroethene (PCE), trichloroethene (TCE), hydrogen peroxide, sand (quartz garnet, ilmenite, hematite, magnetite), anoxic, aerobic, anaerobic

Posters

Sorption, Binding, and Precipitation



STUDY OF METAL ION BINDING TO CHEMICALLY MODIFIED OAT AND WHEAT BY-PRODUCTS

¹V. Armendariz, ²L. Bess-Oberto, ³K.J. Tiemann, and ⁴J.L. Gardea-Torresdey, ^{1,2,3,4}Department of Chemistry and Environmental Science and Engineering, University of Texas at El Paso, El Paso, TX 79968; ⁴Phone: (915) 747-5359, ⁴E-mail: jgardea@utep.edu.

Oat and wheat by-products have demonstrated an ability to bind heavy metal ions in aqueous solutions. Previous studies have shown that different non-living biomaterials have the ability to bind metal ions via carboxyl groups. In order to determine what role carboxyl ligands have on the metal binding by oat and wheat agricultural by-products, chemical modification experiments were performed using acidic methanol to block these ligands. The effects of esterification on the metal ion binding to oat and wheat biomasses were studied at pH 2.0 and 5.0 in batch experiments using 0.3mM solutions of chromium(III), chromium(VI), copper(II), zinc(II), lead(II), cadmium(II), and nickel(II). Results of this experiment showed that there was a decrease in metal binding due to esterification for most of the metal ions studied except for Cr(VI). This data indicates that carboxylic groups are the major binding site in oat and wheat biomass for most of the metal ions studied. This information will be important for determining the potential use of agricultural waste to clean heavy metal ions from contaminated waters.

Key words: oats, wheat, esterification, heavy metals, phytofiltration



STUDY OF THE BINDING MECHANISMS OF HEAVY METALS BY INACTIVATED TISSUES OF *SOLANUM ELAEAGNIFOLIUM*

¹A.E. Rascon, ²K.J. Tiemann, ³K. Dokken, and ⁴J.L. Gardea-Torresdey, ^{1,2,3,4}Department of Chemistry and Environmental Science and Engineering, University of Texas at El Paso, El Paso, TX 79968; ⁴Phone: (915) 747-5359, ⁴E-mail: jgardea@utep.edu.

Contamination caused by heavy metal pollution has been long known, as well as its adverse and toxic effects on the environment and mankind. It has also been observed that some native plants have survived within these areas polluted with heavy metals. This has been observed with *Solanum elaeagnifolium* (silverleaf nightshade), which is considered to be a noxious weed in some states. This woody subshrub has shown to uptake high concentrations of metals. We can take advantage of this singular feature to use the *Solanum elaeagnifolium*'s inactivated tissues as a biofiltration system. First, it is necessary to characterize the mechanism of the binding between the biomass tissues with heavy metals by using chemical modification techniques. These techniques include chemical esterification and hydrolyzation of carboxylic groups, respectively. We have performed studies with esterified and hydrolyzed biomass in order to determine the effects on metal binding. These studies have shown an overall decrease in metal binding for esterified biomass, and an overall increase for hydrolyzed biomass as compared to the unmodified biomass. These experiments were performed with Cu(II), Pb(II), Cr(III), Zn(II), and Ni(II). In addition, experiments conducted with modified biomass at different pH conditions were performed in order to verify these results. Finding the mechanism of the metal binding by the

Solanum elaeagnifolium biomass is the basis on which any bioremediation (biofiltration in this case) system should be built. In addition, we used XANES and EXAFS techniques to elucidate the mechanism(s) of metal ion binding. Results of these experiments will be presented.

Key words: *biofiltration, chemical modification, heavy metals, Solanum elaeagnifolium*



CHARACTERIZATION OF CHROMIUM(VI) BINDING AND BIO-REDUCTION BY AVENA MONIDA (OAT) BIOMASS

¹L. Bess-Oberto, ¹V. Armendariz, ¹K.J. Tiemann, and ²J.L. Gardea-Torresdey, ^{1,2}Department of Chemistry and Environmental Science and Engineering, University of Texas at El Paso, El Paso, TX 79968; ²Phone: (915) 747-5359, ²E-mail: jgardea@utep.edu.

The contamination of chromium(VI) in the environment and the consequences of this potential health threat have become an important issue. Conventional technologies to clean up heavy metal from contaminated waters have been utilized, but they are not cost-effective. Agricultural waste by-products may be a new cost-effective alternative for the removal of chromium(VI) from contaminated waters. Oat by-products from the Juarez Valley in Mexico were studied for the ability to bind chromium(VI) under temperature and time effects. Batch experiments were performed at various time exposures and temperatures to determine their effects on the chromium(VI) binding capacity by oat biomass at pH 2.0. The metal-binding ability of oats was calculated from experimental data collected at time exposures of 1, 6, 24, 48, and 72 hours at each temperature of 8°C, 26°C, and 54°C. These results showed that the binding of Cr(VI) to oat biomass increased with increasing time and temperature. The chromium recovery from oat biomass was performed by treatment with 0.2 M HCl. The strippings were further

analyzed with UV-VIS spectroscopy where it was determined that chromium(VI) was reduced to chromium(III) by the oat biomass. These results were confirmed using x-ray absorption spectroscopy which proved the reduction of Cr(VI) to Cr(III). This agricultural waste by-product could be a good alternative for the removal of chromium(VI) from contaminated waters and for the minimization of the contaminated levels in water due to the reduction of Cr(VI) to Cr(III).

Key words: *chromium(VI), bioreduction, oats, agricultural byproducts, XANES*



ADSORPTION AND RECOVERY OF SILVER IONS FROM AQUEOUS SOLUTIONS BY MEDICAGO SATIVA (ALFALFA) BIOMASS

¹I. Herrera, ¹K.J. Tiemann, ¹K. Dokken, ¹G. Gamez, ¹J.G. Parsons, and ²J.L. Gardea Torresdey, ^{1,2}Department of Chemistry and Environmental Science and Engineering, University of Texas at El Paso, El Paso, TX 79968; ²Phone: (915) 747-5359, ²E-mail: jgardea@utep.edu.

Silver is a widely used metal in electronics, jewelry, medical products, and photographic products. However, silver becomes a waste product after these industries employ it. The photographic industry itself produces waste containing from 3000 to 5000 ppm of silver. Current methods for recovery of silver ions are very expensive and not very effective in this industry. The use of biological systems, such as the alfalfa, have shown to be cost-effective methods to clean heavy metal ions from contaminated waters. This technology may be a plausible approach for recovering silver ions from photographic waste solutions. We have found that alfalfa biomass binds silver in a pH-dependent manner within a period of about 5 minutes. Binding capacity studies were conducted with the alfalfa biomass as well as hydrolyzed, esterified, amino-modified and sulfhydryl-modified in order to determine

the binding sites involved in the binding process. Binding comparison studies were conducted with a weak cation exchange resin containing carboxylic ligand. Temperature studies were conducted to assess the behavior of silver ion binding at different temperatures. Flow studies were performed using silica-immobilized alfalfa biomass at different lighting conditions to observe the effect on silver ion binding. We also determined that the bound silver ion can be removed by using a 0.1 M solution of thiourea acidified. This will lead us to an environmentally friendly system that will recover this precious metal in a cost-effective way.

Key words: silver, weak cation exchanger, alfalfa, adsorption, columns



MODEL DEVELOPMENT AND SIMULATION OF *IN SITU* REMEDIATION IN LEAD-CONTAMINATED SOILS

¹Zhiao Shi and ²Larry Erickson, ^{1,2}105 Durland Hall, Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506; ¹Phone: (785) 532-4323, ¹Email: shiza@ksu.edu; ²Phone: (785) 532-4313, ²Email: lerick@ksu.edu.

Remediation of Pb-contaminated soils has received considerable attention recently. Amending Pb-contaminated soils with phosphate as an *in situ* remediation option has been proposed as an alternative of other remediation options such as soil removal. Research shows that hydroxyapatite [Ca₅(PO₄)₃OH] can reduce the bioavailability of Pb efficiently and thus is considered as an ideal phosphate source. Environmental models are increasingly being relied upon to help identify the limiting factors in such kind of *in situ* remediation.

In the present work, models which include adsorption, diffusion, and reaction have been developed to describe the transformation of lead contaminants to pyromorphite in single particles, aggregates, and soil beds, respec-

tively. Principle factors controlling the time of remediation have been identified.

The contaminated aggregates remediation(CAR) model has been developed and simulated to describe the effect of initial contaminant concentration, partition coefficient, and aggregate radius on the time of remediation.

Key words: modeling, remediation, hydroxyapatite, lead pyromorphite, bioavailability



EFFECT OF PEROXIDASE ADDITION ON SORPTION, DESORPTION, AND BINDING OF PHENOLIC MIXTURES IN SOILS

¹Fangxiang Xu and ²Alok Bhandari, ^{1,2}Department of Civil Engineering, Kansas State University, Manhattan KS 66506-2905;

^{1,2}Phone: (785) 532-7717; ¹E-mail: fxu5398@ksu.edu; ²E-mail: bhandari@ksu.edu.

Peroxidase and phenol-oxidase enzymes can catalyze oxidative coupling reactions that result in the polymerization of phenolic contaminants in aqueous systems. When these enzymes and necessary cofactors are added to soils, they can enhance the rate and extent of contaminant binding to soil organic matter in a process analogous to humus formation. The contaminant is immobilized within the soil matrix and is prevented from transport via surface runoff or leaching into the subsurface. The strong contaminant-soil interactions result in reduced ecotoxicity and, therefore, hold the potential to attenuate health risks without necessarily removing the pollutant from the contaminated media. Another attractive feature of enzyme-based engineered humification is that this approach can be used to treat soils contaminated with mixtures of phenolic chemicals present in a wide range of concentrations. The study presented here focused on evaluating the distribution and binding of phenol-dichlorophenol-naphthol mixtures on two sandy loams belonging to the Haynie

series. One soil was obtained from an agricultural field (1.7% organic matter) while the other was collected from an adjacent forested area (2.6% organic matter). To reduce the influence of dissolved organic matter, both soils were washed several times before use in the experiments. U-ring- ^{14}C -labeled target chemicals were used to improve detection limits and better track the distribution of the pollutant among various soil components. Bottle-point adsorption experiments with constant soil dosage were conducted for a period of 7 days followed by sequential extraction (desorption) with synthetic groundwater. The strongly adsorbed chemicals were removed by multiple extractions with methanol. Next, the soil was extracted with alkali under a nitrogen atmosphere to remove humic and fulvic acids and quantify the contaminant associated with this fraction. Finally, the phenol remaining on the alkali-extracted soil was quantified by combusting the soil at 925°C and counting the $^{14}\text{CO}_2$ on a liquid scintillation counter. The effect of the presence of horseradish peroxidase on the nature and extent of binding was compared to situations when no peroxidase was added. Results showed a dramatic enhancement in contaminant binding in the presence of the enzyme.

Key words: soil, phenols, binding, peroxidase, humification



DETERMINATION OF LONG-TERM STABILITY OF METALS IMMOBILIZED BY *IN SITU* MICROBIAL REMEDIATION PROCESSES

Scott Simonton, Mark Dimsha, George Cathy, Bruce Thomson, and Larry Barton, University of New Mexico, Department of Civil Engineering; Phone: (505) 277-1309; E-mail: simonton@unm.edu.

Most microbial remediation strategies that have been developed for addressing sites contaminated with metals and inorganic radio-

nuclides incorporate anaerobic organisms to achieve *in situ* reduction and precipitation of the contaminants. The pollutants are expected to remain immobilized provided that reducing conditions are maintained in the subsurface formation; however, little information has been developed on the stability of these precipitates over very long time periods. This project has investigated the long-term stability of metals and radionuclides immobilized by microbial processes through use of laboratory research and numerical modeling.

The research has focused on arsenic (As), chromium (Cr), selenium (Se), and uranium (U) as being representative of contaminants found at many DOE sites, including uranium mill tailings sites. The laboratory work has involved operation of columns packed with coarse sand, inoculated with anaerobic bacteria, and fed a simulated groundwater solution containing the metal, or metals, or radioactive contaminants and a soluble organic substrate. Two different organisms have been used, *Desulfavibrio desulfuricans* and *Shewanella putrefaciens*. The purpose of these columns is to generate sand media containing high concentrations of the contaminants for use in subsequent leaching experiments. They have operated for more than one year.

To date, samples of the sand media with immobilized pollutants have been subjected to leaching by deionized water solutions and by weak acetic acid solutions specified in the toxicity characteristic leaching procedure (TCLP). The contaminants immobilized by *D. desulfuricans* culture have been found to be quite stable in a deionized water leach test over a period of time extending into one week. These contaminants are less stable in the weak acid of the TCEP test. Vigorous mixing of the media as called for in the TCLP test diminishes the stability of the immobilized pollutants due to the fragile nature of the microbial floc. Testing is continuing with contaminants immobilized by *S. putrefaciens* culture. Long-term leaching studies are in progress using simulated groundwater to generate information on

the rate of contaminant release. A one-dimensional coupled transport and geochemical kinetic code has been selected to use this information to predict contaminant concentrations down-gradient from a site at which *in situ* microbial immobilization has been implemented.

Key words: *anaerobic microbial reduction, metals, stability*

Posters Risk/Bioavailability



DETERMINATION OF GENOTOXICITY OF WOOD-PRESERVING WASTE-CONTAMINATED SOIL

¹S.S. Garcia, ²G.-D. Zhou, ²K. Randerath, and ¹K.C. Donnelly, ¹Department of Veterinary Anatomy and Public Health, Texas A&M University, College Station, TX 77843-4458; ²Department of Pharmacology, Baylor College of Medicine, Houston, TX.

Soil samples were collected from a site contaminated with wood-preserving waste (WPW) and undergoing bioremediation. WPW is a complex mixture containing several different toxic compounds, including polycyclic aromatic hydrocarbons (PAHs). The objective of this research is to determine whether current risk guidelines based on chemical parameters are protective of human health. Over the past two years, soil samples representing different time points post-treatment (Days 0, 90, 360) have been collected. Extracts of the soils were tested for mutagenicity in the *Salmonella* microsome assay and for formation of DNA adducts in a ³²P post-labeling assay. Chemical analysis was performed by GCMS. For the sum of ten carcinogenic PAHs, results for representative samples from each time period were as follows: Day 0 at 100 ppm; Day 90 at 38 ppm; Day 360 at 32 ppm. In the *Salmonella* assay, each of these

samples produced a positive result (doubling of revertant colonies at two consecutive doses) with metabolic activation by S9 rat liver homogenate. Average revertants at a dose of 1 mg/plate were Day 0 at 98±19; Day 90 at 126±11; and Day 360 at 138±84. For the post-labeling assay, female ICR mice were dosed by painting sample extract dissolved in methylene chloride on a shaved area on the back. Skin, liver, kidney, and lungs were collected. For DNA adducts isolated from skin treated at a dose of 3 mg extract/mouse, the Day 0 sample had a total relative adduct level of 127x10⁹. For days 30 and 360, the RAL were 157x10⁹ and 92x10⁹, respectively. These preliminary results indicate that while chemical concentrations are decreasing over time, genotoxic compounds are still present in this soil.

Key words: *genotoxicity, mixtures, soil*



PARTIAL PRESSURE DATA AS AN INSIGHT INTO MECHANISMS OF DERMAL ABSORPTION OF SOIL CONTAMINANTS

¹Chen-Peng Chen, ²Donald Macalady, and ³Annette Bunge, ^{1,3}Department of Chemical Engineering and Petroleum Refining, Colorado School of Mines, 1500 Illinois Street, Golden, CO 80401; ²Department of Chemistry and Geochemistry, Colorado School of Mines, 1500 Illinois Street, Golden, CO 80401; ¹Phone: (303) 384-2016, ¹E-mail: chenchen@mines.edu; ²Phone: (303) 273-3996, ²E-mail: dmacalad@mines.edu; ³Phone: (303) 273-3722, ³E-mail: abunge@mines.edu.

Dermal absorption is a potentially significant route for human exposure to toxic chemicals present in contaminated soils. Despite its importance, the mechanisms of dermal absorption from such exposure remain largely unknown. However, existing data do suggest

that soil-to-skin transfer may be the controlling step.

The long-term goals of this research are (1) to identify the significant physicochemical mechanisms involved in soil-to-skin transfer, (2) to understand interactions among these mechanisms and the corresponding changes in the dermal uptake of chemicals, and (3) to establish parameters appropriate for developing consistent protocols for assessing the health risks associated with dermal exposure to contaminated soils. In our initial studies, we have focused on two related questions: (1) how does contaminant concentration on/in the soil affect soil-to-skin transfer and (2) is soil-to-skin transfer different from different soils contaminated at the same concentration?

Here, we present results for naphthalene contamination of two soils with different organic carbon (OC) fractions ($f_{oc} = 0.01$ and 0.03). Soil samples were contaminated by direct mixing with powdered neat naphthalene. After 48 hours, the partial pressure of naphthalene in the headspace above the soils became constant and did not change even after several weeks, indicating equilibrium. Naphthalene partial pressure at equilibrium increased with increasing levels of contamination (C_{soil}) to a maximum value, which is equal to the partial pressure from pure naphthalene. The minimum naphthalene concentration producing the partial pressure of pure naphthalene represents an apparent saturation limit for the soil sample (C_{soil}^{sat}). The effect of temperature on C_{soil}^{sat} (23, 40, 50, and 60°C) was comparable to that for the vapor pressure of pure naphthalene. Absorption of naphthalene into silicone rubber, a skin surrogate, equilibrated with contaminated soil was proportional to naphthalene partial pressure. Absorption rates into silicone rubber are also consistent with the partial pressure data. These results suggest that vapor pressure may be a good indicator of availability for dermal absorption, at least for the soil contaminants with significant vapor pressure.

Key words: dermal absorption, soil contaminants, naphthalene



NICKEL INDUCES PLASMINOGEN ACTIVATOR INHIBITOR-1 (PAI-1) EXPRESSION TO INHIBIT THE FIBRINOLYTIC ACTIVITY OF HUMAN AIRWAY EPITHELIAL CELLS

¹Angeline Andrew and ²Aaron Barchowsky,
^{1,2}Department of Pharmacology and Toxicology, Dartmouth Medical School, HB 7650
Remsen, Hanover, NH 03755; ¹Phone: (603)
650-1964, ¹E-mail:
angeline.andrew@dartmouth.edu; ²Phone:
(603) 650-1673, ²E-mail:
barchowsky@dartmouth.edu.

Pulmonary fibrosis is a serious debilitating disease caused by inhalation of certain types of particulate matter. Human epidemiological and animal studies have associated inhalation of nickel dusts with increased incidence of pulmonary fibrosis. However, specific mechanisms for nickel-induced pulmonary fibrosis have yet to be elucidated. We hypothesize that particulate nickel promotes pulmonary fibrosis by inhibiting the fibrinolytic cascade. Since urokinase plasminogen activator (uPA) initiates this cascade, this hypothesis was tested by examining the effects of non-cytotoxic levels of nickel subsulfide on the balance of uPA expression relative to expression of its inhibitor, PAI-1, in cultured human bronchial epithelial cells (Beas-2B). Exposure to the metal decreased secreted uPA protein levels and activity without affecting uPA mRNA levels. In contrast, these same exposures stimulated transcription of PAI-1, causing prolonged increases in both mRNA and protein levels. Despite partial recovery of uPA protein levels, uPA activity remained depressed for more than 48 h after exposure to nickel due to the continued increase in PAI-1 expression. These data indicate that particulate nickel inhibits the fibrinolytic cascade by increasing the ratio of plasminogen inhibitor to activator. Sustained loss of uPA activity may be a primary mechanism contributing to nickel-induced pulmonary fibrosis in exposed populations.

Key words: pulmonary fibrosis, nickel subsulfide, fibrinolysis, respiratory distress, Beas-2B



**Additional Presentations
(Abstracts Received After Publication Deadline)**

**Program One
Wednesday, May 24, 2000
Phytoremediation--Exudates and Metals**



THE USE OF PHOSPHORUS AND OTHER SOIL AMENDMENTS FOR *IN SITU* STABILIZATION OF SOIL LEAD

Ganga Hettiarachchi and Gary Pierzynski,
Department of Agronomy, Kansas State University, Manhattan, KS 66506.

In situ stabilization of Pb-contaminated soils can be accomplished by the addition of P and other soils amendments. *In situ* stabilization would have significant advantages over the standard remediation procedure of soil removal and replacement that is currently used in residential areas. Five contaminated soils having total Pb concentrations ranging from 1180 to 9000 mg/kg were used. Two long-term incubation studies showed a significant reduction in bioavailable Pb (by the *in vitro* bioaccessibility test, also known as Physiologically Based Extraction Test- PBET) upon addition of P (as triple superphosphate, phosphate rock, and H_3PO_4) and other soil amendments in all materials tested. This is

supported by the X-ray diffraction data that indicated the formation of pyromorphite upon P addition, which would reduce Pb solubility. The reduction in Pb bioavailability was evident 3 days after treatment and no further reductions were noted after 1 year of incubation. Adaptation of this technology to remediate lead-contaminated soils would eliminate the need for soil excavation.

Key words: in situ stabilization, bioavailable PB, soil remediation

**Posters
Contaminants in Porous Systems**



TRANSPORT OF METHYL-TERT-BUTYL ETHER (MTBE) IN UNSATURATED SOIL

¹Qizhi Zhang, ²Lawrence Davis, ¹Larry Erickson, ¹Dept. of Chem. Eng., Kansas State University, Manhattan, KS 66506; ²Dept. of Biochemistry, Kansas State University, Manhattan, KS 66506; ¹Phone: (785)532-5584, ¹Fax: (785)532-7372; ²Phone: (785)532-6124, ²Fax: (785)532-7278.

Transport of volatile organic compounds (VOCs) from soil into the atmosphere occurs naturally when volatile contaminants are present in unsaturated soil. MTBE transport in an experimental soil system was investigated by measuring soil water concentrations at different depths in the unsaturated zone and the gas fluxes at the soil surfaces in planted and unplanted chambers. Measured MTBE concentrations at different depths demonstrated a non-linear relationship between the soil water concentration and the depth. A one-dimensional transport model was developed to simulate the transport processes of MTBE in the unsaturated zone. An analytical solution to the model equations is presented. Simulations based on this solution are compared with the measured soil water concentrations and the gas

fluxes at the soil surface. The model gave reasonably good predictions for MTBE concentration profiles within the unsaturated zone and for gas fluxes of MTBE under steady state conditions. Plants enhance the rate of transport of MTBE to the atmosphere by moving water upward and by removing water from the unsaturated zone.

Key words: transport, MTBE, unsaturated soil, modeling, phytoremediation

Posters

Phytoremediation--Organics



LONG-TERM MONITORING TO OBSERVE NATURAL ATTENUATION IN THE LABORATORY

Lawrence Davis, Department of Biochemistry, Kansas State University, Manhattan, KS 66506; Phone: (785) 532-6124.

Earlier studies in this laboratory reported the apparent degradation of several compounds supplied in groundwater to planted channels of alfalfa. However, it was not established whether the degradation process might have occurred without plants or the nutrients and bacterial inoculant that was introduced to the channels at one point in their life history. Therefore, a cylinder of comparable depth was set up in September 1998 and fed with a low level of trichloroethylene. The soil was silty sand from near the closed Riley County Landfill, as used before. The water table was maintained at a few cm from the bottom, producing a saturated zone close to the soil surface. Surface flux rates of TCE and DCE (cis-1,2-dichloroethylene) were monitored as before by sampling vented containers placed on, then pressed into, the surface of the soil. No surface flux of TCE was measurable, even during the first few months; the dominant detectable gas was DCE with some methane. After a further time, the surface flux of DCE

decreased several-fold and methane was no longer observable. Soil sampling indicated that high levels of DCE and some methane both were present in the fully saturated zone. The amount of methane is only a small fraction of the input TCE concentration. After five months, the column was watered from the top with Hoagland's solution for two weeks and then planted with successive crops of sunflowers. It was possible to observe transfer of DCE into the stems of the sunflower plants, as reported elsewhere. Now after ~ one more year, no TCE is detectable in the top 20 cm of soil in the cylinder and surface flux rates of DCE are only < 5% of the amount expected on the basis of water use. This system appears to have evolved into an effective remediation without intentional addition of any specific micro-organisms. It is likely that the same soil could do so in its natural setting, if both anaerobic and aerobic zones were present.

Key words: trichloroethylene, dichloroethylene, natural attenuation, methanogenesis, methanotrophy

Posters

Sorption, Binding, and Precipitation



ADSORPTION OF Pb^{2+} AND Zn^{2+} ON PHOSPHATE MODIFIED MANGANESE DIOXIDE SURFACES

¹Hui Wang and Gary Pierzynski, Department of Agronomy, Kansas State University, Manhattan, KS 66506; ¹E-mail: hwang@ksu.edu.

Sorption of Pb^{2+} onto manganese oxides is an important mechanism for retarding migration in soils, and bioavailability of Pb^{2+} can be decreased by the addition of P. This study was conducted to determine the role of phosphate-modified manganese dioxide surface on the adsorption of Pb^{2+} in $NaNO_3$ solution. The effects of pH, Pb^{2+} concentration,

P concentration, and Pb:Zn ratio in the solution were investigated in room temperature and short-term equilibrium time, due to hypothesis that lead phosphates form and lead adsorption occur rapidly in aqueous systems. The study evaluated two manganese oxides with different kinds of mineral structure, birnessite and cryptomelane. Significant sorption of Pb^{2+} by the phosphate-free oxide sample occurred at low pH level (near the PZC), indicating that the sorption was sufficiently energetic to overcome some electrostatic repulsion. The adsorption edge increased to higher pH as total Pb^{2+} concentration increased in solution. The phosphate-modified manganese dioxide surface can enhance its capability to retain Pb^{2+} and lowered the average pH of the sorption edge. A significant correlation was found between the zero point of charge and the quantity of phosphate applied to manganese oxide surfaces. The capacity of sorbed phosphate to lower the zero point of charge depended on the mineral structure. Increasing the Pb:Zn ratio may also change the sorption edge to a lower pH, but the effect strongly depended on the adsorption space on the mineral surface. The phosphate-modified manganese oxides may be useful for reducing soil Pb^{2+} bioavailability and may improve the new Pb^{2+} remediation method.

Key words: manganese oxides, sorbed phosphate, electrostatic repulsion

Posters Analytical Methods



A SIMPLE, INEXPENSIVE AND RAPID METHOD TO DETERMINE TOXICITY USING A BACTERIAL INDICA- TOR ORGANISM

James Botsford, Department of Biology, New Mexico State University, Las Cruces, NM 88003; Phone: (505) 646-3726, E-mail: jbotsfor@nmsu.edu.

This abstract is also scheduled for an oral presentation on Tuesday, May 23, 2000 at 2:30 p.m. under the session titled "Analytical Methods II," which will be in the Parker Room. Please see page 11 for the abstract text.

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