

**Program One**  
**Tuesday, May 19, 1998**  
**Mine Pit Lakes**  
**Superior B**

**1 THE BERKELEY PIT, BUTTE, MONTANA: SOME ASPECTS OF SPECIATION**

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For over 100 years the Butte Hill was mined extensively for copper and other metals. The mining was confined to underground operations from about 1876 to 1975, when the vein mining was discontinued. In 1955 an open-pit mine (the Berkeley Pit) was commenced, and mining of the supergene orebody continued there until 1982. Another open-pit mine east of the Berkeley was started in 1980 and continues to operate there today. The ground water infiltrating both the Berkeley Pit and the old underground workings was pumped at a rate of about 5,000 gpm before mining ceased in 1982. Since pumping was stopped in that year, the water table has been recovering and the pit and associated underground mines have been filling with water. Initially in 1982 the water level rose over 1,300 ft in the underground workings and in recent years has been rising about 24 ft per year in the Berkeley Pit. In 1996-97 the rise in water level was continuing at a rate of about 14 ft per year above a water depth of about 900 ft. It has been shown in ground water flow models there is the potential for the water level to rise to an elevation where the hydraulic gradient reverses and the pit water migrates into both ground water and surface water systems. It is considered that at some time a water treatment plant may need to be installed to deal with discharge water quality.

The water in the pit has been sampled and analyzed by the Montana Bureau of Mines and Geology and others at regular intervals since 1984. It is acidic (pH~2.7) and contains elevated concentrations of metal ions, sulphate and

arsenic. Although the soluble silica levels are low, but near saturation, it is considered that this component has an important effect on the overall chemistry of the system.

Preliminary investigation of chemical reactions occurring in the pit water, the interaction between pit water wall rock, the sediment depositing in the pit, and biological activity in the pit, are likely to lead to a new understanding of all of these interactions. In many ways the chemistry of the system is similar to that of the formation of the initial supergene orebody and the associated weathering reactions. This paper presents some of the initial findings that relate to chemical interactions and relates these to speciation.

There are a number of computer codes that have been used by different workers for chemical modeling of the Berkeley Pit system. The codes provide species stability and material balance calculations based on free energy (or solubility constant/stability constant) minimization procedures. The data being used (and the species involved) are very dated, and there is a real and urgent need for experimental work in this area of complex multicomponent systems. Interactions between pit water and wall rock need to be understood, and sediment formation also related to the system as a whole.

*Key words: ??????????????????*

**2 CHARACTERIZATION OF DEEP BERKELEY PITLAKE WATER AND SOLIDS**

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Water and solid samples have been collected from the Berkeley Pitlake from 600 and 700 foot depths. Water samples were characterized by determining dissolved oxy-

gen concentration, pH, solution ORP, conductivity elemental concentrations, and valence speciation for arsenic, manganese and iron. Solid samples were analyzed for elemental composition, compound identification, particle size, particle shape, zeta potential, and magnetic fraction. The solid samples were analyzed in the original sample solution whenever possible. Both solid and liquid samples have also been characterized for organic content and bacterial activity; however, these results will only be mentioned in passing and are reported elsewhere in more detail. The results from this characterization study have important implications on natural remediation processes and, as a result, a second sampling event is planned in the near future to expand the above referenced studies to include deep water sediment core samples. A description of the proposed sediment sampling event will also be presented.

*Key words: Pitlake, characterization studies*

### 3

#### TREATMENT OF BERKELEY PITLAKE WATER USING THE GREEN PRECIPITATE PROCESS

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Acid mine drainage (AMD) is usually treated by air oxidation followed by addition of lime to precipitate metal hydroxide and calcium sulfate. Geo2 Limited of Melbourne, Australia, developed and patented a novel alternative precipitation scheme based on the formation of mixed valency, M(II)-M(III), hydroxide sulfate salts. When the composition of AMD has an appropriate ratio of Fe(II):Fe(III), the Green Precipitate Process provides a useful and more effective alternative to conventional liming. Many acidic mine drainage waters consist predominantly of Fe(II) particularly near the source, and it is

these where the Green Precipitate (GP) Process can be used with most positive effect. The GP Process incorporates a pipe reactor to prevent and control oxidation.

The characters and utility of the Green Precipitate Process will be described in terms of the underlying chemistry, and the demonstrations in the United States where Berkeley Pitlake water was treated. A mobile pilot pipe reactor rig which was built by Geo2 to demonstrate the process was used successfully in these trials in the U.S.

In conventional liming processes where the iron in AMD is mostly Fe(III) the "ferric hydroxide" precipitate is either *ferrihydrite* or *schwertmannite*, and the material is poorly crystalline, slow to settle and difficult to filter. In this case the neutralization procedure is often preceded by aeration to oxidize Fe(II) to Fe(III) and this can be a very slow reaction which adds significantly to overall costs.

The Green Precipitate Process involves the formation of an Fe(II)-Fe(III) hydroxide sulfate hydrate compound with the general formula  $\text{Fe}_x^n \text{Fe}_y^m (\text{OH})_{2x+3y-2z} (\text{SO}_4)_z \cdot n\text{H}_2\text{O}$ , which is a green colored precipitate in which either the bivalent or the trivalent iron can be replaced by other bivalent or trivalent metal ions. Many other divalent metals will incorporate into the precipitate structure, and Al(III), which is common in AMD, will substitute as a trivalent metal. It is also possible to have substituting anions such as carbonate and chloride. The compounds that are formed are said to belong structurally to the *pyroaurite-sjogrenite* group of hydroxides with the essentially Fe(II) trioctahedral structured iron hydroxide layers carrying a positive charge, alternating with layers consisting of anions and water. In AMD a significant amount of the predominant sulfate anion is removed from solution in the green precipitate, together with various forms of calcium sulfate when lime has been used as the neutralizing reagent.

*Key words: ??????????????*

## **4 THE USE OF ALGAE AS A NATURAL WATER PURIFICATION PROCESS FOR THE BERKELEY PIT**

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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 selfpurification 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 nutrified with Nitrogen, Phosphorous, or Potassium (eg. Manure or sewage as inexpensive sources), this nutrification 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 on the 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. This first step will be taken through this proposed seed grant research.

*Key words: pitlake, acid mine, extremeophiles, bioremediation, metal*

## **5 IDENTIFICATION OF THE AMOUNT AND TYPE OF ORGANIC CARBON IN THE BERKELEY PITLAKE WATER AND CORRELATION TO POTENTIAL SOURCES**

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Organic carbon, as dissolved organic carbon, has been determined in several water samples from the Berkeley pitlake. The concentration of the organic carbon in these samples was approximately 5 ppm (w/w) and showed little variation with depth. Although the organic carbon concentration is significantly less than many of the metal ions and detected anions, the organic carbon could play a role in the chemistry and biology of the pitlake and potentially could interfere with remediation technologies.

The measured concentrations of organic carbon are similar to those found in natural ground waters from humic substances. The major source of inflow to the Berkeley pitlake is ground water from the surrounding area, and consequently humic materials are suspected as being a contributor to the pitlake organic carbon. Algae, bacteria, fungi, and protozoa have been identified in the surface water on the perimeter of the pitlake. The organic carbon could be decay material for these microbes. However, some of the organisms have been determined to be heterotrophic. Consequently, the organic carbon present could be a food source for these organisms. Rotting timbers and ropes from the time of active surface mining and from the adjoining underground mines have been noted floating in the pitlake. Decay products from these materials could also be the source for some of the detected organic carbon. Significant amounts of petroleum products were used during mining operations in the pit and in the connecting underground mines. Hydrocarbons from spills, leaks, and left with abandoned

machinery in the mines is also likely to contribute to the organic carbon in the pitlake water.

Liquid/liquid extractions and solid-phase microextractions are used in combination with gas chromatography/mass spectrometry to determine the volatile hydrocarbons from the pitlake water. Comparative results from these separations will be presented to identify organic carbon from petroleum fuels.

Extraction of humic substances from the pitlake water suffers from several potential problems. Traditional alkaline extractions result in precipitation of the metal ions. Loss of the humic material due to adsorption on the precipitating metals results in low amounts of the separated humics. Extraction of the humic substances by XAD resins, a reliable method in many natural waters, is affected by the metal ions reacting with the resin.. Comparisons of these and other humic separation methods will be presented.

*Key words: humic substances, dissolved organic matter*

## **6 BERKELEY PIT INNOVATIVE TECHNOLOGIES PROJECT REVIEW**

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

The Berkeley Pit Innovative Technologies (BPIT) Project is managed by Montana Tech of The University of Montana (Montana

Tech) through a subcontract with MSE Technology Applications, Inc. (MSE-TA), which implements the Mine Waste Technology Program (MWTP). The purpose of the BPIT Project is to provide a test bed for innovative and/or high risk technologies for remediating Berkeley Pit water. The Project is focused on bench-scale testing of remediation technologies to help assist in defining alternative remediation strategies for the Environmental Protection Agency's (EPA) future cleanup objectives for the Berkeley Pit waters.

To date, eight technology providers have performed bench-scale demonstrations at Montana Tech. The demonstrators came from Moscow, Russia; Melbourne, Australia; Jerusalem, Israel; Grass Valley, California; Missoula, Montana; Westminster, Colorado; and Rocky Hills, New Jersey. Three to five additional technologies will be demonstrated during the Spring and Summer of 1998.

*Key words: remediation technologies, demonstrations, Berkeley Pit*

## **Program Two Tuesday, May 19, 1998 Fate, Transport, and Modeling Superior A**

### **7 MODELING, VALIDATING, AND OPTIMIZING O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> REACTIONS FOR CONTAMINANT TREATMENT**

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A kinetic model and associated rate expressions for advanced oxidation processes (AOPs) involving reactions of ozone (O<sub>3</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) have been developed and experimentally verified. This model is intended to aid design of test matrix, evaluation of process performance, and optimization

of treatment conditions. The kinetic model involves a complex series of fast free-radical chain reactions as a result of  $O_3$  decomposing in aqueous solution. Rapid formation and depletion of reaction intermediates lead to the formation of low pseudo-steady-state levels of reactive free radicals, most notably  $HO_2/O_2^-$ ,  $HO_3/O_3^-$ , and  $OH/O_2$ , which are employed to attack organic contaminants and carry out remediation. Hydrogen peroxide accelerates decomposition of  $O_3$  resulting in faster formation of potent oxidant such as  $OH$ . While  $H_2O_2$  is generated as an intermediate during ozonation, the addition of high levels of  $H_2O_2$  was tested for treatment benefits and optimal dosage. Investigated parameters of this study include pH, oxidant ( $O_3$  and  $H_2O_2$ ) and scavenger (e.g.,  $HCO_3^-$ ) concentrations. Key results of this study are: 1) a validated kinetic model, 2) derived rate expressions for estimating concentrations of reactive intermediates, thus estimated reaction speeds, under any specified treatment conditions, and 3) recommendations with respect to the appropriate use of hydrogen peroxide in ozonation treatment of contaminants.

*Key words: advanced oxidation process, contaminant, hazardous waste, treatment, kinetics, mechanism*

## 8

### PREDICTABILITY OF HYDRAULIC CONDUCTIVITY AT THE INTERMEDIATE SCALE USING INVERSE MODELING TECHNIQUES

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In ground-water hydrology, appropriate characterization of subsurface heterogeneity has been a perplexing problem. Methods of determining hydraulic conductivity at many scales exist, but their interrelation is not well understood. These relations could be used to

produce more predictive methods of characterizing heterogeneity, in which small-scale information is applied directly to larger scale problems. Progress first requires consideration of situations in which heterogeneity is known. In intermediate-scale experiments the structure of heterogeneity is as known as possible allowing for Precise testing of Predictability.

To investigate hydraulic conductivity predictability of intermediate-scale experiments, data sets from previous experiments were evaluated. The experiments were conducted by Garcia (1995, CU M.S. Thesis) and include head, flow and transport observations. To maintain as much realism as possible, the experiment chosen has five sands distributed in a correlated random field in a 122 X 244 cm tank. The hydraulic properties of each of the sands had been measured via flexible wall flow cell (triaxial permeability) tests and column experiments. In this work, the system is simulated such that the heterogeneity is explicitly represented, and nonlinear regression is used to determine best-fit values of hydraulic conductivity for each of the five sands based on head and flow observations.

Initial results indicate significant differences between flow cell values, column experiment values, and best-fit values. Direct use of flow cell values in the model resulted in flows that were 36% and 22% less than the measured flows for a homogeneous and a heterogeneous packing, respectively. Column experiment values were significantly different than the flow cell values. Use of column experiment values in the model resulted in flows that were 6% and 19% greater than the measured flows for a homogeneous and a heterogeneous packing, respectively. Best-fit values produced flows that closely matched measured flows. These results indicate that the tools, data sets, and (or) modeling used in this work were not adequate to apply the smaller-scale hydraulic conductivities to the simulation of the intermediate-scale experiment, and that improvements in the methods used need to be considered.

*Key words: inverse modeling, heterogenous aquifers, intermediate scale testing*

## **9 SELECTION OF REMEDIAL STRATEGIES BASED ON MODELING OF PLUME DYNAMICS**

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A major shift has taken place in the approach to the remediation of hydrocarbon impacted sites. The natural assimilative capacity of soil and groundwater is being increasingly relied upon to provide low-cost corrective action solutions at hydrocarbon contaminated sites. Intrinsic remediation, the use of scientific principles to evaluate and quantify the natural physical/chemical/biological processes comprising the assimilative capacity of aquifers, is becoming widely used, especially for benzene, toluene, ethylbenzene, and xylene (BTEX) contaminated sites. Models have been developed to aid in conducting intrinsic remediation assessments. In this poster, modeling techniques have been extended to evaluate the use of intrinsic remediation by itself or in conjunction with other technologies to develop an optimal remedial strategy at a given site. This approach uses variations of the Domenico (1987) model to provide a quantitative description of contaminant fate and transport to generate predicted groundwater concentrations over time and space. The model is applied multiple times at a site under a variety of remedial action scenarios to evaluate the improvements in contaminant plume characteristics when a series of remediation technologies, with successively increasing levels of engineering and cost requirements, are applied to enhance intrinsic processes taking place at a site. Both technical and non-technical requirements can be considered on a site-specific basis using this approach. The application of this modeling approach and a technology-assessment

framework are demonstrated through a case study applied at a model field site.

*Key words: ????????????????????*

## **10 NEURAL NETWORK MODELING OF SIMULTANEOUS NAPL AND MOISTURE MIGRATION IN THE UNSATURATED ZONE**

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The problem of modeling migration of non-aqueous phase liquids (NAPLs) in unsaturated soils has been studied extensively in recent years, with particular emphasis on downward migration of fuels from spills or leaking storage tanks, the movement of solvents from uncontrolled storage sites, and on NAPL migration during co-disposal of aqueous and oily wastes in land treatment of refinery and wood treatment wastes. Nearly all models of simultaneous NAPL/moisture migration share the drawback that, for accurate predictions, numerical simulation times can be quite long? due to very steep moisture and NAPL fronts necessitating small time steps and a fine spatial domain discretization

In many analytical situations it is of interest to rapidly assess a large number of scenarios concerning NAPL movement to determine the potential for enhanced migration of trace contaminants as solutes in a mobile NAPL matrix. Full numerical computation of NAPL migration requires long simulation times that can limit the extent of the investigation and make it difficult to couple NAPL migration models with more traditional contaminant fate and transport models due to the stiffness induced by the large differences in simulation time steps. A method, was sought that would accurately represent full numerical solution of NAPL

migration in soils without the long, simulation times.

In this research neural networks were used to approximate the full numerical solutions to a simultaneous NAPL/water migration model to provide a rapid approach for assessing the extent of NAPL migration to extend the capabilities of a vadose zone contaminant fate and transport model (VIP). A number of NAPL/water migration models were evaluated for the approximation sensitivity analyses helped narrow the list of predictive variables for the neural network. training and verification result sets were developed using the chosen model, and the neural network was; fitted to those data. The accuracy of the neural network representation was assessed statistically.

Results showed that under certain ranges of the predictor variables, the neural network provided an excellent approximation to the training data sets. In other cases the approximations were in error by up to 0.05% NAPL saturation at a particular depth, although NAPL penetration depths were well represented under most conditions explored. Representation of the verification data sets was less accurate than that of the training demonstrating that more work needs to be done to improve the neural network approach for this problem. In this paper, the results of the neural network approximations are presented and their accuracy is defined and evaluated.

*Key words:* ?????????????????

# 11

## USE OF SPARSE DATA FOR CHARACTERIZATION OF AQUIFERS TO MODEL WATER FLOW AND CHEMICAL TRANSPORT: INTERMEDIATE-SCALE TESTING FOR THEORY VALIDATION

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The design of remediation schemes for aquifers that are contaminated with chemical wastes is confounded by the ubiquitous spatial variability of the physical properties of the aquifer materials as well as the properties that are affected by the chemical. This spatial variability introduces a significant amount of uncertainty to "sparse" data that is collected to characterize contaminated sites. Also, as a consequence of spatial variability the effective parameters that characterize the field transport behavior become scale-dependent. In the case of entrapped nonaqueous phase contaminants the variability of soil conditions at the spill-site scale exhibit some "random" features introducing scale-dependence to the transport field. The scale-dependence of transport parameters in aquifers is an active area of current research both from a theoretical and experimental perspective. Practical considerations often limit the number of tests that can be carried out at a typical field site. A research study is underway with the broad objective of generating an experimental data base to evaluate the variability and scale-dependence of transport parameters based on controlled intermediate-scale experiments in a laboratory tank. The experimental results and the use of the experimental data to validate theories of upscaling of parameters that control dispersion, retardation due to sorbing of the contaminants and entrapment of non-aqueous phase chemicals are presented. The implications of these findings on practical applica-

tions involving field characterization are discussed.

*Key words: groundwater contamination, upscaling, scale-dependence, intermediate-scale testing*

## 12 RESTRUCTURING SUPERFUND RECORDS OF DECISION: THE TIME IS RIGHT

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- More than a decade of Superfund experience has taught impacted parties and regulators about advantages and limitations of many remediation technologies. More rational and achievable Records of Decision (RODs) are currently being developed based on predicated risks to human health and the environment. Broadened acceptability of "risk-based" cleanup goals mean that RODs, which have unrealistic conditions or goals, are no longer sacrosanct. A number of shifts in public policy and regulatory reform offer support to restructure the ROD process, including: Recognized limits of certain conventional technologies, and openness to alternatives
- Regulatory assistance (rather than control) through streamlined regulatory permitting or approval procedures and multi-state regulatory cooperation
- Broadened support of risk-based decision-making, in part due to improved risk assessment and modeling, which also allows the development of site-specific cleanup targets

In the early stages of Superfund, RODs were written which applied singular technical solutions to highly diverse site problems. Currently it is estimated that various known and proven technological alternatives, better and more representative predictive testing, and

current standards of treatability testing allow us today to determine the most appropriate suite of technologies for given site characteristics. Used together, integrated multiple technologies (or technical approaches) can produce dramatically improved results in terms of greater protection of human health and the environment, reduced cleanup times, and lower remediation costs. Some of these approaches include In Situ Bioremediation, Soil Venting/Vapor Extraction, Surfactant Flushing, and Microbial Fences.

Resource constraints in private and public arenas have encouraged the regulatory community to identify and formalize a variety of more objective and/or achievable remedial solutions. Some of these are characterized by Technical Impracticability, monitored natural attenuation, Risk Based Corrective Action (RBCA), the Hazardous Waste Identification Rule (HWIR), and solutions identified by multi-state regulatory alliances. Currently it is estimated that remediation of over half of all RCRA/CERCLA sites with ground water contamination is impractical using conventional technologies. In fact it is believed that monitored natural attenuation is a sufficient stand-alone remedy in up to 20% of ground water sites contaminated with chlorinated solvents and an even higher percentage of petroleum hydrocarbon contaminated ground water sites. To date, 43 states have been trained in processes which streamline the Superfund ROD development and implementation process.

As a result of these collective, cooperative efforts, states and other agencies are starting to support a restructuring of the ROD process to yield effective, protective RODs which may be implemented and achieved within realistic resource constraints.

*Key words: ROD, RBCA, impracticability, technological alternatives*

## 13 DESIGN OF A GRAPHIC USER INTERFACE FOR A DECISION SUPPORT SYSTEM

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Graphic User Interfaces (GUIs) allow users to interface with complex computer models by simplifying data input and creating pleasing output formats. The design of a GUI depends on a number of parameters including the profile of the intended end-user, parameters needed for the simulation model, and the type of output data desired. A Decision Support System (DSS) is a system that aids in deciding the best solution for a given problem within the confines of the system being simulated. This paper identifies steps involved in the design of a GUI. Information about strategies employed to collect data for GUI development, testing of GUIs, and feedback mechanisms will be covered. An example of a GUI developed for a Decision Support System will also be shown.

*Key words: graphic user interfaces, decision support systems, outreach efforts, modeling*

## 14 EFFECT OF VEGETATION ON MOVEMENT OF GROUNDWATER AND NONAQUEOUS PHASE LIQUID CONTAMINANT

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An aquifer model system was established to examine and delineate the presence, fate and transport of nonaqueous phase liquid (NAPL) contaminants. The system consists of six independent channels with identical dimensions. The channels were constructed

with steel bottoms, side panels and sheet end panels. Trichloroethylene (TCE) was selected as a representative compound to model the NAPL groundwater contaminants in the saturated zone of the aquifer.

The flow regime of groundwater in the saturated zone was investigated by conducting bromide tracer experiment. TCE movement in both horizontal and vertical directions was studied by monitoring its concentration in groundwater effluent stream and soil gas phase after a pulse injection of TCE into each channel. A multistage compartment model was developed to help interpret the experimental data and observations.

*Key words: NAPL, groundwater, movement, vegetation, trichloroethylene*

## 15 AIRCRAFT DEICER FLUID COMPONENT CHEMICAL CONTRIBUTIONS TO AEROBIC BIODEGRADABILITY AND TOXICITY

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Airports and airbases worldwide utilize hundreds of millions of gallons of glycol-based aircraft deicing fluid (ADF) annually. Much of the ADF used in the United States is classified as PG-Type I, which contains 85-90 % propylene glycol (PG), 0.2-0.6 % tolyltriazole (TTA), 9-10 % water, and manufacturer-specific additives comprised of small amounts (< 2 %) of surfactant and corrosion-inhibiting compounds (adpack). More than 50 % of all ADF used is released to the environment during aircraft deicing operations. The environmental fate and impact of ADF, however, has not been well studied. In three separate research efforts, the ADF

formulation was found to be significantly more toxic than PG alone, but no studies have been published investigating the separate and combined effects of the ADF component chemicals. In this research, biodegradation experiments and aquatic toxicity studies were conducted using manufacturer-supplied ADF component chemicals in different concentrations.

In biodegradation experiments, soil microorganisms enriched from ADF-contaminated soils were used to aerobically degrade PG. The resulting baseline degradation rates and specific growth rates were compared to rates from similar experiments in which TTA or adpack was added in varying amounts. The addition of the adpack decreased the PG degradation rate only 5 %, and only slightly inhibited cell growth. The addition of TTA had a more severe negative effect. Growth rate reductions were observed from 31 -76 %, and PG degradation rate reductions were observed from 10 to 61 %. Also, the rate reductions appeared to be additive - that is, experiments conducted with both TTA and adpack showed rate decreases nearly equal to the addition of the rate decreases observed for either constituent separately. Microtox<sup>(R)</sup> 5 and 15-minute aquatic toxicity test results indicated toxicity similar to the biodegradation experiments. The TTA conferred the most toxicity to the Microtox<sup>(R)</sup> test microorganisms (53-69 % more toxic than PG alone), while the adpack was less toxic than the TTA (8-35 % more toxic than PG alone).

Conversely, at environmentally relevant concentrations, higher organisms were more sensitive to the adpack than TTA. TTA was 20 % more toxic to *Ceriodubio daphnia* than PG but the adpack was 188 % more toxic, and the combination fluid containing PG, TTA and adpack was 295 % more toxic than PG alone. Similarly, TTA was 500 % more toxic to *Pimephales promelas* than PG but the adpack was 2,547 % more toxic than PG.

**Key words:** aircraft deicing, biodegradation, toxicity, tolyltriazole

## 16

### THE FATE OF AN AIRCRAFT DEICING ADDITIVE UNDER SUSTAINED ANAEROBIC CONDITIONS

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**Background:** Aircraft deicing practices at commercial and military airports generate millions of gallons of contaminated runoff and concentrated wastes each year. Current management practices to control aircraft deicing fluid (ADF) runoff and treat deicing wastes are unsatisfactory. As a result, the impact of deicing wastes on surface waters, wastewater treatment systems, and groundwater systems is a growing concern in the environmental regulatory community.

The fate and treatment of ethylene glycol-based ADF wastes have been previously investigated. However, a new generation of propylene glycol (PG) based deicing fluids are now in widespread use and are applied with significant concentrations of additives (>2% w/w). Corrosion and flame inhibitors have been implicated to confer significant biological toxicity to ADFs; these compounds have been identified as tautomers of benzo- and tolyl- triazole and are present in ADF at concentrations of 0.2 to 0.6% (w/w).

**Significance:** Investigating the anaerobic degradation mechanisms of ADF is critical, as many sinks for ADF wastes are anaerobic environments. These sinks include saturated soil, sediments, stabilization ponds and anaerobic digesters. The true environmental impact of ADF cannot be established until the fate of ADF additives is resolved and cost-effective management strategies, such as landfarming, pond treatments and anaerobic digestion cannot be safely implemented until the fate of these additives is determined. Tolyltriazole is recalcitrant to degradation under oxidative conditions. This research

examines the fate of tolyltriazole under sustained anaerobic conditions.

**Research:** Under anaerobic conditions, the breakdown products of tolyltriazole remain unidentified. However, there is evidence to suggest that these products include highly carcinogenic, aminated benzene derivatives. High Pressure Liquid Chromatography (HPLC) and Gas Chromatography / Mass Spectrophotometry (GC/MS) are being applied to measure tolyltriazole and its breakdown products under sustained anaerobic conditions similar to those encountered in anaerobic treatment systems and the subsurface. Preliminary observations of anaerobic degradation pathway of tolyltriazole will be reported.

Determining the sorption characteristics of tolyltriazole is critical to estimate its potential for environmental mobility and its availability for degradation. To determine the partitioning behavior of tolyltriazole in the environment, batch tests are being executed under field conditions to predict its sorption characteristics in runway fill, anaerobic digesters and stabilization ponds. Preliminary results from mesophilic anaerobic digester studies, suggest that tolyltriazole sorption to anaerobic biosolids can be approximated using a Freundlich model [ $x/m = 0.046 C_e^{1/3}$ ].

The impact of tolyltriazole on active biosolids from potential anaerobic treatment alternatives is being investigated. To model the fate of ADF additives from deicing operations in anaerobic environments, tolyltriazole is being codigested in mesophilic anaerobic digesters. Toxicity is being measured using accepted methane potential tests and sensitive enzyme assays. The effects of reducing conditions and biodegradation on the stability of tolyltriazole have been experimentally separated and will be reported.

*Key words: deicing, anaerobic degradation, tolyltriazole*

**Program Three**  
**Tuesday, May 19, 1998**  
**Bioremediation**  
**Wasatch B**

**17 SITE CONSIDERATIONS IN  
EVALUATING AIR INJECTION  
SYSTEM PERFORMANCE**

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In-situ air sparging (IAS) and in-well aeration (IWA) are used for remediation of sites with hydrocarbon contaminated soil and groundwater. Both types of in-situ treatment systems require the movement of groundwater for contaminant reduction. Installation of air injection systems at sites without adequate evaluation of soil characteristics governing water and air movement in the subsurface can result in unsatisfactory system performance. Both IAS and IWA systems were installed at a hydrocarbon contaminated site in Layton, Utah. These systems were monitored using an extensive three-dimensional grid. Each monitoring location was sealed from the atmosphere and fit with instrumentation that allowed for continuous monitoring of total head and dissolved oxygen (DO). Discrete samples were collected from each monitoring point for evaluation of contaminant concentration across the grid. In addition, slug tests were used to characterize the hydraulic conductivity at 20 locations, from three depths across the site. Results of the tests with IAS and IWA indicate that under the low hydraulic conductivity conditions existing at this site, neither IAS nor IWA is capable of increasing either physical removal (stripping) or biodegradation of hydrocarbon. Results from this full scale field study suggest that conductivity estimates based on short screen intervals at several depths should be an integral component of

feasibility assessment for air injection remediation technologies.

*Key words:* ????????????????????

## **18 FIELD EVALUATION OF INTRINSIC REMEDIATION AT A CHLORINATED SOLVENT/HYDROCARBON CONTAMINATED SITE EIELSON AFB, ALASKA**

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A two year field study was conducted at Eielson AFB, Alaska to apply a data collection and summary methodology that can be used to provide a comprehensive description of actual and potential rates of intrinsic remediation taking place at TCE/hydrocarbon contaminated sites. A description of this methodology, its application and implications of results from this field study for a specific field site on Eielson AFB is the subject of this presentation .

Field methods used for plume delineation, and data reduction results for contaminant mass estimation and mass center calculations will be highlighted, along with results of documented intrinsic bioremediation taking place at this mixed solvent and petroleum contaminated site. Estimated electron acceptor pool, electron acceptor utilization, contaminant degradation rates, and long-term plume modeling will be summarized. Finally, the case will be made for the selection of intrinsic remediation with long-term monitoring, without source removal, as the preferred groundwater management option for this site.

*Key words: intrinsic remediation, chlorinated solvents, petroleum, field studies, reductive dechlorination*

## **19 COMPLICATING FACTORS IN VERIFYING NATURAL ATTENUATION METABOLITES AT A FIRE TRAINING SITE**

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The use of natural attenuation has become a recognized strategy for in situ remediation of fuel contaminated sites. One challenge associated with site management is verification of the existence of microbial biodegradation. Monitoring of spatial and temporal variations in fuel components, terminal electron acceptors, and groundwater chemistry are inconclusive indicators of biodegradation. An alternative approach that has been suggested is to isolate microbial metabolites from natural attenuation sites. Benzyl succinic and benzyl fumaric acids are considered to be dead-end metabolites of anaerobic fuel degradation, thus the identification of these compounds in groundwater should provide strong evidence of intrinsic remediation. Analysis of metabolites is not typically included in routine monitoring programs due to the need for a complex derivitization procedure to enable GC/MS detection. Consequently, limited field data on the distribution of metabolites in fuel-contaminated groundwater exists to-date. The purpose of this project was to conduct a case study to evaluate the use of metabolite monitoring as field verification of natural attenuation of hydrocarbon contamination.

The focus of this study was a fuel-contaminated decommissioned fire training area at Tyndall Air Force Base in Florida. Analysis of fuel constituents and

electron acceptors from various wells at the site provided evidence that the site was supporting intrinsic remediation. Complicating factors at the site included significant levels of fluorinated surfactants (AFFF) used in fire-training activities. In addition, the surficial groundwater contains high levels of humic and fulvic materials. An array of monitoring wells existed on the site, but no active remediation process had been implemented. Over a two year period, samples were obtained from monitoring wells downstream of the contamination source. Samples were concentrated, derivitized, and analyzed for metabolites. Despite geochemical and isotope evidence of anaerobic activity, benzyl succinic and/or fumaric acid were not detected in any of the sampled wells. To confirm these negative findings, rigorous testing of the separation and analysis procedures was conducted. Additionally, the potential for interferences from fluorinated surfactants was evaluated. The humic and fulvic materials associated with the groundwater at the site were characterized to provide insight into potential bioavailability and transport interferences. The results of this study raise questions about the feasibility of using succinic or benzyl fumaric acids as indicator compounds for natural attenuation .

*Key words: fuel contamination, fire training, anaerobic metabolites, natural attenuation*

**Program Three**  
**Tuesday, May 19, 1998**  
**Biological Processes**  
**Wasatch B**

## 20 EFFECTS OF SURFACTANT SURFACE COVERAGE AND MICELLE FORMATION ON BIODEGRADATION RATES OF PHENANTHRENE

*W.P. Inskeep and R.E. Macur, Department of Plant, Soil and Environmental Sciences, Montana State Univ., Bozeman, MT 59717*

Surfactants have received considerable attention as a potential technology for enhancing the solubility and subsequent bioavailability of nonpolar organic contaminants in soils and aquifers. Recent works including data from our laboratory shows that nonionic surfactants inhibit degradation of polyaromatic hydrocarbons (PAHs) by microorganisms at surfactant concentrations above the CMC (critical micelle concentration). It has been hypothesized that for certain surfactants, micelle-bound PAH is not readily bioavailable. Our previous work showed that decreases in bioavailability actually occurred prior to the onset of micellization suggesting that additional processes may contribute to reduced PAH degradation. We have begun several experiments to determine relationships among surfactant surface coverage and microbial degradation of phenanthrene. Experiments were designed to test effects of surfactant structure and surfactant surface orientation sorbed on microbial degradation of phenanthrene. Results will be discussed in the context of phenanthrene solubility, micellization, and potential effects of sorbed surfactant on microbial attachment.

*Key words: surfactant, bioavailability, sorption, phenanthrene*

## 21 TREATMENT OF SEPTIC TANK EFFLUENT USING SULFUR/LIMESTONE DENITRIFICATION PROCESS

*J. Shan and T.C. Zhang, Civil Engineering Department, University of Nebraska-Lincoln, Omaha Campus, Omaha, NE 68182-0178*

Septic tank systems are widely used in the rural areas as the main means of small community wastewater treatment. Yet these systems produce large amounts of nitrate contamination which is a serious threat to groundwater supplies. The purpose of this project is to evaluate the feasibility of using

sulfur/limestone denitrification process for nitrate removal in septic tank effluent.

The sulfur/limestone method uses autotrophic bacteria to realize denitrification. These bacteria can use elemental sulfur as the electron donor and nitrate as electron acceptor. Since hydrogen ion is generated during this process, limestone is required to provide enough alkalinity. This process needs little maintenance, thus is ideal for small community wastewater denitrification.

Four columns with 4 feet in height and 8 inches diameter were built to simulate the lateral field. Sulfur/limestone layers were placed beneath sand layers. Different thickness of sand layers and sulfur/limestone layers were used to study the degradation rates. The thickness of sulfur/limestone layer are 1.5 feet for both reactor 1 and reactor 3, 1 foot for reactor 2 and 2 feet for reactor 4. Effluent from primary settling tank of a local domestic wastewater treatment plant was used as the influent because its characteristic was similar to septic tank effluent. The hydraulic loading rate of reactor 1 is 1 L/d, which is the EPA standard of the septic tank soil adsorption system. All the other reactors used 5 L/d to study the feasibility of increasing the loading rate. Samples were obtained along the depth of all columns

Significant denitrification was observed after one month of running. The effluent concentration of ammonium and nitrate remained at very low levels. The effluent nitrite was always below 0.01mg/l. The total nitrogen removal efficiency was higher than 90%. There was no significant difference between the removal efficiencies of different reactors. The pH in the columns remained stable between 6.4 - 7.6. The effluent COD were lower than 15mg/l with removal efficiencies of more than 90%. The preliminary study has indicated that using sulfur/limestone method for septic tank effluent denitrification for small communities has a promising future.

*Key words: nitrate, septic tank, sulfur/limestone, denitrification*

## 22 BIPHASIC FERMENTATION FOR ENERGY RECOVERY WITH DESTRUCTION OF HAZARDOUS SUBSTANCES AND PATHOGENS IN SOLID WASTES

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Several billion tons of organic, solid and hazardous wastes are generated annually in the United States. These discarded materials from agricultural, industrial, commercial and municipal activities decompose slowly under anaerobic conditions in open dumps or landfills that emit methane and other gases for decades contributing to global warming and potential fire and health hazards. Pollutants leaching slowly from decomposing solids cause surface and ground water pollution. These pollution concerns motivated European countries to prohibit landfill disposal of wastes containing more than 5 to 10% organic matter.

Since organic solid wastes represent a vast reservoir of potential chemical energy, a management approach that effects methane (energy) recovery and capture with simultaneous stabilization of pollutants in a relatively short period of time merits serious consideration. Anaerobic digestion (AD) offers the potential for liquefying and gasifying solid waste-a heterogeneous mixture of organic materials-in the presence of trash. Redox and pH conditions associated with the steps of sequential liquefaction and gasification processes of AD could promote conversion of hazardous substances to innocuous byproducts with simultaneous destruction of pathogenic organisms to generate a safe and usable residue.

Anaerobic fermentation of high solids-content feeds such as agricultural or municipal solid wastes (MSW) is fraught with the problem of unbalanced acidogenic and

methanogenic fermentations that lead to volatile fatty acids (VFA) accumulation and severe retardation of methane fermentation lasting for 10, 20, or 30 years. The objective of completing solids-to-methane conversion in a few months as opposed to 2040 years in a landfill may be accomplished by separate control of acidogenic and methanogenic fermentations. Bench- and pilot-scale research was undertaken to demonstrate the utility of separate acid and methane-phase fermentations to accelerate and complete the conversion of MSW to methane in several months rather than in several years. The project aims at maximizing bioconversion efficiency, eliminating methanogenic inhibition, and capturing methane gas for captive use to reduce global warming.

In this two-phase process, the first-stage, anaerobic bioreactor contained a bed of MSW packed at a density of 160 kg/m<sup>3</sup> and operated with recycling of the percolated acidogenic bacterial culture through the solid bed; a rapid onset of solids hydrolysis, acidification, hydrogen production, and denitrification was experienced under these conditions. Methane fermentation was completely inhibited in the solid bed, as expected. Even acidogenic fermentation of solids stopped as the total VFA concentration reached 13,000 mg/l at pHs between 4 and 5 and a solid-bed reactor head-gas composition of 75% CO<sub>2</sub>, 20% nitrogen, 2% hydrogen, and 3% CH<sub>4</sub> prevailing at a redox potential of -400 mV.

Organic acids accumulating in the solid bed were moved once a day to a separate packed-bed methanogenic reactor, the effluent of which was recycled to the solid-bed reactor to promote methanogenic conversion to occur in the solid bed. Data will be presented to show that prevalence of a low-pH, acidic environment is conducive to pathogen destruction, and that the presence of molecular hydrogen encourages reductive dechlorination of hazardous organics. Overall biphasic system efficiency was characterized by COD and volatile solids (VS) reductions of 55%,

and gas and methane yields of 0.34 and 0.17 SCM/kg VS, respectively. Chemical composition of the residue in terms of contents of nutrients (NPK), heavy metals, lignin, carbohydrate, protein, and pathogens will be reported.

*Key words: solid waste, hazardous waste, biphasic fermentation*

**Program Three**  
**Tuesday, May 19, 1998**  
**Biological Processes**  
**Wasatch B**

**23 BIOFILM ACCUMULATION AND ACTIVITY IN POROUS MEDIA: BIOBARRIERS**

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A novel strategy for containment of contaminated groundwater consists of a biologically produced EPS barrier within a subsurface formation. These biobarriers have been effective under laboratory conditions for manipulation of porous media permeability. Two pilot-scale lysimeters were designed and manufactured to facilitate evaluation of biobarrier performance in a two-dimensional configuration. Injection ports for nutrient and bacterial addition are downstream from a constant head hydraulic flow reservoir. The hydraulic flow simulates groundwater flow through a contaminated subsurface formation. The injection ports simulate wells drilled down-gradient from a contaminated site. The lysimeters were packed with foundry sand and the flow characterized using chloride tracer studies. The flow was found to contain flow heterogeneities, indicating simulation of a three-dimensional flow configuration. The reactors were inoculated with 2 pore volumes of a culture of *Klebsiella oxytoca*. The bacteria had been prepared for injection into the reactor by nutrient starvation. The resultant bacteria were on the order of 0.5  $\mu$ m in diam-

eter. The bacterial suspension was pumped into the reactor in conjunction with a constant head hydraulic flow. The bacteria were resuscitated on a defined citrate medium. A consistent flow reduction of >99% was achieved over a 60 day period. Subsequent nutrient addition has not been required to maintain the stated flow reduction over a 3 month period. In addition, the barrier has shown no ill effects due to the continuous presence of 1 ppm strontium. This biobarrier test work expands on meso-scale column (3 feet x 6 inch diameter) work that indicates these biobarriers are resistant to heavy metals (Cs, Sr) and chlorinated organics (CCl<sub>4</sub>).

Reactor design has recently been modified to examine biobarrier formation under radial flow conditions. A 4 foot high, 1.5 foot diameter radial flow lysimeter was constructed with piezometer ports situated radially outward from a center injection well. Bacteria and nutrients will be injected into the lysimeter and increased pressure will be an indication of biomass growth. After the development and maintenance of a low permeability subsurface biobarrier has been examined, the radial flow lysimeter will be destructively sampled to correlate biomass growth with reduced permeability.

Results include:

- Evaluation of the effects of nutrient concentration and duration of addition on the stability of the biobarrier.
- Biobarrier development in the vadose zone
- Biobarrier integrity (i.e. permeability) in the radial direction.

This presentation will address methods needed to bring biobarrier technology to field scale. A review of the research performed to date will be included.

*Key words: biobarrier, subsurface, transport, biofilms*

## 24

### EFFECT OF BIOFILM GROWTH ON THE FATE OF CONTAMINANTS IN THE SUBSURFACE

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Biological methods to remediate sites contaminated with organic compounds that are soil sorbed, dissolved, or present as non-aqueous phase liquids (NAPLs) are gaining popularity due to cost effectiveness. However, designs to optimize bioactivity and estimate the control of plume migration are still uncertain. Understanding how biological growth affects subsurface hydrodynamics and predicting the effect of this bioactivity on contaminant fate and transport will help improve bioremediation design and risk management strategies. Modeling these systems will allow the results of laboratory studies to be applied at a field-scale.

In a contaminated aquifer, growth of bacteria attached to soil grains will form biofilms. The dimensions and structure of these biofilms will be dependent both on the contaminant used as the bacterial growth substrate and the flow conditions in the porous media. As biomass growth fills the pore spaces in the soil, changes in the soil's hydrodynamic characteristics (such as permeability and dispersivity) will result. However, the magnitude of these effects under field conditions is not known. For example, as biofilm plugs the soil pores the groundwater flow may divert to areas with less growth, thereby changing both contaminant movement and the nutrient and electron acceptor supply to the bioactive zone. The goal of these laboratory studies and computer modeling was to enhance the understanding of the factors that control contaminant concentrations in groundwater, specifically the effect of biological growth on subsurface hydrodynamic conditions. Predicting these effects on a field scale will allow better targeting of intrinsic remediation strategies which demonstrate risk

management and/or better design of active remediation schemes.

Laboratory studies were conducted to investigate: (1) the hydrodynamic effects of biofilm growth in 1-dimensional packed sand columns (7 cm dia. x 15 cm tall). A variety of growth substrates were tested at different groundwater flowrates and nutrient concentrations in the groundwater. After varying periods of biofilm growth, hydraulic conductivity was measured using a constant head test and dispersivity was approximated from measured breakthrough curves of bromide tracer. Changes in hydraulic conductivity of approximately 2 orders of magnitude have been achieved after 1 to 2 months of growth; substrate (decane versus naphthalene), groundwater flowrate (0.1 to 0.8 cm/min), and nitrogen limitation (C:N ratio of 4: 1 to 100: 1) effect the rate of conductivity changes. Columns were sacrificed to measure the distribution of biomass in the columns, and confirm uniformity. (2) the hydrodynamic effects of localized biofilm growth in a 2-dimensional tank (1.5 m long x 1 m tall x 5 cm thick) containing homogeneous sand. The zone of biofilm growth in the tank (10 cm x 5 cm x 5 cm) was characterized for hydraulic conductivity prior to insertion into the 2-D tank, allowing accurate knowledge of conditions in the tank prior to introduction of the line-source of bromide and dye tracer into the tank.

The 2-dimensional experiments were modeled in Modflow and MT3D, with the input parameters being the independently measured characteristics of the clean and biofilm-containing sections of the sand-packed tank. The model-predicted breakthrough characteristics of the injected tracer were then compared to the experimental results. Differences between the model and experiments were attributed to "up-scaling" effects from the 1-D to 2-D setting. Attempts were made to correct the model for these scaling effects. The magnitude of the scaling effects should provide insight into the ability

of the model to predict full-scale, 3-D conditions.

*Key words: biofilms, porous media, modeling*

## 25 FORMATION OF REDOX-REACTIVE SUBSURFACE BARRIERS USING DIS-SIMILATORY METAL-REDUCING BACTERIA

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The research to be presented focuses on the development of strategies for the in situ biological treatment of groundwater and soil contaminated with chlorinated organics and heavy metals.

Traditional remediation efforts, which have relied on pump & treat technologies or excavation, are in many cases prohibitively expensive. However, recent advances in subsurface redox-reactive barrier technology have demonstrated significant potential for in-place treatment. This remediation concept is based on channeling contaminated groundwater flow (by means of subsurface containment walls, grout curtains, or biofilm barriers) through a zone of low redox potential which serves as source of electrons to drive remediation-related chemical and biological reactions such as heavy metal precipitation and reductive dechlorination. For example, excavated trenches backfilled with zero-valent iron have been successfully used to demonstrate this technology. However, the costs of establishing the redox barrier by excavation and placement of highly reduced metal into the aquifer are high and therefore provide incentive to develop lower cost alternatives. The research to be presented addresses this need by seeking to develop strategies for formation and maintenance of redox-reactive barriers in situ through bioaugmentation with

Dissimilatory Metal Reducing Bacteria (DMRB). DMRB have been found to degrade chlorinated organics and/or precipitate oxidized heavy metals. DMRB can either directly reduce (degrade) these contaminants, or can be used to create a zone of reduced indigenous metals (e.g. ferrous iron from ferric iron) in the path of the contaminated groundwater. These indigenous metals will reductively dechlorinate the organic pollutant and/or reduce the mobile heavy metals to produce immobile crystals of insoluble metal salts (e.g. Cr(VI) to Cr(III)).

The versatile metabolism of DMRB indicates that biologically active redox-reactive zones in the subsurface will facilitate treatment of a wide variety of contaminants. If successfully developed these treatment zones can lead to the complete mineralization of organic contaminants (i.e. aromatic hydrocarbons, and chlorinated organics) as well as the precipitation of heavy metal contaminants under anoxic conditions. The DMRB-metabolism thus represents a potential method for the bioremediation of subsurface environments contaminated with hydrocarbons, radionuclides, heavy metals and halogenated organics.

In situ bioremediation strategies must consider inoculating iron-rich aquifer-zones with pre-adapted or genetically engineered DMRB so as to create and maintain a region of low redox potential. In order to efficiently treat large volumes of soils in situ by injecting bacteria, bacterial transport distances of 10's of meters in the subsurface must be achieved, and the survival and activity of the delivered bacteria in the subsurface must be guaranteed. Several important research questions must be answered before in situ redox-barrier technology can be fully evaluated. These questions include:

1. Can DMRB be effectively transported through the subsurface over field relevant distances (i.e. 10 to 100 m)?
2. Can injected DMRB survive and successfully compete with indigenous bacteria

and how efficiently can DMRB carry out the reduction of ferric iron in situ?

3. What environmental variables influence reduced iron based reductive dechlorination and heavy metal precipitation and can they be controlled?

4. What is the likely influence of subsurface heterogeneities on the field scale application of microbially enhanced redox barrier technology (i.e. what problems must be overcome in order to scale this technology up from the laboratory to the field)?

This presentation will give a summary of the current research results of the transport of DMRB in porous media and microbial iron reduction; an overview of the planned research will be given.

*Key words: transport, biobarrier, starvation, metal, biofilms*

**26**

## **ACCURATE NUMERICAL SIMULATION OF BIOBARRIER FORMATION IN POROUS MEDIA**

*B.M. Chen and H.V. Kojouharov, University of Wyoming, Laramie, Wyoming, 82071*

Biofilm forming microbes have complex effects on the flow properties of natural porous media. 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. Another example of beneficial microbial effects is the formation of biobarriers to inhibit contaminant migration in groundwater.

To describe the population distribution and movement of bacteria in porous media, we consider the convection-dispersion equation with nonlinear reactions. The reactive solute transport equation is one for which numerical solution procedures continue to exhibit significant limitations for certain problems of groundwater hydrology interest. Accurate numerical simulations are crucial to the

development of contaminant remediation strategies.

A new numerical method is developed for simulation of reactive bacterial transport in porous media. The nonstandard “exact” numerical approach is based on nonlocal treatment of nonlinear reactions. It leads to solutions free from the numerical instabilities that arise from incorrect modeling of derivatives and reaction terms. Applications to different biofilm models are examined and numerical results are presented to demonstrate the performance of the proposed new method.

*Key words:* ???????????????

<p><b>Program One</b> <b>Wednesday, May 20, 1998</b> <b>Mine Pitlakes</b> <b>Superior B</b></p>
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**27 ANALYSIS OF SEDIMENTS FROM A COPPER RICH PIT LAKE USING SCANNING ELECTRON MICROSCOPY / ENERGY DISPERSIVE X-RAYS**

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Many conceptual models for the prediction of pit-lake water quality assume that metals released by the oxidation of sulfide minerals will be adsorbed onto sediment surfaces and removed from the lake waters. However, at an existing porphyry copper pit lake in Nevada, dissolved Cu concentrations in pit-lake water may not be controlled by this process.

The Arimetco pit lake in Yerington, NV has pH ranging from 7.8 to 8.2 and dissolved oxygen concentrations ranging from 5.8 to 6.5 mg/L and remains oxic at depth throughout the year. Total dissolved solids concentrations

range from 660 to 694 mg/L. Copper concentrations range from 12 ug/L at the surface to 158 ug/L at 100 m. The pit lake is undersaturated with respect to the Cu minerals azurite, malachite, bornite, and cuprite at the surface and at depth.

X-ray diffraction (XRD) and scanning electron microscopy combined with energy dispersive x-ray spectroscopy (SEM/EDX) of deep pit-lake sediments show sediments are composed of clay minerals resulting from the weathering of wall-rock feldspars. Copper is not present in significant concentrations on these sediment surfaces. However, near the surface of the pit lake, precipitation of Cu carbonates is visible. SEM/EDX analysis shows high Cu concentrations on these surfaces. Since Cu concentrations are below saturation at the near surface, Cu carbonate precipitation may be controlled by Cu precipitating bacteria.

*Key words:* ?????????????????

**28 LATIN HYPERCUBE SAMPLING: APPLICATIONS IN ANALYTICAL MODELING ASSOCIATED WITH OPEN MINE PITS**

*W.L. Niccoli, F. Marinelli, and T.M. Fairbanks, Shepherd Miller, Incorporated, 3801 Automation Way, Suite 100, Fort Collins, CO 80525*

An environmentally progressive, New Mexico mining company, wished to convince the regulatory agencies that after the cessation of mining, evaporative losses from lakes formed in their abandoned open pit mines would not cause a significant impact to ground water. The regulatory agencies were concerned that the uncertainty associated with existing site hydrogeologic information precluded any realistic modeling to support an impact evaluation.

Through sensitivity analysis, Shepherd Miller, Inc. (SMI) deduced which modeling

input parameters most influenced modeling results. SMI then quantified the uncertainty associated with these parameters and incorporated this uncertainty into modeling efforts using the Latin Hypercube sampling technique. This approach addressed the concerns raised by the regulatory agencies without additional expensive and time consuming site investigations.

*Key words: uncertainty analysis, pitlake, groundwater modeling, open pit mine, impact analysis*

## **29 PREDICTING THE WATER QUALITY OF THE FUTURE SOUTH PIPELINE PIT LAKE**

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An investigation coupling field data collection with predictive modeling was conducted to determine whether the evolving water quality in the future South Pipeline pit lake, Cresecent Valley, Nevada may affect local groundwater quality upon infilling, or create a water body with the potential to affect human, terrestrial, or avian life.

Rock characteristic of the wall rock of the Pipeline/South Pipeline ultimate pit surface (UPS) were leached at the site under ambient environmental conditions. The temporally varying leachate chemistry was used to define chemical release functions (CRFs) that describe the water quality of wall rock leachate as a function of Net Carbonate Value (NCV). In addition, humidity cell tests were conducted for the same suite of rock types and for additional rock samples. Both the field test and humidity cell data were carried through the computational sequence. The relative groundwater flows through the UPS derived from the groundwater flow modeling were coupled with the oxidized thickness of the exposed wall rock, and the CRFs for each lithological unit. These data formed the input

to the numerical code PITQUAL, which was used to compute the temporal evolution of the bulk pit lake water quality (chemogenesis) from a juvenile stage through maturity (250 years).

Within PITQUAL, PHREEQC was used to incorporate geochemical reactions from the bulk chemistry at discrete time intervals. Relevant geochemical constraints included variable partial pressure of carbon dioxide ( $P_{CO_2}$ ), precipitation of manganous-calcite and amorphous ferric hydroxide (AFH), sorption of metals to AFH, and evapoconcentration. The juvenile pit lake (after 5 years) for the proposed alternative pit configuration will consist of a pH 8.1 water body containing 755 mg/L TDS. The chemogenetic pathway results in a mature pit lake (at 250 years) with a pH of 8.2 and 1,420 mg/L TDS

The PITQUAL model was verified by comparing water quality of the Cortez Pit Lake, an existing pit lake with similar lithology six miles southeast of the proposed Pipeline/South Pipeline pit. The Cortez pit lake chemistry after 20 years was in good agreement with that predicted for the proposed Pipeline/South Pipeline pit after 20 years. In addition, PHREEQC accurately simulated the chemogenetic pathway of evapoconcentration tests conducted using site groundwater. Based on the of results of the groundwater flow model and on both numerical and bench scale analysis, there will be no impact on groundwater surrounding the Pipeline/South Pipeline pit after infilling, while the pit lake chemogenetic pathway will result in a consistently good water quality, comparable to existing surface waters in Crescent Valley.

*Key words: ????????????????*

## 30 CLOSURE OF PIT LAKES: MODELING, MONITORING AND MITIGATION

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Open pit mines with existing pit lakes, or with the potential to form post-mining pit lakes, must comply with state and/or federal regulations to: 1) meet numerical standards for surface and groundwater; 2) not degrade water resources; and/or 3) prevent potential adverse health affects to human, terrestrial, or avian life. Site-specific characterization of existing, evolving and/or future pit lake water quality requires multi-disciplinary technical information that must be integrated in a coherent conceptual model of physical and chemical processes that may influence interim and final pit water quality. Site-specific conditions such as climatology, hydrogeology, surface water hydrology, groundwater quality, ultimate pit geometry, wallrock physical and chemical characteristics, hydrogeochemical processes and limnological processes may vary significantly from one open pit mine to another. Effective permitting and closure of post-mining pit lakes requires a combination of practical hydrogeochemical modeling, process-focused monitoring and, if required, mitigation of the pit lake and resulting impacts to water quality.

Monitoring of hydrogeologic, geochemical and limnological processes that may have the greatest effect on pit lake water quality, and that may not be adequately addressed by initial predictive modeling, should be conducted as dewatering and mining operations proceed and continued through the post-closure groundwater recovery phase. Changes in hydraulic and chemical effects proximal to the pit lake as regional "steady-state" conditions are reached should be incorporated into recalibrated hydrogeochemical and limnological predictions. Initial modeling, subsequent empirical data and re-modeling to support a closure plan

with mitigation options and cost benefit analyses may result in backfilling with amended waste rock, enhancement of local groundwater recovery by pumping ambient-quality groundwater into the pit, chemical or biological treatment of pit water, or some combination of these mitigative measures. Use of Best Available Demonstrated Control Technology (BADCT) may provide technical solutions to regulatory constraints for pit lake closures.

*Key words: mine closure, pitlake, modeling, monitoring, mitigation, cost-benefit analysis, Best Available Demonstrated Control Technology (BADCT)*

## 31 LEACHING TEST METHODS USED IN PIT LAKE CHEMIS- TRY PREDICTION

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Numerous sources can contribute chemical constituents to lakes that form after closure of open-pit mines. The source that typically has the greatest potential effect on lake chemistry is ground water flowing into the pit through weathered wall rocks. No standard method exists for characterizing this source, and a variety of leaching test methods have been used by investigators at different sites to simulate the chemistry of wall-rock leachate. Test methods that have been used to characterize leachate chemistry at different sites are compared, and potential artifacts of the choice of method discussed. A comparison (from a recent project) of results from two tests of the same material using slightly different configurations of a humidity cell leaching apparatus indicates that the selection of a test method can be a source of significant uncertainty. This uncertainty, which usually is not quantified, carries through to and can be amplified by

geochemical modeling of lake chemistry. Careful selection and design of a leaching test method is therefore important in adequately representing conditions that will exist after mine closure.

*Key words: mining, pitlake, leaching, environmental, testing*

## 32 PITLAKE LIMNOLOGY

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Limnologic processes that influence the evolution of mine pit lakes include biomass production and hydrodynamic mixing. Biological productivity may influence wildlife use, and when combined with lake hydrodynamics, affects the dissolved oxygen distribution and the corresponding chemical reactions within the lake. Lakes can mix either completely (holomixis) or partially (meromixis) on a yearly basis, depending on whether a persistent chemical gradient develops over time. A complete limnological characterization of three existing holomictic Nevada pit lakes is described, followed by a discussion of characteristics that may have led to meromixis in other existing pit lakes.

The three lakes studied in detail represent a range of sizes and configurations typical of Nevada pit lakes. Limnologic parameters (temperature and dissolved oxygen profiles, plankton speciation and abundance, and nutrient concentrations) were measured in the lakes during three seasons. Two of the lakes were thermally stratified during summer sampling and completely vertically mixed during winter, whereas the third lake was completely mixed in summer and winter. The first lake formed when an open-pit copper mine was flooded by rebounding groundwater,

has a maximum depth of 110 m, and is seasonally stratified, well-oxygenated, and oligotrophic. The second lake formed in an open-pit gold mine, has a maximum depth of 17 m, and is a seasonally stratified, eutrophic lake, which develops an anoxic hypolimnion at the end of the summer stratified period. The third lake also formed in an openpit gold mine, has a maximum depth of 7 m, and is an isothermal, saline, well-oxygenated, oligotrophic lake.

Data from the field study were used to develop limnological models of the lakes using the U.S. Army Corps of Engineers hydrodynamic and water quality model CE-QUAL-W2. For the holomictic lakes, the model replicated seasonal variations in temperature and dissolved oxygen concentration. The model could not predict the development of meromixis in lakes, however, because the mechanisms that could lead to meromixis are difficult to determine and incorporate into a modeling study.

*Key words: pitlake, limnology, modeling*

## 20 SULFATE IN PITLAKES

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Understanding the evolution of pit lake water quality requires conceptual models that can reliably predict the concentrations of major constituents in pit lake water. Because sulfate is a major constituent associated with oxidation of pyrite and other sulfide minerals which contain hazardous constituents (e.g. As, Sb), reliable prediction of sulfate concentrations is a useful measure of the utility of a pit lake model. Sulfate (400-2000 mg/L) commonly occurs with elevated calcium concentrations (40-400 mg/L) that is near, or exceeds the solubility product for gypsum (CaSO<sub>4</sub>:

Ksp  $2.4 \times 10^{-5}$  at  $25^{\circ}\text{C}$ ). Current pit lake geochemical models have focused on pit wall oxidation, which generally predict low sulfate concentrations ( $< 200 \text{ mg/L}$ ) in pit lakes. An additional source of sulfate is from sulfide oxidation in dewatered aquifer surfaces in which water has been replaced with air. If all of the oxygen in one acre-foot of air is allowed to oxidize pyrite to sulfate and  $\text{Fe}^{2+}$ , approximately 500 kg of sulfate will be produced. Depending on the dewatering rate, and the exposed sulfide surface, this additional release of sulfate and associated constituents can be a significant source of contaminants into pit lakes and can provide a partial explanation of the sulfate concentrations in existing pit lakes.

*Key words: pitlake, sulfate, geochemical modeling*

## **34 SIMULATION OF GROUNDWATER FLUXES DURING OPEN PIT FILLING AND UNDER STEADY-STATE PIT LAKE CONDITIONS**

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A critical component in determining post-mining pit water quality is knowledge of groundwater fluxes, both as the pit fills and after steady-state conditions have been reached. Simulations of the filling of an open pit in Crescent Valley, Nevada, were made to generate inputs for pit lake chemistry predictions. The simulations show that the water-table recovery is most rapid immediately after pumping stops, when the hydraulic gradients are steepest. The maximum lateral extent of water-table drawdown occurs several years after pumping stops because water continues to be derived from storage as the pit fills. Under steady-state conditions, the lake stage is lower than the steady-state water table in the pit area prior to mining, and groundwater flow is directed toward the pit lake because evapo-

ration from the lake surface causes it to act as a groundwater sink.

*Key words: pitlake, groundwater, water-table*

## **35 AN IMPROVED APPROACH TO MODEL PYRITE OXIDATION IN OPEN PIT WALL ROCK**

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Determination of the pyrite oxidation rate is a critical element in predicting the propensity for acid rock drainage at current and future mining operations. Previously, the Davis-Ritchie approach for modeling pyrite oxidation has been used to model oxidation and acid generation in tailings piles. However, this approach is less successful in modeling pyrite oxidation in open pit wall rock, producing similar predictions for rock under distinctly different conditions. Therefore, the Davis-Ritchie approach was amended to include wall rock geometry (fractures from blasting create pathways for oxygen to travel through) and water content (which could limit the oxidation of pyrite), and use of an explicit numerical scheme to minimize artificial, numerical dispersion. The Fennemore-Neller-Davis (FND) model has been used to model pyrite oxidation in wall rock in arid climates where it provides a more accurate representation of the physical system and improved calibration to field experiments conducted at open pit mines and to laboratory humidity cells.

Comparing the FND and Davis-Ritchie models using identical parameters except for porosity (the FND model used porosity of the rock, while the Davis-Ritchie model used the bulk porosity to account for the fractured surface), demonstrated a 2m oxidation depth after 20 years, while the Davis-Ritchie predicted a 1.5m depth. The greater depth in the FND model is a result of the fractured surface supplying oxygen to a greater surface area.

However, after 50 years the FND model predicted an oxidized depth of 2.75m while the Davis-Ritchie model predicted 4.5m; the greater depth in the Davis-Ritchie model demonstrates the effect of using a bulk porosity model to account for the fractured surface. The FND model results in more representative prediction (i.e., fast oxidation at the heavily fractured surface, but slow oxidation deeper into the pit wall), while the Davis-Ritchie results show oxidation similar to that of a tailings pile or waste rock dump.

*Key words: ?????????????*

## 36 REALISTIC EXPECTATIONS AND RESEARCH DIRECTIONS FOR PREDICTIVE PIT-LAKE WATER QUALITY MODELING

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Models are used widely to predict water quality in open-pit mine lakes and to evaluate the ecological risk associated with these post-mining features. These predictions guide mine planners and regulators in selecting among various closure alternatives that can vary by tens of millions of dollars. Yet, water quality modeling remains largely unverified due to a lack of post-model audits using existing pit lakes. In addition, demands by regulators for accuracy exceed the capability of current analytical models. Regulators and operators can increase the utility of pit-lake modeling by identifying realistic expectations for existing models, improving estimates of prediction uncertainty, and focusing research on improving model accuracy.

Our conceptual model of pit lake water quality evolution (based on studies of seven existing lakes and modeling of water quality in eighteen future lakes) considers six components: chemistry of inflowing groundwater water balance, sulfide oxidation and solute release from wall rock, water/rock interac-

tions, adsorption and precipitation reactions, and metal stability in sediment.

Of the six components, uncertainty in inflow composition, short-term oxidation rates, and wallrock solute release can probably be bracketed with sufficient sampling, and existing probability distributions for thermodynamic values typically bracket chemical reactions. But interactions of wall rock with runoff, infiltration, and lake water are poorly understood. In addition, uncertainty in wall-rock oxidation rates increases with time, because inflow composition can change with variations in flow rates, and water balance can shift with changing climate.

Decision makers should note the following:

- Empirical evidence demonstrates that wall-rock oxidation can be sufficient to acidify pit lakes in any climate (sulfide minerals oxidize faster in semiarid climates than wet).
- Model comparisons to existing pit lakes indicate that probabilistic simulations can bracket most water-quality parameters at early times (e.g., less than 5 years or so after mining ceases), but unquantified uncertainties limit the accuracy of longer-term predictions.

Eventually, model accuracy (and accountability) will emerge from long-term comparisons with evolving pit lakes. To best support policy decisions in the meantime, ongoing research should include a blind "round robin" comparison among existing models to assess consistency among researchers. In addition, studies at existing pits should focus on gathering empirical measurements of the critical model parameters: wall-rock oxidation rates, water/wall-rock interaction, and the rate and quality of precipitation runoff and infiltration.

*Key words: pitlake, modeling, uncertainty, sulfide oxidation, runoff*

**Program Three**  
**Wednesday, May 20, 1998**  
**Phytoremediation**  
**Superior A**

**37 AN INVESTIGATION OF  
PLANT SPECIES NATIVE TO  
THE INTERMOUNTAIN WEST  
FOR USE IN THE  
PHYTOREMEDIATION OF  
LEAD CONTAMINATED  
SOILS**

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Current research on phytoremediation technologies for remediating heavy metal contaminated soils have focused on the use of plants that are not adapted to the growing conditions of sites in the Intermountain West. Phytoremediation of Pb contaminated soils has been especially challenging since few species worldwide have been identified that can accumulate Pb. Therefore, we have approached this problem by characterizing Pb accumulation in a variety of native plant species that have naturally colonized an abandoned mine site in American Fork Canyon, UT. Lead concentrations up to 1000 mg/kg D.W. were measured in above ground tissues of two tree species *Betula occidentalis* (Birch) and *Alnus tenuifolia* (Alder), and one sedge, *Carex microptera* (*Carex*), growing in the field. Controlled laboratory studies were conducted to investigate the effects Birch and *Carex* have on the fate and behavior of Pb in a contaminated soil (Pb = 3000 mg/kg) and tailings (Pb = 15,000 mg/kg) collected from the site. Increased leaching of Pb associated with a drop in pH were observed in planted treatments in the tailings but not in the soil. Significant Pb accumulation was observed in *Carex* (2 1000 mg/kg D.W.) in both soil and tailings treatments but Pb was primarily excluded by Birch. Lead exclusion in Birch

resulted in elevated concentrations of Pb in the rooting zone in both soil and tailings treatments. Total Pb concentrations in the birch rooting zone increased but the results of a CaCl<sub>2</sub> extraction indicated no significant increase in the percent of exchangeable Pb in the Birch rooting zone in the soil treatment. This suggests that the exclusionary behavior of Birch observed in the laboratory study may promote soil Pb stabilization. However, the percent exchangeable Pb concentrations increased in both planted treatments in the tailings. This was consistent with the increased leaching of Pb observed in the planted tailings treatments. Possible explanations for the discrepancy between Birch Pb accumulation in the field and in the laboratory are discussed. Information gathered from the field, laboratory studies, and the literature, were integrated to evaluate the potential use of these species in the phytoremediation of Pb contaminated soils.

*Key words: phytoremediation, lead, hyperaccumulation, birch, carex*

**38 SELENIUM REDUCTION IN  
MINING EFFLUENT USING A  
PASSIVE MODULAR REAC-  
TOR**

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The purpose of this research was to determine if sawdust can be used to support a bioprocess for the remediation of selenium laden streams. In a mining setting, organic substrates required for metabolic activity are usually limiting. Selenium reducing bacteria (SeRB) were found in the sediments and wastes from two mine sites, grown up to higher numbers, and used to increase their levels in mud from each mine. Both inoculated and uninoculated mud was tested in a

reactor design to treat waters from these two mines. Se levels were reduced from 100 ppb to less than 5 ppb for one mine over a 45 day trial period. Se levels were reduced from 700 ppb to below 10 ppb over a 63 day trial period for the second mine. In addition, sulfates, nitrates, and other cationic metals are removed in the same process. The pH values from the streams were increased from values as low as 3 to pH values of 7 consistently.

*Key words: selenium, metals, acid mine drainage*

## **39 EVALUATION OF NORTHERN CHIHUAHUAN DESERT PLANTS FOR PHYTO-EXTRACTION OF HEAVY METALS FROM CONTAMINATED SOILS**

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Heavy metal contamination of the desert environment is a serious concern. The desert ecosystem is very delicate and the introduction of non- native plant species for the purpose of phytoremediation of these contaminated soils may be detrimental to this delicate environment. Therefore, new methods of remediation need to be investigated. The use of native desert plants may be an alternative method. This study was performed to determine the possibility of finding native desert plants that could absorb hazardous heavy metals from contaminated soils. Four different sites were selected for this study. Three of the sites were located near a local smelter, while the other site (a control site) was located approximately 30 kilometers away. This investigation was conducted using some of the four most abundant plant species in the area to determine the copper and lead content of their various tissues. These plants were: *Prosopis glandulosa* (Mesquite), *Salsola kali* (Tumble weed), *Cevalina Spinosa*, and *Solanum*

*Elaeagnofolium* (Purple Nightshade). All plants were separated into leaves, stems, and roots. Subsequently the corresponding plant tissues were washed with de-ionized water and then rinsed with 0.01M HCl to remove any surface metal due to aerial deposition. The plant tissues were then dried and digested following E.P.A. method 200.3. Copper and lead concentrations were determined using a Flame Atomic Absorption Spectrometer. Our results showed that Purple Nightshade absorbed the highest concentration of copper and lead among the four plants studied. The copper levels found within the plant tissues from the most contaminated sites in the roots, stems, and leaves were 745 mg/Kg, 65 mg/Kg, 370 mg/Kg; while the Pb levels were 1875 mg/Kg, 97 mg/Kg, and 380 mg/Kg, respectively. To our knowledge, Purple Nightshade is one of the few or possibly the only desert plant absorbing or phyto-accumulating such high levels of lead. This could be an innovative phytoremediation technique, to remove toxic heavy metals from contaminated soils. The results from these experiments will be presented.

*Key words: heavy metal, phytoremediation, phyto-accumulation, desert plants*

## **40 USING REMOTE SENSING TOOLS TO ASSESS PHYTOREMEDIATION FIELD SITES**

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In order to assess the success of a phytoremediation project, the health of the plants and the movement of the contaminant need to be evaluated. Laboratory Studies have shown that some plant species grown in

hydrocarbon contaminated soils exhibited stunting and chlorosis. Plants grown in heavy metal contaminated soils suffer from stunting, chlorosis, uptake of heavy metals that block natural micronutrient accumulation, and deformations of the leaves and stems. In phytoremediation studies, plants are harvested at intervals and analyzed for greenness, biomass, overall appearance, and chemical analysis of the biomass for contaminant uptake. In field studies, these analysis may need to be performed several times throughout the growing season. For remote field sites, the costs involved in assessing these parameters become prohibitive, especially for large sites where more sampling may be necessary for proper statistical analysis. If the contamination at a field site is non-homogeneous, the use of geostatistical methods may be required in order to assess the remediation of a contaminant and this may require additional sampling. Considering the cost of traveling to the field sites, lodging personnel time, and chemical analyses of samples, the use of remote sensing techniques to assess the same or similar parameters may be a less expensive alternative.

Remote sensing techniques have been used in the agricultural industry to assess the growth of different crop varieties during field studies and have measured similar plant health parameters, as those required in a phytoremediation project. By using satellite or photographic data, the analytical costs may be reduced and the ability to work with very large sites would be possible. This paper presents an overview of remote sensing and its applicability to evaluation of phytoremediation field sites. Data will be presented for several field sites.

*Key words: remote sensing, phytoremediation, evaluation tools, collaborative research*

## 41 PREDICTING LANDFILL LEACHATE REDUCTION USING VEGETATION

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Prediction of water movement through landfill covers is an important parameter in leachate management design. A water balance is generally performed using the Hydrologic Evaluation of Landfill Performance (HELP) model, which is currently the standard in landfill leachate prediction.

In sub-humid to arid environments, water loss due to evaporation and transpiration through plants can be greater than the accumulated precipitation, causing an upward flux of soil moisture. A numerical model has been developed which accounts for the upward flow of water due to evaporation and vegetation. This new model is an improvement over HELP modeling, because HELP does not accurately account for upward water movement due to excessive evaporation rates and vegetation covers. This is due mainly to the unsaturated conditions that exist in the subsurface of sub-humid to arid climates. This new model is used to optimize final cover vegetation to minimize leachate production.

Recently, the use of vegetation to augment conventional leachate management methods has significantly increased. Such applications have been called natural covers or ET (Evapotranspiration) covers, and use natural (intrinsic) processes to store infiltrating water in the soil profile and then remove it from the subsoil through evaporation and the growth of vegetation on the soil cover. This model has been used to evaluate water losses in typical landfill cover systems in South Dakota using various climatic (sub-humid to arid) and vegetative conditions.

*Key words: landfill, leachate, modeling, vegetation*

## 42 PARAMETERS USED IN THE MODELING OF A VEGETATIVE REMEDIATION SYSTEM

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Several computer simulation models have been developed that have the capability of simulating the degradation of hazardous organic contaminants in a rooted soil. Preliminary model comparisons to experimental data have shown that, under certain conditions, the models produce accurate depictions of the fate of hazardous organic contaminants in the root zone of a soil. These comparisons have also demonstrated, however, the need for modification of the model to account for conditions and/or processes that exist at field sites where the models will be utilized.

An exhaustive literature search is currently being performed to more accurately describe process parameters which occur under variable vegetative, all and growth conditions. When a more realistic depiction of optimum growing conditions can be obtained, it will be possible to develop a calibration constant for the model that can more closely simulate site specific growth conditions at field sites under the stress of hazardous organic contamination. This will allow the development of a methodology that can synthesize the modeling data from information that is available about a potential remediation site, and to use the modeling results to systematically arrive at an optimal remediation design based on remediation goals and criteria unique to a site.

*Key words: modeling, vegetative remediation, hazardous organic contaminant*

## 43 ANALYSIS OF TCE AND CHLORINATED METABOLITES IN PLANT TISSUE

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We developed and evaluated methods to analyze plant tissue for trichloroethene (TCE), 2,2,2-trichloroethanol (TCET), trichloroacetic acid (TCAA), and dichloroacetic acid (DCAA) in support of field and laboratory studies designed to evaluate the impact of plants on the fate of TCE in groundwater and soil. The methods were adapted from similar techniques described in the literature for soil, water, and plant tissue. We performed a series of spike recovery studies using leaf, stem and root tissue from six different plant species: hybrid poplar, live oak, castor bean, saw palmetto, mountain maple, and Austrian pine.

Using a sealed vial methanol extraction followed by purge and trap gas chromatography with an electron capture detector (GC/ECD), an extraction efficiency of >95% was achieved for TCE spiked samples with an estimated detection limit of 2.0 ug/kg.

For TCET recovery studies, spiked plant tissue samples were crushed under liquid nitrogen in a mortar prior to extraction with a 0.1N H<sub>2</sub>SO<sub>4</sub>/10% NaCl solution. Phases were separated by centrifugation; the aqueous solution was then extracted with methyl tert-butyl ether (MTBE) and analyzed by direct injection GC/ECD. The extraction efficiency was >95% with an estimated detection limit of 20 ug/kg.

A 0.25N NaOH solution was used to extract TCAA and DCAA spiked into crushed plant tissue samples. After centrifugation, the aqueous extract was acidified with 50% H<sub>2</sub>SO<sub>4</sub> and extracted with MTBE, derivatized with diazomethane, and analyzed by direct injection GC/ECD. The extraction efficiency was >95% for both compounds with an estimated detection limit of 20 ug/kg for TCAA and 70 ug/kg for DCAA. Mass spectrometry

was used to verify the identification of all compounds quantified by GC/ECD.

Method performance, as defined by blanks, matrix spikes and replicates obtained from both field and laboratory studies, will be presented.

*Key words: trichloroethylene, trichloroethanol, trichloroacetic-acid, extraction, phytoremediation*

## **44 FATE OF TCE IN HYBRID POPLAR: STUDIES ON THE UPTAKE, TRANSLOCATION, AND TRANSPIRATION**

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Most studies reported in the literature have concluded that uptake of trichloroethylene (TCE) is significant. We used a high-flow, sealed plant growth chamber system to evaluate the fate of <sup>14</sup>C-labeled TCE and/or its metabolites by hybrid poplar (*Populus deltoides* x *nigra*, DN34). The system was designed to provide complete separation between root and foliar uptake, as well as a non-stressed plant environment. The root zone solution was maintained at a TCE concentration of 0.8mg/L over the 10-day trial period. Systems were run in triplicate and provided high mass recoveries of <sup>14</sup>C-labeled TCE (>95%) with comparable distributions of the label across each chamber system. No gaseous efflux of <sup>14</sup>C-labeled TCE was observed in the foliar chambers. <sup>14</sup>CO<sub>2</sub> was detected in the root zone CO<sub>2</sub> traps at 1%, while no <sup>14</sup>CO<sub>2</sub> was detected in the foliar CO<sub>2</sub> traps. Rhizosphere degradation and mineralization of TCE was 20 to 40 times greater than plant uptake. Foliar concentrations accounted for 0.05% of the applied label, with 0.5% associated with the root tissue. Tissue concentrations as determined by combustion were similar to previously reported concentrations

with leaf tissue concentrations ranging from 3 to 5 mg TCE and/or metabolites/kg, stem concentrations of 1.5mg TCE and/or metabolites/kg, and root concentrations of 33 to 53 mg TCE and/or metabolites/kg. These results suggest that in non-stressed (aerobic) root zone conditions, plant uptake of TCE is negligible in comparison to rhizosphere degradation. We are now comparing TCE uptake by hybrid poplars grown in aerobic and anaerobic root zone conditions.

*Key words: trichloroethylene, phytoremediation, degradation, mineralization, plant uptake*

## **45 PHYTOTOXICITY SCREENING OF CHLORINATED ALIPHATICS**

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Chlorinated solvents are common hazardous waste products in the United States. Phytoremediation may prove to be an inexpensive, effective way to remediate groundwater contaminated with chlorinated aliphatic compounds. High concentrations of solvents, however, may prove toxic to plants and limit the success of plant based remediation. Hybrid poplar trees are widely used in phytoremediation efforts, and knowledge of toxicity limitations will assist in selecting sites appropriate for this technology. General trends in the relationship between chemical characteristics and toxicity should also prove useful.

The relative toxicity of a series of chlorinated aliphatic compounds was assessed in laboratory experiments using hybrid poplar cuttings. Plants were grown with the lower, root portion sealed in individual bioreactors containing hydroponic solutions with varying concentrations of a chlorinated solvent. Hydroponic solution concentrations were monitored and replaced as necessary to maintain exposure to a constant level of compound.

Transpiration rate, change in total biomass, and leaf chlorosis were used as indicators of phytotoxicity. Toxicity experiments were also conducted with axenic poplar cell cultures, and the results compared to tests with cuttings. Compounds tested were chosen with varying number of chlorine atoms, double or single bonds, and a broad range of octanol-water partitioning constants. The effect of these parameters on toxicity to hybrid poplar was determined.

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

## **46 PHYTOREMEDIATION OF TNT-CONTAMINATED SOILS USING PLANTS SELECTED BY A FOUR-STEP SCREENING PROCEDURE**

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We are developing phytoremediation technology for the cleanup of TNT contaminated soil at a specific upland site (the Volunteer Army Ammunition Plant in Chattanooga, TN). Phytoremediation, the use of plants to cleanup contaminated environments, has a great potential for soils contaminated with TNT. Recent discoveries suggest that intrinsic plant enzymes (distinct from microbial processes) can carry out transformation reactions and that plants can take up TNT and convert it into harmless derivatives. Previous work on phytoremediation of explosives has dealt almost exclusively with wetland systems. We will report results of a novel four-step screening procedure to select plants for the upland phytoremediation of TNT:

Step 1-Immunoassay screen to identify plants containing high levels of TNT degradative enzymes. Two antibody assays were used to screen eighteen plant candidates.

The first assay measured nitroreductase enzyme which transforms TNT to triaminotoluene (TAT). The second assay quantifies laccase enzyme, which oxidizes TAT to lignin-like compounds;

Step 2-Whole plant screen to identify plants which carry out high rates of transformation of TNT in hydroponic systems (without accumulation of TNT).

Step 3-Soil phytotoxicity screen to identify plants which can become established in TNT contaminated soil from the VAAP.

Step 4-Phytoremediation screen, a greenhouse study to identify plants which can effectively remove TNT from the soil of interest. The most promising species will be tested in Phase II: a small-scale outdoor phytoremediation study at the VAAP. Although the selection procedure is site specific, the process could be used for soils from any upland site. This project is being supported by a Phase I SBIR award from the US EPA.

*Key words: phytoremediation, TNT, plants, munitions*

## **47 DARAMEND<sup>®</sup> BIOREMEDIATION OF SOILS CONTAINING ORGANIC EXPLOSIVES**

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DARAMEND bioremediation technology, developed by W. R. Grace & Co. (GRACE), has proven effective for bioremediation of soils impacted with chlorinated pesticides and organic explosives. This patented technology relies on application of small quantities of naturally occurring non-hazardous soil amendments (processed plant fibres and powdered zerovalent metals), to facilitate repeated and sequential reductive (anoxic) degradation of chlorinated or nitro-organic compounds. No microbial inoculation is required. Soil is treated in

solid-phase and results in minimal bulking (< 5%).

The DARAMEND technology has been successfully applied to numerous North American soils containing a wide variety of organic explosive compounds. To date, soils impacted by Tetryl, TNT, DNT, nitrobenzene, nitroglycerine RDX, and HMX, have been rapidly remediated using the technology, as determined by HPLC (EPA Method 8330). Treatment has typically resulted in >99% removal of explosive compounds, and removal of soil toxicity.

In a Quebec soil nitroglycerine was reduced from 500 mg/kg to below detectable limits during only 14 days of DARAMEND treatment. In a military soil from Illinois the concentration of DNT was reduced from 5,000 to 16 mg/kg in 84 days of treatment (study still in progress). In addition, the TNT concentration in a military soil from Nevada was reduced from 2,443 to 156 mg/kg within 28 days of treatment (study still in progress). Final results from these applications will be presented. The first field-scale application of DARAMEND will be initiated in early 1998. An update on the field-scale work will be presented.

DARAMEND technology eliminates drawbacks such as supplemental water treatment requirements, handling and storage of large quantities of soil additives, substantial bulking of soil during treatment, and high cost that have previously hindered wide spread application of bioremediation. Cost estimates, supported by data from three successful pilot-scale projects (using the same technology at Toxaphene, 2,4-D, and MetolachlorK-contaminated sites), indicate that relative to alternate bioremediation processes, use of DARAMEND bioremediation could reduce treatment costs by as much as 70%.

DARAMEND<sup>(R)</sup> is a registered trademark of W.R. GRACE.

*Key words: DARAMEND<sup>(R)</sup>, bioremediation, nitroaromatics, explosives, pesticides*

## 48

### **GROUNDWATER TREATMENT PERFORMANCE EVALUATION CASE STUDY: TREATMENT OF INORGANICS AND EXPLOSIVES VIA ELECTROCHEMICAL PRECIPITATION, UV-OXIDATION, AND CARBON ADSORPTION**

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From 1941 to 1978, several million pounds of explosives, principally 2,4,6 TNT and RDX, were washed out of ammunition shells by using a hot water spray at a Tennessee Army site. The water then flowed into a series of unlined settling ponds which had a total area of approximately 5 acres. Because of extremely high levels of explosive compounds (2,4,6 TNT as high as 26,000 ug/L and RDX as high as 18,000 ug/L) detected in ground water and the proximity of the site to a public water supply, it became the Army's top-ranked National Priority List site.

During preparation of the Feasibility Study (FS) in 1992, several potential remedial technologies were identified to treat the ground water. Some of the technologies identified were data-limited concerning their effectiveness in treating inorganics and explosives at the influent concentrations encountered at the site. To address these data gaps, electrochemical precipitation and UV-oxidation bench and pilot scale studies were conducted. Based on the results of the bench and pilot studies, a full scale treatment train consisting of electrochemical precipitation, ultraviolet oxidation, and carbon adsorption was selected for the site in a Record of Decision (ROD) signed in September 1992. Construction of the ground water treatment plant was completed in 1995.

Results of the bench and pilot studies were used to predict full-scale system operations in terms of contaminant removal efficiencies, reagent dosages, and operating costs. This paper will address how accurate these

predictions have proven out after running the full scale system on and off over a two-year period (November 1995 to October 1997). This paper will discuss some of the lessons learned over that same time period. This paper will also discuss the initial rationale for selecting these unit operations.

*Key words: electrochemical precipitation, W-oxidation, solubility, inorganics, explosives*

## **49 INCINERATION OF EXPLOSIVES CONTAMINATED SOIL AT THE FORMER NEBRASKA ORDNANCE PLANT**

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Explosives contaminated soil at the former Nebraska Ordnance Plant was remediated using on-site rotary kiln incineration. Treatment at this site was accomplished in less than a year. This included contract award, mobilization of the incinerator, shake-down, miniburn, trial burn, and the contaminated soil production burn. The remediation was completed quickly and efficiently because of the cooperation and partnering between all involved parties. The project had a minimum of process problems in spite of the early onset of cold weather. This paper summarizes the treatment process and the results of the Mini Burn and Trial Burn.

*Key words: incineration, nitroaromatics, explosives, soil, cleanup*

### **Program Three Wednesday, May 20, 1998 Site Characterization Wasatch B**

## **50 UTILIZATION OF THE KINEMATIC RUNOFF AND EROSION MODEL IN PREDICTING THE EFFECTS OF VEGETATION ON SEDIMENT CONTAINMENT**

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In southeast Kansas, where mining activities ceased in the middle half of the twentieth century, residue materials have created surface contamination problems. The erosion losses of chat material, a byproduct of mining activities, has elevated levels of cadmium, lead and zinc in nearby farmland to phytotoxic levels for the crops normally planted. Selective vegetation is being examined as a means of controlling the loss of sediment material and containing the further spread of the metal contaminants. The kinematic runoff and erosion model, KINEROS, is examined to investigate the role vegetation plays in controlling erosion from an 800 acre watershed, near Galena, Kansas. The results of the model are compared with predictions made by another non-point source model, the Agricultural Non-Point Source Pollution model, AGNPS.

*Key words: erosion, metals, modeling, vegetation, watershed*

## 51 CHARACTERIZATION OF NAPL CONTAMINATED SITES USING TRACER TECHNIQUES: INTERMEDIATE SCALE EXPERIMENTAL VALIDATION

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Site remediation can be significantly impacted by the quality of characterization data. Determining the distribution of contaminants in heterogeneous aquifers requires accurate site data at the appropriate scale. Parameters used to characterize sites contaminated with entrapped nonaqueous phase liquids (NAPL) are typically measured or modeled at a scale other than that which dominates the relevant physics. Application of parameters evaluated at the wrong scale result in significant errors in the design of remediation schemes

A series of experiments were designed to evaluate the use of conservative tracers as a method of evaluating NAPL entrapment in the subsurface. A 10 X 1.5 X 0.05 meter tank was filled with a heterogeneous packing of five different sands. The distribution of sands satisfied statistical properties similar to a heterogeneous alluvial aquifer. The total packing represented 16 horizontal correlation scales and 20 vertical. Measurements included pressure at 46 locations, tank effluent, conservative tracer breakthrough curves (BTC) and gamma spectroscopy to map the NAPL distribution

Initial tracer tests were performed to determine the baseline response of the heterogeneous packing and to demonstrate repeatability. This was followed by a series of NAPL spills. A light NAPL (Soltrol) was injected into the bottom of the formation. After redistributing and becoming entrapped, the conservative tracer test was repeated and the BTCs recorded. This process was repeated to produce a series of BTCs as a function of

increasing NAPL entrapment in the formation. Experimental results are presented and their implications for the use of tracer tests are briefly discussed.

*Key words:* organic waste, nonaqueous phase liquids, site characterization, tracer methods, inverse modeling

## 52 GEOSTATISTICAL ANALYSIS OF GROUND PENETRATING RADAR DATA

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A critical step in assessing groundwater flow and/or contaminant transport at a site is to obtain an accurate model of the hydraulic properties of subsurface. Such a model should include estimates of the magnitude of hydraulic properties and should also contain information about the spatial variability or heterogeneity at the site. Of specific interest in our research is the geostatistical analysis of ground penetrating radar (GPR) data as a means of characterizing the spatial heterogeneity of the subsurface. This can contribute to the development of accurate models of the subsurface, and also provide information of use in planning for drilling and direct sampling.

Ground penetrating radar is a high resolution, near-surface, geophysical technique that images variation in the electrical properties of the subsurface. We collect GPR data at a site, using 100 MHz or 200 MHz antennas, and trace spacing on the order of 20 cm. We use a geostatistical analysis of the GPR data to obtain experimental variograms which quantify the correlation length of the GPR reflections. We have developed an interactive program that allows us to select various

regions within the GPR image for analysis, to construct either a 2-D variogram or a variogram along a specific direction. Our working hypothesis is that GPR data sample the spatial variability of the subsurface in such a way that the correlation structure of the GPR image can be taken to represent the correlation structure of the subsurface.

GPR data have been collected in regions underlain by sedimentary units deposited in a number of different deltaic, barrier spit, and glaciofluvial environments. We find that the variograms obtained from the GPR data can be modeled with a spherical or exponential variogram model. In all cases, there is excellent agreement between the data and the model. The correlation lengths that we have obtained range from approximately 1 m in channel deposits to 40 m in a coastal barrier spit.

The results obtained from different sedimentary environments, with cliff-face "calibration exercises", suggest that GPR can be used to characterize the sub-meter- to meter-scale variability at a site. We conclude that the methodologies which we have developed and applied in the analysis and interpretation of GPR data can lead to the improved use of GPR data in site characterization.

*Key words: characterization, geostatistics, geophysics, radar*

**Program Three**  
**Wednesday, May 20, 1998**  
**Monitoring and Analysis**  
**Wasatch B**

**53**

**ON-SITE DETERMINATION  
OF TRICHLOROETHYLENE  
(TCE)/PERCHLOROETHYL-  
ENE (PCE) IN WATER BY  
UV-INDUCED COLORIMETRY**

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Halogenated volatile organic compounds (VOCs) such as trichloroethylene (TCE) and perchloroethylene (PCE), are some of the most frequently occurring contaminants found at RCRA and DoD sites. On-site characterization of halogenated VOCs in real time and at low cost is important for environmental decision making.

An on-site colorimetric method for the detection of TCE/PCE has been developed by EnviroI, Inc. The method utilizes a novel extraction procedure to remove TCE/PCE from water. Quantitative determination of the extracted analytes is accomplished by a photochemical reaction which produces coloration proportional to the concentration of the analytes. The method detection limit (MDL) is 5,11g/L for both TCE and PCE in water. The method allows determination of TCE/PCE concentrations in less than 20 minutes at a fraction of the cost of standard analytical methods. EnviroI's TCE/PCE test system has been used for determination of TCE/PCE concentrations in water samples from several contaminated sites. Results obtained with EnviroI's TCE/PCE test method are compared with results obtained with standard methods.

*Key words: trichloroethylene (TCE), perchloroethylene (PCE), field method, water*

## 54 RAPID SELECTIVE MONITORING OF BACTERIA IN WATER BY FERROGRAPHIC ENUMERATION

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The need for improved methods to rapidly enumerate bacterial concentrations is driven by bacterial contamination of food and water. Immunomagnetic separation (IMS) can be used to selectively concentrate bacteria in suspension, but IMS alone does not determine bacterial concentrations, at least at low cell counts. Strategies to enumerate bacteria at low cell counts include filtration onto 25 mm diameter filters followed by laser scanning of the entire area of the filter to identify and count bacteria. Although effective, this strategy requires sophisticated and expensive equipment. Our objective is to introduce a method which offers a low-cost alternative. The method utilizes a Bio-ferrograph to focus deposition of magnetically-conjugated bacteria onto an exceedingly small area, which is then easily examined visually under an epifluorescence microscope to determine bacterial concentrations at low cell counts. Experiments examining *Escherichia coli* XL1 Blue correctly determined cell concentrations at  $100 \text{ cell mL}^{-1}$  and  $1000 \text{ cells mL}^{-1}$  using only 1 mL of suspension in both pure water and water of high ionic strength (1E-3 M). The ability to determine lower cell concentrations by processing larger volumes of solution is presently being examined. Rapid selective ferrographic enumeration offers the ability to enumerate low cell concentrations in only a few hours.

*Key words: bacterial transport, pathogen monitoring, ferrography, immunomagnetic separation, Escherichia coli*

## 55 USE OF ICP-MS TO DETERMINE ELEMENTAL COMPOSITION OF AIR PARTICULATES IN EL PASO/JUAREZ AIRSHED

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Air quality is one of the most fundamental environmental challenges in urban areas along the U. S. Mexico border. In the El Paso, Texas/Juarez, Mexico airshed particulate matter is a serious problem. Despite this, current understanding of the composition, toxicity, and origin of these particulates is limited.

In this project we are using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) to determine the elemental composition of particulates in ambient air filters collected in El Paso and Juarez over a 30-year period. ICP/MS permits the simultaneous determination of the concentration of up to 65 elements in a liquid or dissolved solid, typically at ppb levels in the solution. ICP/MS is considered the current "ultimate weapon" in the search for low detection limits. This technique also provides useful isotopic information for appropriate toxic elements such as lead.

So far we have found relatively high levels of copper, lead, arsenic and chromium in the Juarez-El Paso particulate matter. The metal distribution seems to vary depending on sampling year and on season. It appears that there may be two point or limited area sources responsible for the presence of these metals, one in Juarez and one in El Paso. We are currently attempting to link the metal concentrations to their possible sources. Results of our investigation will be presented.

*Key words: particulate matter, air quality, El Paso/Juarez, ICP-MS*

**Program Three**  
**Wednesday, May 20, 1998**  
**Remediation Processes**  
**Wasatch B**

**56 CHEMICAL-BIOLOGICAL  
TREATMENT OF PYRENE**

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Pyrene is one of the persistent polycyclic aromatic hydrocarbons (PAHs) that are a group of organic compounds containing two or more fused aromatic rings. PAHs are ubiquitous compounds formed naturally during thermal geologic reactions associated with fossil-fuel and mineral production and during the burning of most organic matter. PAH-contaminated sites are associated with the past and present processing, combustion, and disposal of fossil-fuels. The US EPA has listed 16 PAHs as priority pollutants due to their toxic and mutagenic nature. Five of the listed priority pollutant PAHs are known to be carcinogens. In this study, both packed column and batch reactors were used to examine the degradation pathways of pyrene subject to ozonation in the aqueous phase. Samples from both reactors were collected at treatment time intervals, analyzed for organic contents, and further inoculated to determine biodegradability. Tests of BODs, 20-day BOD, COD, toxicity, and qualitative and quantitative GC/MS analyses of pyrene, intermediates, and products were performed after different consecutive chemical and biological treatment stages. The objectives of this research were to: 1) provide mechanistic details in the degradation of pyrene subject to ozone treatment, 2) test the combined technique of AOP pretreatment followed by biological degradation, and 3) test a proposed pretreatment configuration that promotes biodegradability as well as efficient use of chemical oxidants. Results showed that ring

cleavage occurred at the 4,5-bond and 9,10-bond of pyrene. A biodegradation rate constant ( $k_o$ ) of 0.243 day<sup>-1</sup> was measured for the treated column effluent. This paper includes a verified degradation pathway of pyrene in the aqueous phase under ozonation. The treatability of pyrene using a combined chemical-biological treatment approach will be evaluated. The sample toxicity, intermediate, and products at different treatment stages will be discussed.

*Key words: advanced oxidation process, ozone, PAH, chemical, biological, treatment, pyrene*

**57 DETERMINATION OF ACTI-  
VATION ENERGY IN THE  
REDUCTIVE DECHLORINA-  
TION OF CARBON TETRA-  
CHLORIDE WITH ZERO-  
VALENT ZINC**

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Zero valent metals have been used for the reduction of a variety of halogenated hydrocarbons. An active area of interest is the remediation of contaminated groundwater supplies. Zinc metal has shown excellent results and is able to reduce carbon tetrachloride completely to methane. Proposed mechanisms invoke oxidative addition of the chlorocarbon to the metal, followed by hydrogen addition, then elimination of a hydrogenated intermediate which degrades further. The details of these steps is unclear. The goal of this project is to elucidate mechanistic details of these systems. Current work is the determination of activation energy of the rate determining step of chlorinated methanes. The principle analytical tool is gas chromatography via the head space of these volatile compounds.

*Key words: carbon tetrachloride, zinc, dehalogenation, kinetics, mechanism*

## **58 REMOVAL OF NITRATE/ ATRAZINE CONTAMINATION WITH ZERO-VALENT IRON PROMOTED PROCESS**

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This research project is designed to study the feasibility of removing or remediating nitrate/atrazine in groundwater using the zero-valent iron treatment. Zero-valent iron is selected because it is cheap, non toxic and field testing can easily be accomplished with the construction of an iron wall to intercept nitrate/atrazine contaminated groundwater. Several batch and column studies were conducted with different types of iron powder to determine nitrate/atrazine removal efficiencies.

Batch experiments were conducted using lab grade iron powder (about 0.02 micron in size), industrial grade iron powder (about 0.5 micron in size) and industrial grade iron powder pretreated with 2N H<sub>2</sub>SO<sub>4</sub> acid (about 0.5 micron in size). These experiments were conducted in 160 mls dilution bottles with 5% (w/v) of the various type of iron powders. When lab grade iron powder was used, about 75% of the atrazine was reduced while about 20% reduction in nitrate was observed. When industrial grade iron powder was used, only about 28% of the atrazine was reduced while about 10% reduction in nitrate was observed. When industrial grade iron powder pretreated with acid was used, only about 40% of the atrazine was reduced while about 70% reduction in nitrate was observed. When a combination of nitrate and atrazine solution were used, the removal rates for nitrates remained relatively the same but a slight decrease was observed in the atrazine removals. The results tend to indicate a possible atrazine inhibition in the presence of nitrates.

To simulate an iron wall treatment, acrylic tubes with a diameter of 1.5" and a height of 12" were constructed as continu-

ously fed reactors. Mixing two parts of fine sand with one part of iron powder prevented plugging (observed when only iron powder was used). In addition to preventing plugging, removal rates improved. More than 98% of the atrazine were removed by lab grade iron powder with less than 2 days detention time. On the other hand nitrate removals were dependent on pH. High nitrate removals were observed at low and high pHs while less than 50% removals were observed near neutral pH.

Based on the preliminary results obtained from this research, it appeared that iron powder can reduce nitrates and atrazine in the groundwater. For field testing, it is recommended that iron powder be mixed with sand to form the treatment wall to prevent plugging and improve removal rates.

*Key words: zero-valent iron, atrazine, nitrate*

### **Program Three Wednesday, May 20, 1998 Sorption and Mobility Wasatch B**

## **59 PCE SOLUBILIZATION AND MOBILIZATION BY COM- MERCIAL HUMIC ACID**

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The limited ability to remove sorbed and non-aqueous phase contaminants from subsurface materials using simple pump-and-treat technology motivates research into the use of agents to solubilize these contaminants in order to facilitate their removal. Foremost among candidate agents being examined for this purpose are surfactants. In contrast, dissolved humic substances (DHS) have received little attention as potential remediation agents, although they strongly bind hydrophobic organic compounds (HOC), and are readily available by simple extraction from swamp materials such as peat. In this

paper, several possible advantages of DHS use in the remediation of subsurface media contaminated with HOC are described, including the ability of DHS to solubilize HOC irrespective of the DHS concentration, and potential lesser tendency of DHS to depress the interfacial tension between non-aqueous phases and water relative to surfactants. This paper examines the ability of a commercial humic acid (Aldrich humic acid) to solubilize and mobilize tetrachloroethene (PCE) residual in porous media. The constant for solubilization of PCE by Aldrich humic acid is shown to be a factor of two to thirty times less than that published for dodecyl alcohol ethoxylate surfactants, showing that Aldrich humic acid is less capable than some non-ionic surfactants at solubilizing residual PCE. The depression of PCE-water interfacial tension in the presence of DHS is shown to be significantly less than published values for a non-ionic surfactant, and surfactant mixtures, corroborating the hypothesis that DHS are less prone to cause mobilization of non-aqueous phase liquids relative to surfactants.

*Key words: DNAPL, DHS, humic substances, mobilization, dissolution*

## 60 THE INFLUENCE OF HUMIC ACID ON THE BIODEGRADATION OF POLYAROMATIC HYDROCARBONS

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Although sorption to soil organic matter (SOM) has been well documented as inhibitory to biodegradation of many pollutants, the effect of dissolved organic matter (DOM) on biodegradation has not been determined. The few studies that have addressed this issue have produced contradictory results. Therefore, the effect of hydrophobic organic compound (HOC) binding to DOM on the availability of the HOCs to biodegradation was investigated.

The DOM studied was humic acid extracted from a local site (RC humic acid), and the HOCs used were fluorene, naphthalene and phenanthrene, three PAHs of varying hydrophobicity. Biodegradation experiments used a mixed microbial culture isolated from a Superfund site at which PAHs were present. Isotherms were measured for fluorene and phenanthrene sorption to both a commercially available humic acid (Aldrich) and RC humic acid for humic acid concentrations from 17 mg/l to 166 mg/l. Aldrich humic acid log K<sub>oc</sub> values in ml/g were measured as  $4.29 \pm 0.02$  for phenanthrene and  $3.67 \pm 0.01$  for fluorene. RC humic acid log K<sub>oc</sub> values in ml/g were found to be  $4.50 \pm 0.03$  for phenanthrene and  $4.16 \pm 0.04$  for fluorene. In PAH mixtures, competitive sorption effects were not observed. Batch biodegradation experiments were performed both with and without 80 ppm RC humic acid, the maximum level observed in the environment. Although at this humic acid concentration 60% of the phenanthrene and 35% of the fluorene were associated with the humic acid, no significant change in biodegradation rates was detected. From this we infer that sorption of these PAHs to dissolved organic matter at environmentally relevant DOM levels does not reduce their availability for biodegradation. Further experiments will explore in more detail the interactions between PAHs in biodegradation and test other possible DOM influences such as solubility enhancement of HOCs.

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

*Key words: biodegradation, humic acid, sorption*

## 61 ENGINEERING THE IMMOBILIZATION OF COUPLABLE ORGANICS IN SOILS AND THE SUBSURFACE

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Phenolic contaminants can become bound to soil organic matter via oxidative coupling reactions catalyzed by soil enzymes or oxides of transition metals. The bound chemicals have been shown to possess attenuated environmental mobilities and reduced bioavailabilities. The purpose of this study is to a) evaluate the factors affecting binding of phenols to natural soils, sediments and aquifer material, and b) utilize this information to develop innovative engineering applications of oxidative coupling for the remediation of contaminated soils and subsurface materials. Phenol, o-cresol and chlorophenols (p-chlorophenol and 2,4,5-trichlorophenol) are being studied as target contaminants and their binding is being investigated on a shale, an aquifer material and two near surface soils. Model system studies are being conducted to evaluate the effects of pH and ionic strength on the enzyme and metal oxide mediated polymerization of aqueous phenols. Finally, knowledge gained from the natural and model experimental systems is being utilized to develop engineered systems such as reactive barriers designed to intercept contaminant plumes in the subsurface and transform the migrating contaminant into soil bound residues.

*Key words: ?????????????????*

## 62 CONTRIBUTION OF LIPIDS TO THE EARLY SORPTION OF HYDROPHOBIC CONTAMINANTS TO SOIL

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Contaminant sorption and desorption from soil commonly displays strong hysteresis with rapid initial sorption followed by slow desorption. Soil organic matter fractionated by the MIBK method produces, among other fractions, two organic soluble fractions, comprising less than 20% of the total soil organic matter, referred to as bitumen (or extractable lipids) and bound lipids (which are not extractable from the whole soil). The bound lipids play a major role in the fate of bound hydrophobic organic contaminants. The bitumen may be responsible for the initial uptake of hydrophobic contaminants into the soil organic matter. Once taken up into the bitumen, the contaminant may slowly diffuse or sorb into other organic domains. It is the diffused or sorbed contaminant in these other domains which may be at least partially responsible for slow desorption of contaminant from the soil as well as the formation of bound residues. Results from experiments using PAHs and PCBs testing this hypothesis are be discussed.

*Key words: PAH, PCB, bound residues, hydrophobic contaminants*

**Program One**  
**Thursday, May 21, 1998**  
**Metals**  
**Superior B**

**63 IN SITU STABILIZATION OF  
PB IN SOILS USING PHOS-  
PHORUS**

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Soils contaminated with Pb and other metals pose significant risk to humans as well as to terrestrial and aquatic ecosystems. Within the United States, large areas with metal-contaminated soils occur in both urban settings and in rural areas from a variety of causes, most notably from the mining and smelting of nonferrous metal ores. Many Superfund sites have metal-contaminated soils. Current remediation activities in residential areas have utilized soil removal as the primary strategy. Soil removal is a disruptive activity that has significant disadvantages in terms of cost, the need for a contaminated-soil repository, and the need for a clean source of replacement soil. Phosphorus amendment has recently been proposed as an in situ alternative to soil removal for Pb-contaminated soils. The primary benefit is a reduction in Pb bioavailability such that the primary receptor of concern, the human child, will show less of an increase in blood Pb concentration after incidental consumption of soil that has received P compared to unamended soil. The proposed mechanism is the conversion of Pb to pyromorphite, an insoluble Pb phosphate mineral. Many issues and concerns need to be addressed before P amendment is formally accepted as a remediation alternative. The influence of P level, chloride additions (to facilitate chloropyromorphite formation,

which is less soluble than hydroxypyromorphite), time, soil pH management, and competing cations on reductions in soil Pb, Cd, and Zn bioavailabilities induced by P need to be addressed. A variety of techniques are being used to evaluate the influence of P on Zn, Cd, and Pb bioavailability. Laboratory incubation studies have been designed to assess the influence of P source, P rate of addition, and time. Mineralogical analyses confirm the formation of pyromorphite and suggest additional pyromorphite formation over time, although this procedure is still under development. Sequential extraction results suggest significant reductions in Pb bioavailability upon addition of P with lesser effects on Cd and Zn. Solubility equilibrium studies with P amended samples suggest equilibrium with pyromorphite for Pb with octavite and smithsonite controlling Cd and Zn activities, respectively. Data from an in vitro bioaccessibility test for Pb will be presented.

*Key words: lead, cadmium, zinc, bioavailability, stabilization*

**64 REDUCTION RATES OF AR-  
SENATE IN BATCH ACID  
COLUMN ENVIRONMENTS**

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The chemistry and subsequent bioavailability and transport of arsenic (As) in soils and natural water systems is complicated by effects of oxidation-reduction reactions on As speciation. It is commonly assumed that As exists predominantly as arsenate (As V) in oxidized systems, and as arsenite (As III) in reduced environments. Arsenic sulfide phases are also a possible reaction product in reduced environments containing sulfide. Our work has focused primarily on measuring rates of arsenate reduction in a variety of controlled

environments, including sterile systems necessary to understand abiotic reduction rates in the presence of  $N_2(g)$  and  $H_2(g)$  and biotic systems where C oxidation rates drive redox processes. We have also studied the reduction rate of arsenate in the presence of Fe oxides, where arsenate is present predominantly as a surface species. Controlled redox vessels were designed to study arsenate reduction at constant temperature, pH and EH using a pH stat in combination with gas delivery (either  $O_2$  or  $H_2$ ). Biotic systems were inoculated with microorganisms harvested from an As contaminated soils in the presence of 2-10 mM glucose or lactate to serve as a C source (electron donor). Rates of C oxidation were monitored as a function of time, including analysis of the As(V)/As(III) and Fe(III)/Fe(II) redox couples. Results show that rates of arsenate reduction are quite slow (week time scales) in the abiotic conditions we investigated [using  $H_2$ , Fe (II), S(-II) as potential electron donors]. Conversely, reduction rates in the presence of microorganisms is considerably faster (time scales of hours to days) and depends in part on the C oxidation rate. Rates of arsenate reduction are apparently suppressed when arsenate is present as a sorbed species (on Fe-oxides), perhaps due to the slow desorption of arsenate or the preferential use of Fe(III) as an electron acceptor. Other factors controlling arsenate reduction in nature systems will also be discussed with specific reference to comparison of platinum-EH values and EH values computed from As(V)/As(III) speciation.

*Key words: arsenic, oxidation-reduction, electron acceptors, iron*

## 65 PHOTO-ASSISTED REMOVAL OF ARSENIC FROM ACID MINE WATER

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Acidic arsenic-bearing water draining from abandoned mines has been identified by the United States Environmental Protection agency as a significant environmental hazard in the western United States. In these mine waters, arsenic can occur in both trivalent arsenic(III) and pentavalent arsenic(V) forms, usually with dissolved iron as iron(II) or iron(III). Before arsenic can be effectively removed from solution in water by precipitation it must be in the pentavalent form, so any arsenic(III) should be first oxidized.

Since oxidation of arsenic(III) by air or oxygen is extremely slow, a chemical oxidant such as chlorine or permanganate is normally utilized.

The Cooperative Research Centre for Waste Management and Pollution Control Limited (CRC) in Sydney, Australia, funded the original work at ANSTO where it was shown that the rate of arsenic(III) oxidation by air can be increased by up to ten thousand fold by a UV light source such as sunlight or UV lamps with the presence of certain dissolved photocatalysts. In a demonstration supported by MSE Inc. of Butte, Montana, this patented photo-oxidation process was used successfully to oxidize arsenic(III) in the presence of a large excess of dissolved iron(II) in acid mine water from the Susie Mine, an abandoned gold-silver-lead mine near Rimini, Montana. In this demonstration, the oxidized arsenic was then removed from solution by an iron coprecipitation process thus effectively utilizing the iron in the mine water to immobilize the arsenic and other metals. Process residues from the Rimini demonstration passed the standard U.S. EPA leach test for landfill

disposal, as well as the ANSTO long-term leach test in aerated water.

The process based on sunlight is currently being applied by ANSTO for the removal of arsenic from well water in Asian countries. Oxidation of arsenic is only one of a number of photochemical processes being developed by CRC and ANSTO to treat other contaminants in water.

*Key words: arsenic, oxidation, photochemical processes, coprecipitation*

## **66 UTILIZATION OF THE KINEMATIC RUNOFF AND EROSION MODEL IN PREDICTING THE EFFECTS OF VEGETATION ON SEDIMENT CONTAINMENT**

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In southeast Kansas, where mining activities ceased in the middle half of the twentieth century, residue materials have created surface contamination problems. The erosion losses of chat material, a byproduct of mining activities, has elevated levels of cadmium, lead and zinc in nearby farmland to phytotoxic levels for the crops normally planted. Selective vegetation is being examined as a means of controlling the loss of sediment material and containing the further spread of the metal contaminants. The kinematic runoff and erosion model, KINEROS, is examined to investigate the role vegetation plays in controlling erosion from an 800 acre watershed, near Galena, Kansas. The results of the model are compared with predictions made by another non-point source model, the Agricultural Non-Point Source Pollution model, AGNPS.

*Key words: erosion, metals, modeling, vegetation, watershed*

## **67 INTERFERENCE STUDIES FOR MULTI-METAL BINDING BY MEDICAGO SATIVA (ALFALFA)**

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Previous studies have shown that alfalfa shoot biomass has the ability to bind a significant amount of various individual metals from aqueous solutions. Since most heavy metal contaminated waters contain more than one heavy metal, it was necessary to determine the binding abilities of the alfalfa biomass with multi-metal solutions. Multi-metal binding capacity experiments resulted in the following order of affinity for the multi-metal binding by the alfalfa biomass: 43.3mg/g for lead(II), 8.2mg/g for chromium(III), 3.4mg/g for copper(II), 1.5mg/g for cadmium(II), 1.3mg/g for Zinc(II), and 0.5mg/g for nickel. In order to better understand how this system may behave with hard cations such as magnesium and calcium which are found in contaminated waters, batch laboratory interference studies were performed with various calcium and magnesium concentrations (0.1 mM - 1 M). The information obtained will be useful for the future development of an innovative technology to remove heavy metal contaminants from polluted ground waters. Results of our experiments will be presented.

*Key words: interferences, multi-metal, heavy metal binding, phytofiltration, alfalfa*

## 68 THE INFLUENCE OF PREVIOUS EXPOSURE ON TOLERANCE OF BENTHIC INVERTEBRATES TO HEAVY METALS

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We investigated the direct and indirect effects of heavy metals on benthic macroinvertebrates in the Arkansas River, a Colorado stream severely degraded by heavy metals from historic mining operations. We conducted surveys of benthic macroinvertebrates, chronic toxicity tests, metals analyses, and bioaccumulation studies from 1989 to 1995 at stations upstream and downstream from California Gulch, a U.S. EPA Superfund Site. A large-scale restoration program was initiated in 1992 and provided an opportunity to investigate recovery of the Arkansas River. We compared biomonitoring results before and after remediation of Leadville Mine Drainage Tunnel (LMDT) and California Gulch (CG), the two primary sources of metals into the Arkansas River. After remediation, we observed reduced metal levels in water and benthic macroinvertebrates and increased abundance of metal-sensitive taxa downstream from LMDT. Recovery was less pronounced downstream from CG because large pulses of metals during spring runoff reset benthic communities to pre-remediation conditions.

To investigate tolerance of benthic communities to heavy metals, we compared the effects of a mixture of Cd, Cu, and Zn on communities collected from the Arkansas River and an unpolluted reference stream (the Cache la Poudre River). As expected, communities from the Arkansas River were more tolerant of heavy metals; however, our results suggested that costs are associated with

increased tolerance. Preliminary results using RAPD-PCR showed lower genetic diversity in mayfly populations (*Baetis tricaudatus*) downstream from California Gulch. In addition, experiments conducted in stream microcosms indicated that metal-tolerant communities were more susceptible to novel biotic (stonefly predation) and abiotic (UV-b radiation; acidification) stressors. Our results suggest that biotic and abiotic factors interact to structure benthic communities in metal-polluted streams. Ecosystems disturbed by contaminants, particularly those that have been polluted for relatively long periods of time, provide excellent opportunities to study interactions between biotic and abiotic factors

*Key words: aquatic insects, biomonitoring, metals, streams, tolerance*

### Program Two Thursday, May 21, 1998 Remediation Processes Superior A

## 20 ADSORPTION OF COMMON AIR POLLUTANTS BY METAL OXIDES

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Various methods have been widely applied to improve air quality, and reduce pollutant content in both indoor and outdoor environments. Some chemicals are suspected of causing human cancer, or other clinical diseases. In our research, we have employed high surface area materials (mainly metal oxide nanocrystals in consolidated powder form) to adsorb several air borne pollutants, for example, magnesium oxide adsorbs ketones, aromatics, acid gases etc. Under normal conditions, auto-clave prepared samples are observed to be more efficient than their conventionally prepared counterparts, due to the exposure of more active surface sites. Gravimetric methodology and experimental results will be discussed in detail, comparisons with

high surface area activated carbon samples will also be discussed.

*Key words: adsorption, metal oxides, pollutants*

## **70 BIOAVAILABILITY DEFINED: PRACTICAL CONSEQUENCES FOR BIOREMEDIATION**

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Bioavailability is herein defined as the potential for chemical interaction with a biological receptor in a bioavailable phase. This definition will be cast in terms of both conceptual and mathematical (quantitative) models. Chemical potential is defined in terms of "water fugacity," the tendency for a hydrophobic chemical to escape from the aqueous phase. Thus, chemical potential relies heavily on a compound's solubility and hydrophobicity, the key characteristics that govern its equilibrium sorption and mass transfer phenomena. This concept will be extended using the Resistance Model for Bioavailability (RMB) that quantifies bioavailability in terms of a single, time-dependent parameter (the Bioavailability Factor). An extension of the model to surfactant-enhanced bioremediation will be presented to illustrate the importance of clarifying key processes in the design of systems employing this emerging technology. Experimental data will be presented that illustrates the model's utility in predicting key bioavailability processes.

*Key words: bioavailability, surfactants, HOC, bioremediation*

## **71 A COMPARISON OF PACKED COLUMN AND LOW PROFILE AIR STRIPPERS CHOOSING THE CORRECT TYPE FOR THE APPLICATION**

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Packed column and low profile sieve-tray (perforated plate) air strippers are widely used in the remediation of contaminated ground water. The demand for low profile air strippers has increased dramatically in the past few years. Are they better than traditional packed column air strippers or not? The answer is probably no. There are advantages and disadvantages of each that must be considered in making a selection during design. One advantage of low profile air strippers is that they are easier to clean out if they become fouled. One disadvantage is that they use more air than packed column air strippers. This will increase the cost of off-gas treatment, if required. This paper will describe both styles of air strippers, the advantages and disadvantages of each, and provide information on how to size each style. The listener will gain the information needed to select and design the proper kind of air stripper for each application.

*Key words: air stripper*

**Program Two**  
**Thursday, May 21, 1998**  
**Technology Transfer**  
**Superior A**

**72 CONTEXTUALIZING THE  
LEARNING EXPERIENCE:  
CREATION OF AN INTE-  
GRATED PEST MANAGE-  
MENT (IPM) VIDEO CUR-  
RICULUM**

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The learning experience can be greatly enriched through video technology. The Haskell Environmental Research Studies Center's Integrated Pest Management video curriculum project has integrated several fundamental insights about how human beings learn to create a video curriculum that is unique. A presentation of a segment of the video curriculum will be used to illustrate some simple, but creative, ways in which video instruction can be greatly improved. In an age where much technology transfer could be accomplished using this almost ubiquitous technology, the panel will discuss some basic curriculum design insights that will greatly improve the production of any technology transfer materials for video.

*Key words: Native American, minority, technology transfer, hazardous substances*

**73 OPPORTUNITIES FOR WASTE  
SITE TECHNOLOGY TRANS-  
FER IN SLOVAKIA AND CEN-  
TRAL EUROPE**

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The U.S. Environmental Protection Agency (USEPA) and the Slovak Environmental Agency (SAZP) collaborated on a three-year risk assessment/risk management pilot project. The objective was to demonstrate the use of the risk paradigm, as practiced in the U.S., to waste, air, and water problems in Slovakia. The method required the SAZP to identify appropriate cases, the USEPA to suggest tools and technologies (such as those developed through the HSRC Program,) transfer these tools through workshops, and collaboratively work on the application of the tools to the cases. As a final step, the SAZP analyzed the results for potential widespread use within Slovakia.

Municipal, industrial, and abandoned waste sites were found to be similar in both countries. The techniques for site characterization and restoration are similar. To the extent that U.S. innovative technologies offer price and performance advantages compared to standard practice, innovative technologies are attractive in Slovakia. The Slovak environmental work force is highly motivated and well trained in the basic environmental sciences. The workforce is a national asset that will simplify the introduction of new technologies.

Slovak national environmental laws are protective and in many instances similar to U.S. law. National program strategies for implementing environmental law are more prescriptive than in the U.S. The well-defined nature of problems to be solved, market size, and priorities over time encourage the use of

“market pull” rather than “technology push” techniques of technology transfer.

*Key words: technology transfer, characterization, remediation, solid waste, international programs*

### **Program Three**

**Thursday, May 21, 1998**

### **Field Research**

### **Wasatch B**

## **74 REVEGETATION OF A MINE TAILINGS IMPOUNDMENT USING MUNICIPAL BIOSOLIDS IN A SEMI-ARID ENVIRONMENT**

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Municipal sewage sludge, also termed “biosolids,” has been shown to be an excellent soil conditioner for the reclamation of mine tailings. A large-scale (approximately 30 ha) field experiment on the Kennecott Utah Copper Corporation mine tailings impoundment, west of Salt Lake City, Utah, USA, demonstrates the usefulness of a one-time application of biosolids to improve vegetative growth in a difficult, semi-arid environment. Relatively few such studies have been performed in the semi-arid climate that is typical of the state of Utah. Rainfall averages about 36-cm yr<sup>-1</sup> in the Salt Lake valley. Two types of biosolids were used in the project: anaerobically digested and aerobically treated, alone or with limestone and wood residues, as secondary treatments. Biosolids were applied at four application rates: 0 (as a control), 11.2, 22.4, and 33.6 Mg ha<sup>-1</sup> on a dry solids basis, and were planted with a dryland seed mix. Results through the third year of the study show that biosolids were successful in enhancing plant biomass and areal cover without a significant increase in tissue metal concentrations in the planted species. After the first year, biomass production increased from 43.0

g m<sup>-2</sup> in the control plots to a maximum of 554.4 g m<sup>-2</sup> when 33.6 Mg ha<sup>-1</sup> of biosolids were applied. The total plant cover increased significantly from 7.3 % at 0 Mg ha<sup>-1</sup> to 62.8 % at the 33.6 Mg ha<sup>-1</sup> biosolids application rate. There were no differences in metal concentrations in plant species from the control and biosolids-amended plots, and with few exceptions all metal concentrations were below phytotoxic levels. Further, it has been shown that a self-sustaining ecosystem has been established on the tailings impoundment sites when at least 22.4 Mg ha<sup>-1</sup> were applied.

*Key words: reclamation, biosolids, mine tailings, mining*

## **75 REVEGETATION OF A PB/ZN SMELTER SITE USING POPULAR TREES**

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Non-ferrous metal mining activities across the world have produced a variety of environmental problems including the generation of trace element contaminated sites that are often sparsely vegetated and represent a significant human and ecological hazard. Numerous remediation options exist for such sites including soil removal, capping, solidification, vitrification, soil washing, and vegetative remediation. Vegetative remediation involves the establishment of a vegetative cover of grasses, forbs, or trees that is complete enough to prevent wind and water erosion and that will remain viable for extended periods of time. Advantages include the minimization of wind and water erosion, lower cost as compared to other remediation options, improvement of aesthetics, a lack of waste products produced in the process, minimization of water percolation through the

site, improvement of soil chemical and physical properties, and the potential to serve as a temporary remediation until more suitable methods are developed or funded. The purpose of this study was to evaluate the revegetation of an abandoned Pb/Zn smelter with poplar trees. A smelter ash material covers a portion of the site. This material has from 18750 to 86875 mg/kg total Zn, 1875 to 35000 mg/kg total Pb, and 32 to 237 mg/kg total Cd in the upper 15 cm. The pH ranges from 5.1 to 6.7. Total metal concentrations decreased with depth. In March 1995 poplar trees were planted into trenches arranged in a split-plot design. All material excavated from the trenches was amended with lime and P fertilizer. The main plots were manure treatments with half of the plots receiving manure such that the weight of the manure was approximately 25% of the weight of the material excavated from the trench. The other half of the plots did not receive manure. The split plots were one of four tree types. After the first growing season there was no significant difference in survival between the types of poplar trees. The manure treatments significantly increased the growth and survival of the trees. In year two the manure treatments had significantly higher survival than the nonmanure treatments and significant differences occurred between tree types. In year three nearly all trees in the nonmanured treatments had died with survival averaging approximately 30% with manure. Leaf tissue analysis suggested Zn phytotoxicity may have been a problem. A destructive sampling of the trees was conducted at the end of the 1997 growing season. Data will be presented on metal concentrations in wood, bark, twigs, and leaves.

*Key words: zinc, cadmium, lead, poplar, trees*

## 76 PERFORMANCE OF ANIMAL WASTE LAGOON LINERS

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Containment of animal waste in lagoons in Southwest Kansas has been an issue of intense political and public debate over the recent years. The technical viability of isolating waste in lined lagoons has been doubted by some sectors of the public. In response to the growing debate, a comprehensive research program has been undertaken to examine the issues surrounding the impact of waste containment in lagoons on groundwater quality. In this paper, results from an experimental investigation will be presented to document the seepage quantities and qualities from compacted clay liners made of representative soils from Southwest Kansas and permeated by animal waste streams. An important question that is answered is whether the Kansas soils are clay enough to yield seepage quantities less than 0.25 inch/year (current regulation set by the Kansas Department of Health and Environment, KDHE) when properly compacted.

All of the three representative soils examined in this study yielded seepage quantities less than 0.25 inch/year under operating conditions of field lagoons. Nitrate, Phosphorous, and Ammonia concentrations were monitored in the effluent samples from permeameters. Nitrate and Phosphorous concentrations were insignificant; however, Ammonia concentrations were considerably high in the case of swine waste. Microbial counts of the effluent samples did not indicate any microbial growth in the samples. Bioclogging was not observed.

Some implications of the seepage quantities and qualities will be presented in terms of their impact on deeper groundwater resources. The adequacy of KDHE regulations in protecting groundwater resources will also be discussed.

*Key words: compacted clay liners, fate and transport, waste containment, waste lagoons*

## 77 RF/SVE-LABORATORY OVEN TO FIELD DEMONSTRATION

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A field demonstration of enhanced soil vapor extraction (SVE) using radio frequency (RF) heating to remove semi-volatiles from the subsurface has been completed. The site, a fire training area consisting of well-graded sand and silt, had initial petroleum hydrocarbon concentrations up to 30,000 mg/Kg. The sampled volume contained 561 Kg of diesel range organics (DRO, C-12 to C-20). Vapors were extracted from a central well while RF energy was supplied by two applicators positioned in vertical wells located on either side of the extraction well. Temperatures in the center of the treatment zone reached 139°C and at a 2 m radius reached 100°C to 120°C. The condensed off gas contained DRO with constituents up to C-20. Mass balance evaluations indicated that more than 292 Kg of DRO were removed from the site (52% reduction). The total petroleum hydrocarbons were reduced from 4221 Kg to 3231 Kg (a 24% reduction). Ninety-two Kg of DRO was captured in the condensed off-gas leaving 900 Kg of TPH unaccounted for in the mass balance. Mass closure analyses were difficult due to incomplete off-gas data and the possibility of some biodegradation. Further complicating the analyses was the fact that the treated volume was an open system. In-situ respiration studies conducted in the site soils before and after RF/SVE indicated an active microbial population suggesting that biodegradation of the site organic could have been one cause of the unaccounted for TPH and DRO.

The RF/SVE project was conceived, developed, managed, and led by a team at The University of Texas at Austin (UT). The team consisted of researchers from three departments: Civil Engineering, Electrical Engineering and Petroleum and Geosciences Engineering. UT collaborated with Brown and root

Environmental (BRE), Oak Ridge TN; KAI Technologies, Inc. (KAI), Portsmouth NH; and Kirtland Air Force Base (KAFB), Albuquerque NM. BRE was the prime contractor for the fieldwork and KAI was the radio frequency heating contractor. The demonstration was located at Kirtland AFB.

The Advanced Applied technology Demonstration Facility (AATDF) facilitated the collaboration of the teams from industry (BRE and KAI), academics (UT), and government agencies (DoD, Kirtland AFB). Each team member contributed in ways the others could not, thus making the overall project more complete than a single entity could have achieved.

The field demonstration was the culmination of six years of research, development, and collaboration beginning with heating soil in a conventional laboratory oven and pulling a vacuum through it while measuring moisture loss in the soil. The work progressed to using laboratory RF to heat the soil and finally monitoring removal of chemical compounds in the off-gas of the soils heated by RF in the laboratory. Initial project funding was \$5000 for the laboratory investigation (ESP Program at UT) and was continued with funding through the US EPA's Gulf Coast Hazardous Substance Research Center. The field demonstration was funded through AATDF/DoD.

*Key words: RF heating, soil, vapor, demonstration*

## 78 SOIL WASHING AND LEACHING AS A REMEDIATION ALTERNATIVE: FRUSTRATIONS, SUCCESSES, AND PROMISES

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This presentation will examine soil washing and leaching as a remediation technology that showed promise as a cost effective

method for treating metals contaminated soil. Past performance, a changing regulatory environment, and remediation technology advances have dampened the reception that the technology has been receiving. But the technology has a place in the toolbox of remedial technologies available to metals contaminated sites.

**History:** Soil washing has been used in Europe for far longer and much more frequently than it has been used in the U.S. Since 1980, soil washing as a remedial technology has had several successes and many failures. The process, which is very effective at reducing volume, concentrating contaminants, and recovering metals, is very demanding. The successes that have been experienced belong to companies with expertise in materials handling plus chemical processing.

In 1993, soil washing was combined with soil leaching to remove and recover metal contamination from an Open Burn/Open Detonation site at the Twin Cities Army Ammunition Plant in New Brighton, Minnesota. Though a success, another site with only metal contamination has not emerged as a likely candidate for soil washing and leaching. The new challenge is to treat metals when in the presence of explosive residues, such as TNT and DNT.

**Frustrations:** Each failure to apply soil washing successfully has impoverished the image of the technology in the eyes of the generator, regulator, or design engineer. Soil washing heavy organics like creosote has a success in the southeastern U.S. yet a major failure in the west. Soil washing a battery site in the western U.S. was a complete failure, while a major Superfund site in the mid-Atlantic states was a tremendous success. Due to the failures, however, soil washing has been included in less and less Records of Decision (RODs).

**Successes:** Two major project successes are King of Prussia and Twin Cities Army Ammunition Plant (TCAAP). The first was soil washing, the second soil washing and

leaching combined. At the King of Prussia site, Alternative Remedial Technologies washed 20,000 yd<sup>3</sup> of soil and was able to concentrate the metals into 2,000 yd<sup>3</sup>.

At the TCAAP, soil washing was combined with soil leaching for the first time for the cleanup of an Open Burn/Open Detonation site containing seven heavy metals. Soil was cleaned to below background and the soil was left on site. The agreement with the regulator was that no deed restriction would be required if background levels were achieved.

**Promises of Soil Leaching:** One problem remediating soil is the requirement of large unit operations that must be mobilized to the site. Looking to eliminate that cost and significantly reduce the labor cost associated with field remediation, The Doe Run Company purchased the equipment and technology to leach metals contaminated soil at its Buick Resource Recycling Facility in Boss, Missouri. The Doe Run Company had been recycling lead from ammunition manufacturing, firing ranges, batteries, and other sources for over 7 years at the Buick facility and over 50 years at its primary lead smelter facility. The cost experienced remediating the Open Burn/Open Detonation site at TCAAP (with UXO removal included) was about \$170 per ton of contaminated soil. Projected costs at the Buick Resource Recycling Facility are about \$100/ton. The facility should have received a modification to their Part B permit by the time the HSRC meeting occurs.

*Key words: soil washing, soil leaching, metals, lead, recycle*

## 79 A COMPREHENSIVE EVALUATION ON THE USE OF OXYGEN RELEASE COMPOUND IN BIOREMEDIATION

*S.S. Koenigsberg, Regenes Bioremediation Products, 27130A Paseo Espada, Suite 1407, San Juan Capistrano, CA 92675*

ORC is a unique formulation of magnesium peroxide that releases oxygen slowly when hydrated. The compound is insoluble and releases oxygen while being converted to ordinary magnesium hydroxide which is also insoluble. ORC is packaged in exchangeable filter socks and is contacted with contaminated groundwater via an array of wells or trenches. ORC can also be made into a slurry for permanent applications in the saturated zone, or dispersed as a free powder for the in-situ or exsitu treatment of soil. These methods help optimize the natural bioremediation of aerobically degradable compounds and are being used on over 2600 sites worldwide as a low-cost, passive bioremediation protocol.

ORC mediated oxygenated zones generally last four months to a year as a function of contaminant flux. The objective of the "oxygen barrier" is plume cut-off; however, any significant reduction of contaminant mass will bring the control point back to the source and reduce risk. A broad array of treatment points, in which ORC is backfilled or injected, has been shown to be an effective source treatment. The points can be implemented with low-cost, small-bore technologies to achieve full remediation or risk reduction objectives. Free powder has traditionally been used by direct mixing of ORC into biopiles or in the floor of tank pit excavations to address residual hydrocarbons.

An overview of the history of the environmental applications of ORC, and the evolution of the strategies for site closure involving direct treatment of contaminant sources and control of plume migration, will be presented. This will include 1) a compendium of oxygen barrier field results featuring

several large-scale, fully monitored demonstrations, 2) results from several large-scale, fully monitored source treatment applications and 3) results from a variety of in-situ soil applications. All of these projects were directed at BTEX remediation and showed that the use of ORC is a highly effective bioremediation protocol. Preliminary evidence for the use of ORC in the remediation of other hydrocarbons and MTBE will also be presented and the potential for treating certain chlorinated hydrocarbons will be discussed.

*Key words: oxygen, bioremediation, enhanced natural attenuation, groundwater remediation, in situ treatment*

### Posters

#### Golden Cliff

#### Modeling/Fate and Transport

## P1 USE OF THE DOD GROUNDWATER MODELING SYSTEM IN SITE CLEANUP

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Activities at Department of Defense (DoD) installations have produced contamination of groundwater resources which may pose problems for human health and the environments adjacent to or on these posts. Estimates for environmental remediation of these sites ranges from tens to hundreds of billions of dollars. The U.S. Army Engineer Waterways Experiment Station (WES), in concert with the Army Environmental Center (AEC) and Headquarters, Army Corps of Engineers (USACE), leads a consortium of Tri-Service, Department of Energy (DOE), Environmental Protection Agency (EPA), industry, and academic researchers in the development of the DoD Groundwater Modeling System (GMS). The GMS provides a single, comprehensive means for DoD to use advanced environmental quality modeling and simulation assets in site characterization, contami-

nant transport/fate assessment, and in the evaluation of differing remedial action strategies at DoD installations. The capabilities of this system to support site cleanup will be presented. Future development plans for the GMS will also be presented.

*Key words: subsurface modeling, remediation, site characterization*

## **P2 A MODEL OF IN SITU BIOREMEDIATION WHICH INCLUDES THE EFFECT OF RATE-LIMITED SORPTION AND BIOAVAILABILITY**

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In situ bioremediation is a technology that is currently being studied (and increasingly, implemented) in the hope that it may be useful in remediating the nation's hazardous waste sites. One factor affecting the feasibility of in situ bioremediation is the availability of the contaminant to the indigenous or introduced microorganisms which degrade it. It is typically assumed that the contaminant is only available for biodegradation in the aqueous phase. However, many organic contaminants of interest are sorbed to soils in the subsurface. The sorbed fraction is presumably unavailable for bioremediation. If bioremediation is being attempted, the rate of desorption of contaminant from the sorbed phase is a factor in determining the availability of the contaminant to the degrading microorganisms and hence, the efficacy of the remediation. Most models of contaminant transport in the groundwater neglect the rate of desorption, even though desorption rate may be crucial in determining bioavailability, and hence efficacy of remediation.

In this work, a transport model is presented which incorporates the following processes: (1) multi-dimensional flow, (2)

advection/dispersion, (3) rate-limited sorption (described by either first-order kinetics or Fickian diffusion), and (4) biodegradation. Biodegradation will be described using either Monod kinetics or cometabolic transformation kinetics. The model will have a number of features not incorporated in previous models, such as the ability to simulate multi-dimensional transport, diffusionlimited sorption, and cometabolic transformation kinetics. The model will be run, using realistic parameter values obtained from a recent field evaluation of in situ aerobic cometabolic bioremediation at Edwards AFB, to determine the potential impact of ratelimited sorption and other phenomena on bioremediation efficacy.

*Key words: modeling, bioavailability, sorption, cometabolism, bioremediation*

## **P3 SIMULATORS FOR IN-SITU REMEDIATION EVALUATION**

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As part of the Strategic Environmental Research and Development Program (SERDP), a suite of four in-situ remediation simulators (NUFT3D, SEAM3D/MT3DMs, UTCHEM, OS3D) is being enhanced, documented, and incorporated into the Department of Defense (DoD) Groundwater Modeling System (GMS). The GMS is a graphical user interface for multiple groundwater flow and transport models, with integrated tools for subsurface conceptualization, grid generation, feature mapping, and visualization.

Incorporation of multiple simulators into a common interface will provide unique modeling capabilities to expedite evaluations of remediation alternatives as well as the design, implementation, and optimization of remedial actions. The goal is to reduce cleanup costs by enhancing the probability of

optimal technology selection and implementation, while reducing the replication of modeling efforts. Addition of these well documented codes to the GMS suite will reduce impediments to the acceptance and application of faster, effective, though often complex, innovative technologies.

The incorporated models will simulate the following remediation technologies: (1) the natural attenuation of explosives and petroleum hydrocarbons; (2) in-situ bioremediation; (3) in-situ chemical treatment, particularly zero-valent iron barriers; (4) surfactant/cosolvent flushing for NAPL recovery; and (5) soil vapor extraction, bioventing, and air sparging. Pump-and-treat, containment, and simple barrier technologies also can be simulated. Models will be enhanced as needed and undergo rigorous documentation, including benchmark applications to controlled laboratory and/or field experiments.

Features of each simulator and example results are presented from each of our project partners, including the Department of Energy, the Air Force, and several universities. The example applications include: simulation of transport and natural attenuation of TNT in a column with soils from the Louisiana Army Ammunition Plant using UTCHEM; simulation of reactive transport with OS3D to reproduce the column studies from the design phase of the zero-valent iron, funnel-and-gate investigation at Dover Air Force Base (AFB); NUFT3D simulation of soil vapor extraction of TCE at a Lawrence Livermore National Laboratory cleanup site; surfactant enhanced aquifer remediation simulation for removal of DNAPL at Hill AFB using UTCHEM; and demonstration of the sequential electron acceptor model (SEAM3D) bioreactions and simulation of a tritium plume at Columbus AFB with SEAM3D'S companion transport code, MT3DMS.

*Key words: groundwater, simulators, remediation, in situ, GMS*

## **P4 MODELING AND SIMULATION OF VOLATILE ORGANIC COMPOUNDS IN SOIL-ROOT ENVIRONMENTS**

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A model is developed to investigate the fate of trichlorethylene (TCE) transport in soil-root system. Steady state is assumed. One dimensional transport of TCE in soil and two dimensional transport of TCE in root are described. Root structures are applied in the model development. Experimental values are used to estimate the parameters in the model. Coupled governing equations are solved by numerical methods. Simulation results are compared with experimental data sampled from the experimental channels.

*Key words: trichloroethylene, root, soil, diffusion, model*

## **P5 TRANSPORT STUDIES OF ZINC IN ONE-DIMENSIONAL COLUMNS UNDER INFLUENCE OF ADSORPTION PROCESSES**

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Heavy metal contaminants released into the soil environments cause a serious problem to the human population in the vicinity of these sites. These contaminants may be released due to various careless practices during mining and smelter operations. The transport of metal contaminants through river sediments and eventual deposition as alluvial soils cause a serious problem to the local vegetation. Metals undergo different fate processes such as adsorption, ion-exchange, and precipitation during their transport process in soils. Zinc is one such representative heavy metal contaminant of concern in the soil environments. In order to understand the various fate processes

of zinc during its transport in soils, one-dimensional column studies were undertaken for this study. Four columns were constructed and packed with soils. Three columns were packed with different soils collected from various depths from a site near a landfill in Riley County. Zinc bromide solution was the feed to these soil columns and a comparison of zinc transport results from various columns was made. The fourth column received  $\text{CaCl}_2$  solution along with the feed solution in order to study the transport of zinc when the soil adsorption sites were saturated with  $\text{Ca}^{2+}$  cations. The various comparison results will be presented in this paper.

*Key words: heavy metals, zinc transport, ion-exchange, precipitation*

## **P6 THE EFFECT OF VEGETATION ON WATER MOVEMENT THROUGH A CONTAMINATED SOIL**

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Heavy metal contamination can spread from contaminated soils to surrounding areas due to wind and water action. Vegetation of these soils can reduce this movement by stabilizing the soils against erosion, but the introduction of Vegetation can also change the way soil water moves through the soil. The accumulation of organic matter due to the death of roots and the presence of root exudates can influence soil water movement by changing the water holding capacity of the soil. The presence of roots can lead to preferential flow paths. Vegetation will evapotranspire soil water in various amounts due to climate, soil, and plant conditions. This paper looks at changes in the movement of moisture through a heavy metal contaminated soil during a growing season. Results of a

laboratory study will be presented along with modeling predictions.

*Key words: vegetation, heavy metals, soil, water, mechanisms*

## **P7 TURBULENCE FLOW MODELING OF INDUSTRIAL CHEMICAL WASTE**

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The transport of chemical or industrial wastes that are disposed of in dilute quantities are usually accomplished by using extended pipeline systems, and then jetting it at high velocities in spray form into the oceans. The inherent presence of solid particles in the system complicates this process, and the direct consequence thereof is incorrect pipeline sizing, wrong pump specification, and the cost thereof is exorbitant. Very often deposition of these particles set in lower down the pipeline, and this leads to blockages which are difficult to rectify. The essence of the problem is identifying a method of modeling the flow behavior of this fluid, to more accurately predict it AEs performance under a range of different conditions. Rapid disposal of industrial or chemical waste utilizing these means, is desired. The only method of achieving that, as well as impeding the settling out of the solid particles in suspension, is by operating the flow within the turbulent regime. The prediction of turbulent flow headloss for fluids which stray from classical Newtonian behavior, has remained one of the most difficult theoretical and practical problems, both from the point of view of the fundamental physics of the phenomenon, and from applied engineering practice. Recent interest in the field has produced several new approaches to the problem. The objective of this research is to review these new approaches, as well as those from earlier work, compare their performance

under practical application, and formulating a concept called "Particle Roughness Turbulence" into an alternative and more accurate method of modeling. The traditional problem areas are discussed and the strengths and weaknesses of the various approaches are examined. These models are then applied to a database of experimental results accumulated by the slurry flow research program at the Cape Technikon, involving a number of tertiary institutions in South Africa, and work done at the University of Cape Town.

The principal dilemma at present is whether the turbulent flow headloss can be predicted from the rheology (traditional flow behavior) of the slurry only, or whether other properties are required. Various rheological approaches from simple to complex are employed to illustrate the dilemma. Guidelines for the accurate prediction of turbulent flow headloss for fluids exhibiting non-Newtonian characteristics are formulated.

*Key words: turbulent, headloss, non-Newtonian, suspension, rheology, roughness*

## **P8 RESEARCH WELLFIELD FOR CALIBRATING GEOPHYSICAL MEASUREMENTS AGAINST HYDROLOGIC PARAMETERS**

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A wellfield is being developed for hydrologic and geophysical research in a shallow, unconfined, aquifer consisting of unconsolidated, coarse (cobble-and-sand) braided-stream deposits adjacent to the Boise River. Preliminary analysis of ground penetrating radar (GPR) images suggests that the wellfield is underlain by three or more cobble-bar sequences separated by subhorizontal bounding surfaces. research will focus on developing methods for using non-invasive geophysical techniques to map variations in permeabil-

ity. Responses to surface geophysical techniques (e.g., seismic, GPR and TEM) will be calibrated against a highly characterized volume (the wellfield) with determined 3-dimensional distributions of hydrologic, geologic, geophysical, and multivariate properties, and geostatistical characteristics. Well coring and construction methods, and the well arrangement in the field, are designed to provide detailed control on lithology (facies distribution and sediment properties) and to support a variety of single-well (borehole geophysical logging, permeability logging, vertical seismic and radar profiling,...) cross-hole (seismic, radar and resistivity tomography, tracer tests,...), and multiwell (pumping and tracer tests, seismic borehole-to-surface tests,...) experiments. The wellfield will have a central well surrounded by two rings of six wells each and outer "boundary" wells. Wells will be nearly fully screened with 4 in-diameter PVC to about 20 m depth. Permeability will be measured directly with the flow meter and pumping method in each well, and with a series of tests where successive intervals will be pumped in a given well while multiple zones will be monitored in surrounding wells. Wellfield dimensions and design specifics are based on experience at a nearby remediation site in the same aquifer; a Monte Carlo search was used to optimize well-pair distances and azimuths for definition of correlation lengths and, to the extent possible, anisotropy of parameters of interest. The wellfield will be aligned with anticipated axes of anisotropy at the site.

*Key words: characterization, hydrogeology, geophysics, permeability, heterogeneity*

## Posters

### Golden Cliff

#### Metals/Radionuclides/Inorganics

## P9 THE MOUNT MORGAN PIT LAKE, QUEENSLAND, AUSTRALIA: HISTORY AND CURRENT STATUS

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Active exploration of the historic Mount Morgan mine site by Joint Venturers, Perilya Mines NL and Aumin Technology and Development NL is showing hope of finding another viable orebody that may change the course of history yet again for Mt. Morgan. The company currently manages the environmental and heritage aspects of former operations at the site under contract for the Queensland Department of Mines and Energy (QDME).

The colourful history of this mine has been well documented since mining commenced in 1882 with the company records preserved in the Central Queensland University Library ~t nearby Rockhampton. As early as 1890, however, there were concerns about acid water associated with the pyritic ores polluting the Dee River. Balancing heritage values and long-term effects of the mining activities are now the focus of the Department's site planning.

Although 40% (150 Ha) of the disturbed area has been rehabilitated there is still considerable acid mine drainage produced by the remaining 370 Ha which require rehabilitation. As a short-term control measure a pump-back system aims to intercept as much of this seepage as possible before it reaches the Dee River and pumps the contaminated water back to the open cut. The open cut contains 28 Mt of re-treated tailings covered

by a pit lake holding 9 000 ML of acidic water. Four million dollars was spent by the former operators to cap tailings dams, and to install surface drainage works and the pump-back system. Operating and maintaining the system costs QDME \$300 000 each year.

Contamination of the Dee River, which drains to the Fitzroy River, is the major off-site impact and has directed research commissioned by the QDME to date. Characterisation of the pollution in the Dee River at low and moderate flows has been conducted by the Commonwealth Scientific and Industrial Research Organization (CSIRO) Minesite Rehabilitation Research Group. Baseline biological studies to assess the impacts on the ecosystem have been performed by Central Queensland University Centre for land and Water Resources

If the current exploration is successful and mining proceeds the company will assume more responsibility for environmental management. The Department is continuing to investigate ways to implement a cost effective long term rehabilitation strategy, especially for areas of the site unlikely to be involved in any new operation. The annual cost of the pump back system will be on-going until the causes of the acid mine drainage are addressed.

*Key words: Mount Morgan, acid mine drainage*

## P10 CHEMICAL INTERACTIONS OF THE WATER IN THE BERKELEY PIT AND ITS SURROUNDING AREAS

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Since 1982, when the Anaconda Company stopped its copper mining operation, both the Berkeley pit and the adjacent underground network began filling with acidic massive toxic mine waste. The water samples

from the pit, from the surface inflow, and from ground water (mine shafts and monitoring wells) have been taken, measured and analyzed at regular intervals since 1984.

The research will compile and present the collected data, and model and interpret interactions that may be happening in the water. For the Berkeley pit water itself, the interactions include the formation of the surface water, the transport of the water within the pit, and the interaction between the water and the wall of the pit. For the underground water, the study will concentrate on the interaction between the water and the ore deposit. For surface inflow, the study will investigate the mixing between inflow and the pit water.

*Key words: Berkeley pit water, water chemistry, water interaction, modeling*

## **P11 PREDICTION OF ARSENIC CONCENTRATIONS IN MINE PIT WATERS AT GETCHELL MINE, HUMBOLDT COUNTY, NEVADA**

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Currently many Nevada mining operations are exploiting disseminated gold deposits from open pit mines which extend below the water table. When mining operations cease, water will flow into these pits forming lakes. One of the most important environmental issues facing the gold mining industry in Nevada is the quality of water in the newly formed pit lakes that results from interaction between pit waters and wallrocks over time. Water/rock interaction with sulfide wallrocks in an oxidizing environment can potentially result in high levels of arsenic and conditions of low pH in pit waters. Therefore, the objectives of this study are to (1) in-

crease understanding of the hydrologic and geochemical processes which are active in mine pit lakes, (2) represent these processes in geologically reasonable conceptual models of pit lake systems, and (3) utilize hydrologic and geochemical modeling techniques to develop and test methods which will accurately predict future water quality in mine pit lakes.

Getchell Gold Corporation's open pits were chosen for study because of the availability of hydrologic and geochemical data for three historic pit lakes which existed at the mine site from 1968-1983. Using these archival data, we have attempted to reconstruct the hydrologic and geochemical characteristics of the historic pits, and these reconstructions will provide useful analogs with which to compare our model predictions. This poster describes the history of the Getchell pit lakes and the assumptions and considerations that are included in a conceptual model of a pit lake system. This poster also presents preliminary results of geochemical modeling efforts to predict arsenic concentrations in future pit waters over time and compares model results to historic data.

Initial findings regarding arsenic concentrations in pit lake waters can be summarized as follows: (1) arsenic and iron concentrations in the hypolimnion of a pit lake can be controlled by sulfide mineral saturation (realgar and pyrite) provided the redox conditions of the hypolimnion waters support sulfide mineral stability; (2) total arsenic concentrations in hypolimnion waters are dependent on a number of factors including pH, arsenic concentrations of groundwaters filling the pit lake, and composition of the pit wallrocks; (3) arsenic concentrations in the epilimnion of a pit lake are not controlled by saturation of As-bearing mineral phases. Instead, arsenic concentrations appear to be controlled by either adsorption of arsenate to colloidal Fe-oxyhydroxide surfaces or precipitation of arsenate salts; and (4) dissolution of pit wallrocks that are depleted in Fe-bearing

mineral phases may not release sufficient amounts of Fe into pit waters to become saturated with Fe-oxyhydroxide phases. As a result, high background arsenic concentrations in regional groundwaters may not be naturally remediated by adsorption processes within some pit lakes.

*Key words: arsenic, geochemical, groundwater, EQ3/6*

## **P12 REMOVAL OF DISSOLVED ARSENIC SPECIES THROUGH AN INNOVATIVE ELECTRO-CHEMICAL PROCESS**

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Occurrence of arsenic in drinking water sources along, with recent health studies have paved the way for the reduction of the current drinking water standard for the metal. Problematic areas in the United States and in West Bengal India have spawned worldwide attention to the problem. Solubilized inorganic arsenic species found in numerous drinking water systems throughout the world and the western United State, have been correlated with increased skin cancer.

Recent epidemiological studies suggested that skin cancer may occur at arsenic concentrations at or above 2 ppb The World health organization (WHO) has responded by setting a provisional guideline of 10 ppb in 1993 in order to enhance research. Canada has already lowered its maximum allowable arsenic concentrations to 10 ppb. In the United States, a new arsenic standard between 5 and 20 ppb is expected to be promulgated by the year 2001. Although few utilities are at or near the current 50 ppb limit, approximately 7,126 rely on potable sources whose concentrations are in the 5-20 ppb range. The USEPA has responded by proposing a revision of the current Maximum Contamination Level (MCL) for arsenic in drinking water.

This revised MCL could be lowered from the current 50 ppb down to 10 ppb.

Arsenic does occur naturally in many aquifers throughout the world. In particular, Utah is known to have at least 61 systems with arsenic concentrations over 20 ppb The Spiro Tunnel outlet in Park City Utah has been the object of particular concern among the State of Utah's Division of Drinking Water. Park City's search for water resources is essential to its future growth The aforementioned tunnel was formerly a silver mine in the Park City area, whose water contains concentrations of arsenic typically ranging from 30-50 ppb) This source was developed in the 1970s when winter sports facilitated development and population growth Utilization of the Spiro source was initially delayed due to arsenic levels of 65 ppb on average

Current technologies for removal of dissolved arsenic species have proved expensive for smaller communities and somewhat ineffective for arsenite (AsIII) Typically, arsenite removal is accomplished by oxidizing, it to arsenate (AsV) via expensive oxidizing agents and pH adjustment. Arsenate may then be readily removed from the water by the addition of salts sorption ion exchange or filtration. Exploration of electrochemistry by various researchers has led to the development of several processes capable of a spectrum of environmental applications

Recent studies conducted by Magnus Schroeder Technologies on drinking water from Park City Utah indicate that the use of an electrochemical cell comprised of iron electrodes, effectively oxidizes and precipitates all dissolved arsenic species without the addition of oxidizing agents or pH adjustment Neutral arsenic-laden water was successfully treated, without pH adjustment or the addition of oxidizing agents by passing it through a rudimentary electrochemical cell comprised of iron electrodes Reduction of arsenic levels from 50 ppb to non-detection (below 2 ppb) was achieved in pilot studies where up to 50 gallons per minute of water was treated

*Key words: arsenic, precipitation, electro-chemical, maximum contamination level, drinking water, Park City*

### **P13 TRANSCRIPTION OF CYANOBACTERIAL CLASS II METALLOTHIONEIN AND MOLECULAR CHAPERONE GENES IN RESPONSE TO DIVALENT METAL CATIONS AND THE OXYANIONS OF ARSENIC**

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The cyanobacterium *Synechococcus* sp. PCC7942 is a single celled photosynthetic prokaryote. A number of studies have been performed aimed at understanding the mechanisms used by this bacterium for coping with heavy metal exposure. A better understanding of these resistance mechanisms could guide genetic engineering attempts to develop this organism for use in bioremediation. In particular, we have been interested in the extraordinary resistance this organism shows against arsenate. Cells in culture are unaffected by concentrations of arsenate as high as 1M. Possible mechanisms for this resistance include exclusion from the cell, intra and extracellular binding and potential interactions with cellular proteins such as the metallothioneins. Metallothioneins are sulfur rich polypeptides expressed at high levels in response to cellular challenges with divalent metal cations such as  $\text{Cd}^{++}$ ,  $\text{Cu}^{++}$  and  $\text{Zn}^{++}$ . These polypeptides bind and thus potentially detoxify these metal ions. We have found that *Synechococcus* sp. PCC7942 expresses messenger RNA for metallothionein protein in response to a variety of concentrations of these divalent metal cations and interestingly, in response to the oxyanions arsenate and arsenite as well. The response to arsenate however, occurs only in cells previously limited for phosphate. This finding suggests that under phosphate sufficient conditions,

arsenate is excluded from the inside of these cells. We are examining the hypothesis that arsenate, once allowed to enter phosphate limited cells interacts with the thiol groups of cysteine residues found in the regulatory protein responsible for the expression of the metallothionein gene. We are also studying the expression of the more generalized stress response protein GroEL. This gene is expressed at high levels by cyanobacterial cells. In response to a number of physiological stresses including temperature and light intensity. We have also shown that the transcription of the gene for this protein responds within 15 min to various concentrations of the divalent metal cations  $\text{Cd}^{++}$ ,  $\text{Cu}^{++}$  and  $\text{Zn}^{++}$ , but not to either arsenite or arsenate - even in phosphate depleted cultures. Thus the conditions which induce expression of the general stress protein GroEL and the metal binding protein metallothionein are somewhat different.

*Key words: metals, arsenic, metallothionein, cyanobacteria*

### **P14 INVESTIGATION OF METAL BINDING IN ALFALFA BIOMASS THROUGH CHEMICAL MODIFICATION OF AMINO AND SULFHYDRYL LIGANDS**

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Heavy metal pollution of the environment has become a serious problem, and as a result, there has been a great deal of attention given to new technologies for remediation of heavy metal ions from contaminated waters. Although alfalfa biomass has shown to be very effective at removing heavy metal ions from aqueous solutions, the mechanism of metal ion binding has yet to be fully understood. To better comprehend this mechanism, amino and sulfhydryl groups were chemically modified individually to block the metal

binding ligands in order to determine their contribution to the metal uptake process by alfalfa biomass. Acetylation of the amino ligands on the alfalfa biomass resulted in a small reduction of metal binding for copper(II) and nickel(II), while no significant change was observed for lead(II) at pH 5.0. In addition, succination of the biomass was performed. This process adds a carboxylate group onto the possible nitrogen ligand. This resulted in an increase in binding for copper(II), nickel(II), and lead(II), indicating that carboxyl groups play an important role in metal binding. Also, this suggests that amino groups are indeed present but play a less significant role on the binding of these metals. Sulfhydryl ligands on the alfalfa biomass were chemically blocked resulting in no significant change in metal binding for copper(II), nickel(II), and lead(II). By determining the metal binding sites in the alfalfa biomass, a new treatment technology of heavy metal contaminated ground waters can be further understood and developed.

*Key words: chemical modification, heavy metal binding, alfalfa, metal ligands*

## **P15** ENHANCED METAL BINDING CAPACITY OF NaOH TREATED LARIREA TRIDENTATA LEAF TISSUE

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*Larrea tridentata*, or creosote bush, is a common desert plant that inhabits the Chihuahuan desert. Due to its great abundance and high growth tolerance of heavy metal contaminated soils, it was chosen as the primary candidate for this study. Previous experiments conducted on inactivated and untreated sodium hydroxide (NaOH) *Larrea tridentata* leaf tissues showed that it effectively bound metal ions from aqueous solutions. These pure metal ion solutions consisted

of copper(II), cadmium(II), nickel(II), lead(II), zinc(II), and chromium(III). In order to understand the effects of NaOH modification on the creosote bush's metal ion binding ability, batch modification studies were conducted. Results from these modification studies showed that there was an increase in metal binding for every metal tested. We believe that the enhanced metal binding ability of the NaOH modified biomass of *Larrea tridentata* is due to the conversion of methyl esters to carboxylic groups. Carboxylic groups have a higher affinity to bind metal ions at pH 5 since they are deprotonated and thus promote the approach of positively charged cations. Data from these experiments suggests that NaOH modification may be a process to further improve heavy metal binding by creosote bush tissues.

*Key words: Larrea tridentata, heavy metal binding, creosote bush*

## **P16** INNOVATIVE TECHNOLOGY TO RECOVER GOLD(III) FROM AQUEOUS SOLUTIONS BY USING MEDICAGO SATIVA(ALFALFA)

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There is a need for the development of a system that can extract gold out of aqueous solutions without the use of hazardous chemicals. A biorecovery system using alfalfa biomass may be the answer for the recovery of gold(III) from aqueous solutions in an environmentally friendly manner. Batch laboratory experiments indicate that Alfalfa binds gold(III) quickly and in a pH independent manner. Gold(III) binding capacity experiments performed with the alfalfa roots and shoots have shown the following results: 40.9

mg gold per gram of shoot tissues; 18.7 mg gold per gram of root tissues. We were able to recover up to 99.1% of the bound gold metal by treatment with acidic thiourea. Surprisingly we discovered that the bound gold turned purple in color, meaning that gold(III) had been reduced to gold(O). This was confirmed by transmission electron microscopic analysis (TEM). In addition, column experiments were performed with silica immobilized alfalfa to determine the gold(III) binding ability under flow conditions. This in turn could constitute an innovative pollution prevention technology to reclaim gold from natural and industrial processes and prevent the use of hazardous chemicals that might contaminate ground waters.

*Key words: pollution prevention, heavy metal binding, gold, phytofiltration, alfalfa*

## **P17 PATTERNS OF ACCUMULATION OF HEAVY METALS IN NON-WOODY VEGETATION ESTABLISHED ON ZINC-LEAD SMELTER CONTAMINATED SOILS**

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Soil columns for two soil types obtained from an abandoned lead and zinc smelter at Dearing in Montgomery County, Kansas were vegetated by means of a grass/ legume seeding mixture. Herbaceous shoot and root material was analyzed for zinc, lead, and cadmium by ICP spectrometry. Results indicate that for both types of substrate there was significant accumulation of all three metals by root systems with relatively low concentrations of any of these metals being partitioned to the shoots. Partitioning between shoots and roots for all three metals on both soil types averaged 1:5 (shoot:root). There was little correlation between root and shoot concentrations of any of these metals. Implications of these observations for phytoremediation of smelter sites are considered.

*Keywords: shoot-root partitioning, zinc, lead, cadmium, phytoremediation*

## **P18 ALKALINE-RECHARGE EXPERIMENTS EMPLOYING LIME SLURRIES FOR IN-SITU REMEDIATION OF AQUIFERS PRODUCING ACID-MINE DRAINAGE, WEST VIRGINIA**

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Perched aquifers form from resaturation of coal overburden and develop extremely-heterogeneous groundwater flow systems above the original pit floor. A series of experiments were performed at a West Virginia research site using lime slurry solutions to recharge the spoil aquifer by artificial methods, to cause reduced acidity and removal of metals in situ. Benefits of this mode of treatment, if successful, would be reduced sludge handling, reduced frequency of water sampling for NPDES compliance, and reduced chemical costs. In initial experiments, treated AMD was pumped from an NPDES discharge site onto the top of the spoil deposit and mixed with fresh lime hydrate [the mineral portlandite  $\text{Ca(OH)}_2$ ] in a 6x6 m hydraulic structure. Goals were to evaluate feasibility of lime-slurry recharge from surface leakage and to estimate the percentage of applied alkalinity that reaches the aquifer. The alkaline recharge solution (pH 12.3), at saturation with portlandites forced to infiltrate into the aquifer through a series of artificial recharge structures. Despite high pH (8.8-9.3) of the NaOH treated water used to dissolve the lime, an additional 18 milliequivalents/liter were added to the slurried solution by lime dissolution. In addition, an indeterminate amount of suspended lime was forced into the aquifer through macropores. Excess lime was retained at the surface of the recharge structures, available for later dissolution by runoff. Calcite formation was induced by the extreme

pH in the slurry but limited by initial  $\text{Ca}^{2+}$  concentrations in the treated water ( $<200 \text{ mg/L}$ ). Even early in the period of response, downgradient changes in chemistry, were observed in wells surrounding the recharge basin pH was raised from an initial value of 3.5-3.8 to as high as 6.. At the springs, iron was reduced from 30-70 to  $<10 \text{ mg/L}$ . AL was somewhat higher (10-30  $\text{mg/L}$ ) but well below the higher values observed in the aquifer ( $>190 \text{ mg/L}$ ). Additional chemical changes are anticipated as the center of the alkaline recharge plume reaches the springs. The method may represent a cost-effective alternative to point-of-discharge chemical treatment and sludge removal.

*Key words: acid mine drainage, in situ remediation, groundwater geochemistry*

## **P19 SELENIUM REDUCTION IN MINING EFFLUENT USING A PASSIVE MODULAR REACTOR**

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The purpose of this research was to determine if sawdust can be used to support a bioprocess for the remediation of selenium laden streams. In a mining setting, organic substrates required for metabolic activity are usually limiting. Selenium reducing bacteria (SeRB) were found in the sediments and wastes from two mine sites, grown up to higher numbers, and used to increase their levels in mud from each mine. Both inoculated and uninoculated mud was tested in a reactor design to treat waters from these two mines. Se levels were reduced from 100 ppb to less than 5 ppb for one mine over a 45 day trial period. Se levels were reduced from 700 ppb to below 10 ppb over a 63 day trial period for the second mine. In addition, sulfates,

nitrites, and other cationic metals are removed in the same process. The pH values from the streams were increased from values as low as 3 to pH values of 7 consistently.

*Key words: selenium, metals, acid mine drainage*

## **P20 CHARACTERIZATION OF AN ANAEROBIC SOLIDS BLANKET REACTOR SYSTEM FOR THE BIOLOGICAL REDUCTION AND REMOVAL OF SELENIUM FROM WASTEWATER**

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Two anaerobic solids blanket reactors in series were evaluated for the potential of biologically reducing and removing selenate oxyanions from a synthetic wastewater. Each column contained a total aqueous volume of 1.1 L and the entire system was operated at a hydraulic retention time of 2 days. Selenate was utilized as the electron acceptor, while acetate served as the electron donor and carbon source. The synthetic wastewater contained 25  $\text{mg/L}$  selenate-selenium. The influent acetate concentration was in excess of the theoretical stoichiometric requirement for selenate reduction to elemental selenium. In addition, nitrogen, phosphorus, trace minerals and vitamins and 2% (v/v) anaerobic digester supernatant were added to the influent. For this study, the selenium species measured in the effluent included selenate, selenite, total selenium, and volatile selenium. Selenium concentrations were quantified using manual hydride generation atomic adsorption spectrophotometry. Average aqueous effluent concentrations of selenate, selenite, total selenium, and volatile selenium from the first column were  $8.22 \pm 8.77 \text{ mg/L}$ ,  $7.98 \pm 4.41 \text{ } \mu\text{g/L}$ , and  $47.9 \pm 76.1 \text{ } \mu\text{g/L}$  respectively. Average concentrations of selenate, selenite, total selenium, and volatile selenium in the aqueous effluent of the second column were

2.80 ± 1.84 ug/L, 2.96 ± 2.94 ug/L, 6.47 ± 4.67 ug/L, and 27.9 ± 22.5 ug/L. respectively. A longitudinal profile of selenium concentrations in the aqueous phase of the two columns indicated that approximately 98% of the selenium reduction and removal occurred within the first column. In addition, tracer tests were conducted using fluoride to determine if channeling or hydraulic short-circuiting was occurring. Results showed that these effects were negligible, and the system operated in a plug flow regime as expected.

*Key words: selenium, anaerobic microbial reduction, bioreactors*

## **P21 BIOLOGICAL REDUCTION OF PERCHLORATE TO THE CHLORIDE ION USING AN ANAEROBIC FLUIDIZED BED REACTOR**

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Perchlorate, used as an oxidizer in rocket fuels, represents a significant contamination problem in groundwater near numerous aerospace and defense industries. Due to its potential health effects on the thyroid and bone marrow, the California Department of Health Services (CDHS) has issued an "action level" of 18 ppb for perchlorate in drinking water. An anaerobic fluidized bed bioreactor (FBBR) with recycle was evaluated to determine its potential to biologically reduce perchlorate to the chloride ion at low perchlorate concentrations. The system consisted of a 5 foot long, 3 inch I.D. glass column with 9 sampling ports. Celite<sup>R</sup>-633 (30x50 mesh) provided the catalyst carrier and was fluidized to 100% expansion. The FBBR was operated with a 2-day hydraulic retention time. Perchlorate was utilized as the electron acceptor and cheese whey provided the electron donor and carbon source. The influent was further enhanced with nitrogen, phosphorus, trace minerals, and 1% (v/v) anaerobic digester

supernatant. The pH was adjusted to levels between 6.6 and 7.5. Sodium perchlorate at 1.3 mg/L as ClO<sub>4</sub> in the influent was fed into the reactor at the diluted concentration of 1.4 ug/l due to the high recycle to influent ratio (900:1). The FBBR was allowed to operate under these conditions for several months until steady-state conditions were reached. The effluent samples were sent at 4 °C to a certified laboratory for analysis using the ion chromatography ~method developed by the CDHS. Quantification of the aqueous effluent concentration proved to be below the method detection limit for perchlorate of 4 ug/L. It is assumed that biological processes are the cause of this reduction otherwise perchlorate concentration in the FBBR would have built up, approaching 1.3 mg/L, over time. Subsequent tests on the chloride ion revealed significant increase, up to 250% in effluent concentrations 3S compared to influent concentrations; likewise, indicating the occurrence of biodegradation. The authors are optimistic that anaerobic biotreatment is a viable alternative for perchlorate reduction and can be used to meet the current action level of 18 ppb. Additional investigations are being conducted to further quantify system parameters and performance.

*Key words: perchlorate, anaerobic bioreduction, fluidized bed*

## **P22 FEASIBILITY OF BIOAUGMENTATION OF FE(0) WITH HYDROGENOTROPHIC DENITRIFIERS FOR REMOVAL OF NITRATE FROM GROUNDWATER**

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Nitrate is a ubiquitous priority pollutant that can cause methemoglobinemia. Many physical-chemical and biological processes for nitrate removal are marginally cost effective and/or result in undesirable effects on water quality. Consequently, there is a need to explore novel alternatives that address both

biological and chemical advantages and constraints. Till et al. (1998) explored the combination of  $\text{Fe}^0$  with autotrophic, hydrogen-utilizing bacteria to remove nitrate. It was previously shown that  $\text{Fe}^0$  can reduce nitrate stoichiometrically to ammonium and that nitrate removal can be enhanced by autotrophic denitrifiers that utilize cathodic  $\text{H}_2$  (produced by  $\text{Fe}^0$  corrosion) to reduce nitrate to more desirable nitrogenous gases. This project builds on Till's work and addresses the feasibility of bioaugmentation of  $\text{Fe}^0$  barriers to remove nitrate from different types of aquifer material.

Aquifer microcosms were prepared in duplicate using 200 mL serum bottles capped with Mininert valves. All microcosms were amended with 90 grams of either 2.5% org-C soil or 0.1% org-C sand plus 100 mL of mineral medium containing 30 mg/L  $\text{NO}_3\text{-N}$ . Biological and abiotic transformations were studied separately and interactively by including or excluding  $\text{Fe}^0$  (IOg Fisher Fe-filings) and denitrifying hydrogenotrophs (10 mL of *Paracoccus denitrificans*, ATTC# 17741 suspension, OD<sub>600</sub>=0.06). Abiotic removal was assessed per  $\text{NH}_4^+$  accumulation, and biological denitrification was quantified per  $\text{N}_2\text{O}$  accumulation in acetylene-blocked microcosms.

Neither bioaugmentation or  $\text{Fe}^0$  addition to high-carbon soil increased the efficiency of nitrate removal relative to the no-treatment control (i.e. no  $\text{Fe}^0$  and no *P. denitrificans* added). Apparently, the indigenous consortium effectively utilized the naturally occurring organic carbon to denitrify the added nitrate within 5 days. In many aquifers, however, denitrification is often limited by the availability of suitable electron donors. In such cases,  $\text{Fe}^0$  addition and/or bioaugmentation with specialized strains holds great promise to enhance nitrate removal. This was demonstrated in the low-carbon, sandy microcosms, where no nitrate removal occurred in no-treatment controls. Yet, the best results were observed in  $\sim 10\%$ -amended,

bioaugmented microcosms, which exhibited not only faster nitrate removal rates, but also lower ammonium accumulation.

Interestingly,  $\text{N}_2\text{O}$  was detected in acetylene-blocked sandy microcosms amended with  $\text{Fe}^0$  alone. This indicates that there is a potential for an indigenous hydrogenotrophic population to eventually develop around  $\text{Fe}^0$  barriers to fill a metabolic niche associated with denitrification in low-carbon soils. Bioaugmentation of  $\text{Fe}^0$  barriers with hydrogenotrophic denitrifiers under low-carbon conditions may shorten the adaptation period and enhance short-term denitrification potential, thus improving overall nitrate removal efficiency.

*Key words: autotrophic denitrification, hydrogen, nitrate, bioaugmentation*

## **P23 SELECTION OF CHELATING AGENTS FOR REMEDIATION OF RADIONUCLIDE-CONTAMINATED SOIL**

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Soil contamination by heavy metals and radionuclides is a common problem encountered at many contaminated sites of DOE. Lead, chromium, copper, arsenic, uranium, technetium, strontium, cesium, and actinides were among the most often found. Metals and radionuclides in soil pose a serious risk to public safety and groundwater supplies. Once reaching the soil matrix, they can be strongly retained, ensuring prolonged adverse impacts on environmental quality and human health. Chelating extraction has already been shown to have potential for the remediation of heavy metal contaminated soils either as on-site soil washing agents or for in-situ remediation. Chelation extraction is well suited as a remediation technique for radionuclide-contaminated soils.

This paper will communicate our progress in efforts to develop a predictive tool for the selection of effective chelators for the target radionuclide contaminants, and for assessing chelation remediation efficiency based on barest essential test results. This predictive modeling tool is thus technically and economically beneficial to the Mound project and other DOE sites awaiting remediation. Results to date of this project are a list of chelators suitable for the extraction of target contaminants including U, Ra, Th, Ba, Ce, Sr, and Tc. The selection of chelators is based on aqueous phase equilibrium determination of the chelators's complexation ability, selectivity, and recoverability with respect to the target contaminants. A regression/empirical model is being developed that predicts radionuclides extraction efficiencies based on input parameters including equilibrium properties of the chelators, laboratory sequential extraction results, and soil characteristics such as composition, texture, organic content, soil pH, cation exchange capacity, carbonate content, mineralogy, and other significant factors.

*Key words: metals, radionuclides, soil remediation, chelation extraction*

## Posters

### Golden Cliff NAPLs

## P24 ASSESSMENT OF SOURCE MASS AND SOURCE LIFETIME AT AN LNAPL SITE

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Active remediation of petroleum contaminated aquifers is becoming less common across the country as Risk Based Corrective Action methodologies and Natural Attenuation remedies are being selected for low-risk sites even when free product exists in the

source area. A major question that remains to be answered at many sites, however, is how long the free product and residual contamination will remain,

and how long monitoring will be required if no active source removal is carried out.

Procedures for the estimation of the mass of residual contamination existing at a site based on soil core, product, and groundwater analysis will be discussed in the presentation. Example calculations for residual mass estimates, product weathering rates using site hydrogeological data and free product chemical analyses,

and source lifetime estimates will be presented using field data from a State-lead UST site in south Salt Lake Valley. The results of these calculations will be put into perspective relative to a Natural Attenuation remedy for the site, and options for and the impact of active source removal will be presented.

*Key words: ??????????*

## P25 EFFECTS OF AQUIFER HETEROGENEITY AND GROUNDWATER FLOW DIMENSIONALITY ON UPSCALING OF NATURAL AND SURFACTANT ENHANCED DISSOLUTION OF NONAQUEOUS PHASE LIQUID WASTE CHEMICALS

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Mass transfer from entrapped nonaqueous phase liquids (NAPL) at field sites takes place under three-dimensional flow. However, most laboratory studies of mass transfer have been conducted under one-dimensional flow. Under realistic conditions, heterogeneous distribution of NAPL ganglia and reduced water permeability due to entrapment impact mass transfer. Dissolution experiments in

two-dimensional flow field are used to evaluate the effects of flow dimensionality. Evidence of dissolution fingering was found from measured concentration profiles. A flow and transport model with added capability to simulate dissolution was used to determine parameters of a phenomenological model. This model predicts less quasi-steady state mass transfer compared to one-dimensional experiments. Comparison of model results with data from an intermediate scale tank demonstrated the improvement in accuracy obtained by representing the flow dimensionality realistically. This findings have implications on the possible errors in using phenomenologically dissolution models based on column data in field applications.

Extending this work to enhanced dissolution using surfactants, a series of two-dimensional experiments were conducted in a bench scale dissolution cell in which a surfactant solution was pumped from the inlet of the tank. Continuous gamma scanning of the NAPL source provided data on active dissolution length, change in NAPL saturation with time and dissolution fingering. Data collected enabled to overcome deficiencies identified in the prior research of enhanced dissolution such as flow one-dimensionality, homogeneity, local equilibrium assumption and idealized transient mass transfer. Through numerical modeling, mass transfer rate coefficient for the enhanced dissolution case was correlated to porous media parameters, Reynolds number and entrapped NAPL saturation. These results will be useful in upscaling surfactant based remediation techniques from the laboratory to the field.

*Key words: nonaqueous phase, surfactants, dissolution, heterogeneity, mass transfer*

## **P25 SCALE-DEPENDENCE OF HIGH-FREQUENCY SEISMIC RESPONSE IN UNCONSOLIDATED POROUS MEDIA TO THE PRESENCE OF NAPL CONTAMINANTS**

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Geophysical methods are an essential, albeit under-utilized, tool for the evaluation of remediation options and monitoring of contaminated groundwater aquifers. By providing areal or three-dimensional distributions of physical properties between boreholes, infinitely more information is obtained compared to borehole sampling. The capability of high-frequency cross-hole seismic tomography to provide velocity and attenuation distributions at a resolution matching the heterogeneity scale of interest for contaminant transport, on the order of tens of centimeters, has been demonstrated for liquid-saturated conditions. However, the challenge in this application is to relate the change in velocity and attenuation distributions to parameters of interest for remediation, which in this case is the distribution on non-aqueous phase liquid(NAPL) contaminants.

Our laboratory measurements in sand columns show significant changes in compressional and shear wave velocity and attenuation due to the presence of varying fractions of immiscible liquids, specifically water and NAPL. The effect of the NAPL on wave attenuation is consistently greater than the effect on velocity. Our current work addresses the issues of (1) whether these effects will occur at scales larger than the 4 cm long columns (i.e. at frequencies lower than 500 kHz), and (2) whether we can resolve the three-dimensional distribution of the NAPL

(as opposed to the one-dimensional conditions of the column tests).

We are conducting a series of controlled NAPL spills in a 61 cm diameter by 76 cm long confining vessel to measure the seismic response at a frequency range that is one order of magnitude lower than the column studies. The tank is designed for confining pressures up to 150 psi (1 Mpa). Six 3 cm diameter wells are located just inside the vessel wall for the crosshole seismic data acquisition, and a NAPL injection port is located in the center of the vessel.

The crosshole seismic data is obtained using source and receivers mounted in acrylic tubes that are water-coupled to the borehole wall through a water annulus trapped between two O-rings (to prevent the generation of borehole tube waves). The source consists of a bar piezoelectric crystal (PZT 5400 Navy I; resonance frequency 123 kHz) that is excited by a 60 kHz single-cycle tone amplified to 50 V peak-to-peak. This frequency corresponds to P-wave wavelengths in the water-saturated sand of approximately 2–3 cm. The receivers which are currently being used are commercial high frequency accelerometers (PCB 309A; resonance frequency >120 kHz). The waveform from the accelerometers are preamplified to 40db, stacked 200 times, and stored on a hard drive of a digital oscilloscope. Presently, scanning is performed manually by moving the source and receiver tools in 1 cm (i.e., 2/3) intervals.

In our first experiment, the tank is packed with coarse sand and saturated with water. A lighter than water NAPL (n-dodecane) is injected from the bottom of the tank and allowed to finger upward. This distribution is analogous to the case of a denser-than-water NAPL (DNAPL) fingering downward. The tank is scanned before and after the NAPL injection. The acoustic visibility of the NAPL plume is determined by tomographic imaging using the recorded waveforms. The measured variation in P-wave velocity in the water-saturated tank due to packing heterogeneities

is on the order of 3%. Column measurements predict that the presence of NAPL will cause a 10% change in P-wave velocities, and as much as a 40% change in wave amplitudes. The imaged NAPL distribution is compared to the measured NAPL distribution obtained from the excavation of the vessel.

*Key words:* ?????????????

## **P27** DNAPL SOURCE ZONE CHARACTERIZATION USING A STOCHASTIC AGGREGATION MODEL

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DNAPL source zone characterization is important for risk assessments, feasibility studies and identification of appropriate remediation technologies. If sufficient DNAPL is released into the subsurface, it can penetrate the water table because of its relative density to water. When the DNAPL is also less viscous than water, an inherently unstable DNAPL-water displacement occurs. Descriptions of DNAPL source zones that accurately characterize these unstable pathways at the pore scale have as yet been unattainable with commonly used modeling techniques.

Stochastic aggregation models are a variant of diffusion limited aggregation model. These models have been used to model such unstable processes as dielectric breakdown diffusion-controlled polymerization, chemical dissolution processes, solute leaching, fluid-fluid displacement in Hele Shaw cells and viscous fingering in porous media. The authors of this paper have developed a stochastic simulation model for DNAPL source zone characterization. The proposed approach uses fluid properties, porous media properties and macroscopic flow rates as inputs. This paper will summarize the approach used compare model simulations to

two-dimensional laboratory flume experiments and discuss the advantages and disadvantages of this modeling approach.

*Key words: DNAPLs, site characterization, modeling, groundwater*

## Posters

### Golden Cliff

### Semi-Volatile Organics

## **P28 BIODEGRADATION OF PHENANTHRENE AND PENTACHLOROPHENOL IN CREOSOTE CONTAMINATED AQUIFER MATERIAL**

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The Champion International Superfund Site in Libby, Montana is a former wood preserving facility. It is among approximately 400 wood preserving waste contaminated sites in the U. S. The subsurface environment at the Libby site is contaminated with polycyclic aromatic hydrocarbons and pentachlorophenol due to accidental spills and improper disposal of waste preservative. In situ bioremediation is used to treat contamination in the upper aquifer at the site. The effects of temperature, sampling depth, nutrient addition and oxygen on the biodegradation potential of phenanthrene and pentachlorophenol in aquifer samples using radiolabeled chemicals were studied. Over a 56 day incubation period, 14% of the phenanthrene and less than 1% of pentachlorophenol were mineralized. There was no significant difference in phenanthrene mineralization at 10° and at 20° C. The annual average temperature the aquifer is approximately 10° C and the microbial community at the site are probably acclimated to this temperature. Average volatilization of phenanthrene and pentachlorophenol did not exceed 2%. The majority of the radiolabeled chemical was either solvent extractable or

soil bound following the 56 day incubation period.

*Key words: bioremediation, hydrocarbons, pentachlorophenol, phenanthrene, groundwater*

## **P29 ADSORPTION OF GROUNDWATER CONTAMINANTS UTILIZING MATRIX-ANCHORED ORGANOCLAY**

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Wood-preserving waste is a common groundwater contaminant; its components have been detected at a Montana Superfund site. In this study, groundwater from this site was used to investigate the ability of montmorillonite clay that was modified with cetyl pyridinium (CP/LPHM) to adsorb toxic chemicals present in highly contaminated water. Samples were prepared in accordance with EPA Method 3510B, then examined on GC/MS to determine the identity of contaminants as well as concentrations of PAHs and total petroleum hydrocarbons (TPH). This method was utilized to prepare samples which were treated with 0.5% w/w CP/LPHM in a batch process for 21 h and analyzed for a contaminant profile and concentrations of PAHs and TPH. Baseline pentachlorophenol (PCP) levels exceeded 10 ppm; in CP/LPHM treatment groups, PCP levels were non-detectable. Concentrations of those PAHs encountered in the baseline analysis showed a decrease in treatment groups; naphthalene levels were reduced from 261 (+ 5.4) ug/ml to 31 (+ 6.1) ug/ml. The concentration of TPH was reduced by 77%. An environmental concern in the use of CP/LPHM for water purification was the desorption of CP, the modifying cation. Using a 3 CP-sensitive Hydra bioassay, the NOAEL for CP was determined to be approximately 0.125 ug/ml and below. To diminish the release of GP, CP/LPHM and the base clay (LPHM) were chemically anchored and immobilized to a porous matrix.

Columns for water filtration were prepared using 200 mg of immobilized CP/LPHM, followed by an equal weight of immobilized LPHM as a polishing step. Effluent from the CP/LPHM columns alone was extremely toxic to Hydra. Using both CP/LPHM and LPHM columns, no adverse effects were observed. In further studies, the Chicken Embryo Toxicity Screening Test confirmed the reduction of toxicity of contaminated water following treatment with CP/LPHM. Matrix-anchored clays may facilitate inexpensive and field-practical purification of groundwater (supported by NIH P42-ES04197 and TAES H6215).

Key words: ??????????????

### **P30 VARIATION AMONG SIX PLANT SPECIES IN PHYTOREMEDIATION OF THREE SOURCES OF PETROLEUM HYDROCARBON CONTAMINATED SOILS**

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Phytoremediation utilizes plants to enhance the clean up of soils contaminated with hazardous chemicals. As a new remediation technology, little is known about the best plant species to use in the phytoremediation of petroleum hydrocarbon contaminated soils or whether similar species will be useful for many sources of contaminated soil. Petroleum hydrocarbon contaminated soils vary in the source of the contamination and the length contaminated soils have aged. Both of these factors are likely to affect the potential for plants to enhance dissipation of the contamination. It would be useful to determine plant species that are generally useful for phytoremediation under a variety of contamination conditions.

In a previous greenhouse study, we demonstrated variation among nine plant

species for their impact on hydrocarbon dissipation of a soil artificially contaminated with 0.5% crude oil. Tall fescue, Palmer amaranth, barley, and switchgrass were the four species with the highest degradation of total petroleum hydrocarbons in the study. As a follow-up study, these four species were selected for a second greenhouse trial utilizing three sources of contaminated soil: soil freshly contaminated with crude oil, aged diesel contaminated soil, and aged sediments contaminated with petroleum refinery wastes. We wanted to determine if plant species selected for dissipation of one source of contaminated soil will also work well for other sources of contaminated soil. Two additional plant species were included in the experiment along with an unplanted control treatment. The additional species' included lettuce variety 'buttercrunch' and sweet clover. Lettuce is used as a bioassay of the toxicity of contaminated soils and sweet clover is a nitrogen fixing legume.

The experiment was designed as a randomized complete block design with four replications. There were seven species treatments and three soil types. Lettuce was also planted in uncontaminated soil to make 22 total treatment combinations per replication. There were 84 total pots in the trial. Each pot of contaminated soil was also spiked with 100 ppm of phenanthrene to serve as a common contaminant marker in each pot. Seeds of each species were germinated in peat pots containing clean soil. One week after germination seedlings were transplanted to pots with the contaminated soil. A sample of each contaminated soil source was sampled and dried to determine concentrations of initial contamination. The greenhouse was maintained at 30C during the day and 20C at night with a 14-hour day-length. After four months of plant growth each pot was evaluated for plant height, aboveground biomass, and root biomass. The soil was separated from the roots, dried, and sampled to determine the concentration of total petroleum hydrocarbons.

Hydrocarbons were extracted in methylene chloride using a sequential shaking method. TPH was determined using GC analysis. Data were analyzed by analysis of variance.

*Key words:* ?????????????????

### **P31 EFFECTS OF PAHS ON MICROBIAL DIVERSITY IN FRESHLY CONTAMINATED AND WEATHERED SOILS**

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Soils contaminated with polycyclic aromatic hydrocarbons (PAHs) are of interest to the Environmental Protection Agency due to their carcinogenic nature. Bioremediation of PAHs is aimed at increasing the natural rates of degradation. Microbial bioremediation promotes the natural processes by which microorganisms can take up and/or degrade organic molecules and their metabolites. Microorganisms convert organic molecules to cell biomass and release products such as carbon dioxide and water to the environment. The changes in microbial biomass and CO<sub>2</sub> evolved are measured and used as indices of degradation. In situ bioremediation utilizes indigenous microorganisms and/or involves addition of microorganisms with specific enzymatic capabilities (such as enhanced oxidative functions) in order to establish conditions that favor microbial degradative activities. The overall goal of this study was to assess the effects of target PAHs, such as pyrene and phenanthrene, on spatial diversity of microbes and overall microbial activity. Comparisons of microbial diversity and activities between clean, freshly contaminated soils, and previously contaminated, weathered soils will be presented. Carbon substrate utilization is one estimate of microbial functional diversity used in this study. Phenotypic functional diversity will also be evaluated using the Biolog<sup>(R)</sup> assay system. Biodegrada-

tion rates of pyrene and phenanthrene in these soils, as well as, toxicity of pyrene and phenanthrene to microorganisms will also be discussed.

*Key words:* hydrocarbons, bioremediation, pyrene, phenanthrene, soil decontamination

### **P32 PHENANTHRENE DESORPTION KINETICS IN SOIL MEDIATED BY BACTERIAL EXTRACELLULAR POLYMERS**

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Bioavailability of Polycyclic Aromatic Hydrocarbons (PAH) in the environment is often limited by their low solubility and sorption to the solid surfaces. The purpose of this study was to quantify the effect of bacterial extracellular polymer on the desorption of a model PAH Phenanthrene in soil. The extracellular polymer produced by a bacterium isolated from soil (designated 9702-M4) has been employed in laboratory studies of the desorption kinetics. The soil isolate was selected based on a series of screening experiments in which the polymers of many different bacteria were evaluated for their ability to bind Phenanthrene. The experimental results show that the 9702-M4 extracellular polymer significantly enhances the rate of release of soil-bound Phenanthrene. A kinetic model was developed as an aid in interpreting the release rate alterations accomplished through polymer addition. The model employs a statistical array (i.e., a gamma distribution) to describe PAH mass transfer rates from soil to water, and assumes instantaneous binding of Phenanthrene to polymer and of polymer to the test soil. The relevant distribution coefficients and statistics for Phenanthrene desorption rates were determined in independent experiments. Using these measured parameters, the model

provides an excellent prediction of Phenanthrene release from soil to water at a polymer concentration of 50 mgTOC/L.

*Key words:* phenanthrene, desorption, kinetics, extracellular polymers

### **P33 EFFECT OF INORGANIC OXIDANTS ON PHOTOCATALYSIS OF 2-CHLOROBIPHENYL IN AQUEOUS SUSPENSIONS OF TITANIUM DIOXIDE**

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2-Chlorobiphenyl (2-CB) was decomposed photocatalytically in air-equilibrated aqueous TiO<sub>2</sub> dispersions under UVA-340 irradiation. The addition of inorganic oxidants such as H<sub>2</sub>O<sub>2</sub>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, and IO<sub>4</sub><sup>-</sup> increased the rate of 2-CB degradation in the following order: H<sub>2</sub>O<sub>2</sub> < IO<sub>4</sub><sup>-</sup> < S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. The apparent quantum yield increased quickly with the increase of H<sub>2</sub>O<sub>2</sub> concentration up to 10<sup>-2</sup> M. A decrease in rate enhancing effect per H<sub>2</sub>O<sub>2</sub> concentration was observed when H<sub>2</sub>O<sub>2</sub> concentration was higher than 10<sup>-2</sup> M. The presence of 10<sup>-2</sup> M H<sub>2</sub>O<sub>2</sub> remarkably expedited not only the initial 2-CB disappearance but also the degradation of the intermediates and CO<sub>2</sub> formation; the irradiation time needed for the complete mineralization was significantly shortened. The inhibition of electron and hole recombination by scavenging the photogenerated electron and the direct participation of the inorganic oxidants in 2-CB oxidation contributed to the rate enhancing effect. The additional homogeneous OH and other radical source as the result of oxidant addition were also responsible for the acceleration effects.

*Key words:* 2-Chlorobiphenyl, TiO<sub>2</sub>, photocatalysis, H<sub>2</sub>O<sub>2</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, KIO<sub>4</sub>

### **P34 BENZOTRIAZOLES: TOXICITY AND DEGRADATION**

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Benzotriazole and 5-methylbenzotriazole are heterocyclic compounds that contain three nitrogen atoms in a five membered ring. They are used in large quantity as corrosion inhibitors in antifreeze and airplane de-icing/anti-icing fluid, and it is mainly through this use that they become environmental contaminants. According to an EPA report, benzotriazole and methylbenzotriazole are of very low toxicity and low health hazard to humans, but they have a toxic effect in the aquatic environment. In addition, it is our observation that both benzotriazole and methylbenzotriazole are toxic to plants. There is a limited information on the fates of benzotriazole and methylbenzotriazole released into the environment. Due to their resistance to oxidation under environmental conditions and stability, it is believed that they will persist in the environment for a very long time. To date there is no evidence showing the biodegradation of benzotriazole and methylbenzotriazole. Investigation is underway to study the degradation of benzotriazole and methylbenzotriazole through chemical or microbiological approaches. Fenton reagent has been found to be able to degrade these contaminants.

*Key words:* benzotriazole, methylbenzotriazole, toxic, degradation, environment

### **P35 TOLORANCE TOWARDS EXPLOSIVES IN AQUATIC AND WETLAND PLANTS**

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Munitions material such as 2,4,6-trinitrotoluene(TNT) and hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX) and their combustion and decomposition products can enter the environment from production activities and field usage and disposal. The presence of these substances is of concern because of their potential toxicity and mutagenicity. Technology is sought to remove explosives from contaminated groundwater, and constructed wetlands are considered an option to perform this task. Plants to vegetate these wetlands are currently sought.

Toxicity of explosives to plants was investigated by determining dose-response curves under laboratory conditions. Toxicity of explosives was demonstrated to vary with parent compound and differed per plant species, with sensitivity varying no less for submersed than for emergent plants. Overall toxicity was highest for TNT, lowest for 2NT, and intermediate for 24DNT, 26DNT and RDX over the range of 0 to 40 mg L<sup>-1</sup> tested. Toxic effects became apparent during the third and sometimes during the fourth week of exposure. Toxicity of aqueous explosives to plants was influenced by irradiance (light vs darkness; presence of UV) and by manner in which plants were cultivated (hydroponic or planted in sediment).

*Key words: phytoremediation, nitroaromatics, aquatic macrophyte, groundwater*

### **P36 FEASIBILITY OF BIOAUGMENTATION OF Fe(0) WITH ANAEROBIC SLUDGE TO REMOVE RDX FROM SOIL AND GROUND- WATER**

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Careless disposal of RDX-laden waste from the manufacture of munitions at many sites across the country has created serious soil and groundwater contamination problems. In the past, the water used to wash RDX production equipment was often discarded into trenches or lagoons where contaminants were allowed to accumulate to very high levels in the soil and groundwater. RDX is very recalcitrant once it enters the environment, and clean-up is very expensive. RDX has been shown to cause unconsciousness and epileptiform seizures in workers exposed to RDX-laden air. A more serious toxicity problem associated with RDX may be its degradation products, some of which have been shown to be potent carcinogens and mutagens (e.g. 1,1- and 1,2-dimethylhydrazine, dimethylnitrosamine, and azoxymethane). Research conducted at the University of Nebraska has shown that treatment with Fe(0) can remove RDX from soil, and that indigenous microorganisms participate in the clean-up process. Our work corroborates that reductive treatment of RDX with Fe(0) might be a viable cleanup alternative, and suggests that this process can be significantly enhanced by bioaugmentation with anaerobic bacteria.

Batch reactors were prepared using 250 mL amber serum bottles capped with Mininert valves. Bottles were filled with 100 mL of an acetate-enriched anaerobic culture (250 mg/L VSS) and fed RDX at 12 mg/L. Five reactor sets were prepared in triplicate: sterilized (HgCl<sub>2</sub> poisoned) culture, sterilized culture plus Fisher Fe(0) powder (10g), viable culture alone, viable anaerobic culture plus hydrogen gas (15 mL at 1 atm), and viable culture plus Fe(0) powder. Reactors fed hydrogen gas were

used as positive controls to determine if the cathodic hydrogen (produced during anaerobic corrosion of Fe(0) by water) could serve as an electron donor for microbial reduction of RDX.

Following a 1.5-day incubation period, RDX was significantly removed in all reactors containing either viable culture or Fe(0), but not in Fe(0)-free sterile controls. Residual RDX concentrations in reactors prepared with viable bacteria or Fe(0) alone were between 2 and 5 mg/L. Yet, no RDX was detected in reactors amended with both viable bacteria plus Fe(0). Interestingly, HPLC analysis (W detector ~254 nm) found heterocyclic metabolites (e.g., TNX, DNX, and MNX) in reactors prepared with viable bacteria or Fe(0) alone. However, no metabolites were detected in reactors amended with both viable bacteria plus Fe(0), suggesting that a more complete degradation of RDX (beyond ring fission) occurred. This suggests that the combination of Fe(0) and anaerobic bacteria offers significant advantages over approaches where either process is used alone. Specifically, this combination might be synergistic in terms of enhancing both the rate and extent of RDX transformation. Therefore, bioaugmentation of Fe(0) barriers might be a valuable tool for the control of RDX-contaminated groundwater.

*Key words: RDX, bioaugmentation, iron*

### **P37 A COLORIMETRIC METHOD FOR THE ON-SITE DETERMINATION OF 2,4,6-TRINITROTOLUENE (TNT) IN SOIL**

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Evaluating TNT contamination in soils from field sites, using standard laboratory analytical methods, is lengthy, slow, labor-intensive and expensive. Colorimetric and immunoassay methods have proven to be

effective for on-site analysis of TNT and other munitions. Commercially available colorimetric methods for TNT are based on the procedure developed by Jenkins and Walsh. This procedure is not selective for TNT, but is broadly class sensitive, responding to a variety of polynitroaromatics. Researchers at Enviroil, Inc. (North Logan, UT) have modified the procedure developed by Jenkins and Walsh to produce a field soil test system that is specific for TNT. In the Enviroil TNT test system, the colorimetric reaction yields a peak at 630 nm that can be used to detect and quantitate TNT. With the modification, no peaks were observed above 600 nm for 2,6-dinitrotoluene, m-dinitrobenzene, 1,2-dinitrobenzene, 2-amino-4,6-dinitrotoluene, 4-amino-4,6-dinitrotoluene, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Analysis of field-contaminated soils showed that concentrations of TNT determined using the modified test system were comparable with standard laboratory analytical methods. Test systems based on the unmodified Jenkins and Walsh method exhibited positive interference in the presence of 2,4-dinitrotoluene or other nitroaromatic compounds. This interference was not observed with the new TNT-specific field test. Standard quality control procedures were used to characterize the performance of the Enviroil TNT test system. The method detection limit for the Enviroil test system is 2.4 mg/kg TNT in soil with a dynamic range up to 100 mg/kg TNT. Accuracy and precision for the analysis of TNT in soils were comparable to standard laboratory methods. This new field test method for TNT adequately fulfills the requirements set by the U. S. Environmental Protection Agency for field methods and is suitable for use in the specific analysis of TNT contaminated soils.

*Key words: 2,4,6-trinitrotoluene, field method, validation, soil*

## Posters

### Golden Cliff

#### Volatile Organic Contaminants

## P38

### SIMULTANEOUS FIELD SITE WATER WELL SAMPLING OF DISSOLVED HYDROGEN, METHANE, AND VINYL CHLORIDE

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A groundwater sampling technique was devised for determining concentrations of the biodegradation process components hydrogen, methane, and vinyl chloride. The technique will be used to assay fieldsite monitoring wells.

Method development studies in the laboratory involved pumping water from a reservoir through a nearly filled 250 mL glass gas sample bulb with a 20 mL headspace. When equilibrium was attained between the water and headspace, aliquots of the headspace were collected into gas-tight syringes. The aliquots were then analyzed by gas chromatographic techniques. Concentrations as low as 10 ppb or less could be detected for all three dissolved gases using this method.

Laboratory data will be presented on the influence of water flow rate, headspace volume, water temperature, equilibration time, and differential pressure between the headspace and the ambient atmosphere. A description and diagrams of the sampling apparatus will be presented.

*Key words: groundwater sampling, biodegradation, monitoring wells, gas chromatography*

## P39

### SORPTION OF TRICHLOROETHYLENE AND OTHER HALOGENATED ALIPHATICS ON AND IN PLANT MATERIALS

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One concern in plant based bioremediation of chlorinated aliphatic contaminants is the possibility of intermedia transfer. The extent of transfer of trichloroethylene (TCE) through plants and the possibility of its metabolism within plants are points of debate at present. Recently we showed clearly that at high concentration, TCE does move through plants with a transpiration stream concentration factor consistent with its octanol-water partition coefficient (Davis et al, J.Haz. Mat. Res, 1998). Evidence will be presented to indicate that the plant behaves like a capillary chromatography column with a fixed capacity. Thus at low concentrations of TCE in the root zone, the contaminant is sorbed to organic material within the plant, until the binding capacity is exceeded, at which time the contaminant breaks through and is released from the plant to the atmosphere in the transpiration stream. The octanol-water partition coefficient is greater than 100 and the binding capacity is large so that very large volumes of slightly contaminated water may pass through the plant without breakthrough. A similar situation is likely to pertain to other strongly sorbed materials. Effective systemic agrochemicals may be exceptions to the more general sorption phenomenon.

*Key words: ???????????????*

## **P40 PHYTOREMEDIATION OF TRICHLOROETHYLENE: A FIELD EVALUATION**

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Reports of both insignificant and significant plant uptake, transpiration and/or degradation of TCE have appeared in the literature. Most of these results have come from laboratory studies.

The objective of this poster is to present the results of an Air Force Center for Environmental Excellence sponsored study designed to determine if mature trees and shrubs are involved in the uptake, transpiration and/or degradation of TCE from a shallow contaminated groundwater plume located at Ordnance Support Facility 1381 at Cape Canaveral Air Station (CCAS), Florida. Dissolved-phase TCE concentrations in the vicinity of the vegetation ranged from 414 to 90,500  $\mu\text{g/L}$ . Three representative plant species identified near the plume were studied: live oak, castor bean and saw palmetto. Portable flow-through chambers were used to collect transpirational gases for TCE analysis by GC/ECD and/or GC/MS. Plant tissue samples (leaves, stems and roots) were also collected and analyzed for TCE and its reported metabolites (2,2,2-trichloroethanol [TCEt], 2,2,2-trichloroacetic acid [TCAA] and 2,2 dichloroacetic acid [DCAA]) identified in previous laboratory studies. To better understand the fate and transport of TCE in the plant/soil system, groundwater and soil samples were also collected and analyzed for TCE and its potential metabolites. In addition, soil gas and surface flux measurements were collected to quantify the amount of TCE volatilizing directly from the soil surface.

TCE efflux from the live oak leaves averaged 9  $\mu\text{g}$  per liter of water transpired. TCE efflux from the other two species was significantly lower or not detected. Extrapolat-

ing to a typical transpiration rate during the entire growing season the TCE efflux from the leaves would be a maximum of 9  $\mu\text{g}$  per  $\text{m}^2$  per year. The average TCE efflux from the soil surface was determined to be 43  $\mu\text{g}$  per  $\text{m}^2$  per year. The concentrations of TCE and metabolites ranged from below detection limits to 1100  $\mu\text{g}$  per kg (dry weight) of plant leaves for the 3 species studied. The potential impact of plants on the remediation of TCE at this site will be discussed.

*Key words: TCE, plants, uptake, transpiration, degradation*

## **P41 PHYTOREMEDIATION OF TRICHLOROETHYLENE USING HYBRID POPLARS: NON-STRESSED VS. STRESSED UPTAKE**

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Trichloroethylene (TCE) is a common groundwater due to its widespread use in degreasing operations. Phytoremediation, the use of plants and their associated microbiota to take up, sequester, and degrade environmental contaminants, may be a cost-effective alternative to current remediation strategies. Both significant and insignificant uptake and degradation have been reported in the literature. Most of these results were obtained in laboratory studies using  $^{14}\text{C}$ -labeled TCE. Mass recoveries ranged from 43 to 85%. Possible reasons for the varying results include: system leaks, plant age, and increased membrane permeability caused by plant stress. Plant stress may be caused by high root zone TCE concentrations, co-solvents used in dosing, or anaerobic root environments. Using growth chambers specifically designed for high mass recoveries and precise environmental control, Imperial Carolina hybrid poplar trees (*Populus deltoides* x *nigra*, DN34) were

exposed to a root zone solution of 1 ppm TCE over a 10-day period. Uptake, transpiration, and mineralization of  $^{14}\text{C}$ -labeled TCE were measured under non-stressed (aerobic root zone) and stressed (anaerobic root zone) hydroponic plant growth conditions. Recoveries of  $^{14}\text{C}$ -labeled TCE were greater than 95%. Initial results indicate little uptake ( $<0.05\%$ ) and some measureable rhizosphere mineralization (1%) under non-stressed conditions.

*Key words: trichloroethylene, phytoremediation, degradation, mineralization, plant uptake*

## **P42** DESIGN OF A PLANT GROWTH CHAMBER FOR STUDIES ON THE UPTAKE OF VOLATILE ORGANIC COMPOUNDS

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Both significant and insignificant uptake of volatile organics have been reported in the literature. Discrepancies may be attributed to differences in growth chamber design. Mass balance recoveries for  $^{14}\text{C}$ -labeled TCE have ranged from 43 to 85%. We have designed and implemented a high flow, sealed growth chamber that provides mass recoveries greater than 95%, complete separation between root and foliar uptake, and a favorable plant environment. Root and foliar chambers are separated by both a physical seal and by a pressure differential (10 inches of water) to prevent the volatilization of organics from the root chamber to the foliar chamber. The root and shoot chambers are each 0.5m long to accommodate plant growth during long-term studies. High flow rates present difficulties in the trapping of volatile organics and are thus seldom incorporated into system designs. Our design provides continuous high flows (5-10 L/min) in the foliar chamber to prevent high humidity

caused by transpiration. Traps were designed and evaluated to efficiently capture volatile organics and  $\text{CO}_2$  at these high flow rates. Continuous flow (0.02-0.05 L/min) through the root zone environment enables us to dose the system via the inlet gas stream, ensures mixing of the contaminant, and continuously replenishes root zone  $\text{O}_2$ . A favorable plant environment is crucial in uptake studies. Stressed plant roots may be more permeable to organics. In addition, excessive humidity levels in growth chambers cause reductions in transpiration and may reduce contaminant uptake. Plants in this system exhibit normal transpiration levels (approximately 100 mL/day) and grow rapidly throughout the experimental period.

*Key words: growth chamber, organics, uptake, phytoremediation, trapping*

## **P43** REMOVAL OF VOCs FROM GROUNDWATER USING AIR-SPARGED HYDROCYCLONE STRIPPING TECHNOLOGY

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The air-sparged hydrocyclone (ASH) technology offers the unique opportunity to achieve efficient removal of volatile organic compounds (VOCs) from contaminated water at a high specific capacity, many times that of conventional air stripping technologies. Originally developed for the fast and efficient flotation of fine particles from suspensions, VOC stripping is the first application of the ASH as a contacting reactor rather than a flotation device. The effectiveness of the ASH system for this application has been demonstrated through a number of laboratory and field experiments which indicate the ASH technology to be competitive with other conventional stripping technologies in areas including removal efficiency, capacity, and resistance to biological and inorganic fouling.

Prior to late 1997, ASH stripping technology had been tested and proven only in the

University of Utah pilot plant. Then in November-December 1997, the first stage of field testing took place at the Tooele Army Depot north site. The site, which has approximately 38 billion gallons of trichloroethylene (TCE) contaminated groundwater, is currently being treated via two packed column air strippers at a rate of 7500 gpm. Up until that time, it was uncertain whether the ASH system would provide positive results under actual field conditions, where VOC removal capabilities had the potential to be affected by varying contaminant concentrations, groundwater chemical makeup, and ambient air temperatures. Objectives of the first phase of field testing were to determine the feasibility of using the ASH technology for removal of VOCs from groundwater under actual field conditions and to compare the effectiveness of the ASH technology to packed column stripping technology in use at the site. Plausibility of biological and/or inorganic fouling of ASH system components was also examined.

Preliminary results of the first phase of field testing show that treatment using a 2-stage ASH system has a removal efficiency comparable to a packed tower air stripper (>96%), but requires an operating space many times less. As a result, preliminary estimates show that a significant savings in capital costs are possible. Or, alternatively, a considerable reduction in clean-up time could be projected for a system of larger capacity, ultimately reducing long-term operation and maintenance costs. Additionally, site specific services for small volume flows could be provided with a compact mobile system. Although the potential for fouling of the ASH system components over long-term operation remains uncertain at this time, initial observations indicate that control of hard-scale build-up has the possibility to be less problematic than with traditional aeration techniques. There is, however, a need for more long-term field testing to confirm this observation.

*Key words: air-stripping, VOCs, hydrocyclone*

## **P44 USING VEGETATION TO TREAT METHYL-TERT-BUTYL ETHER CONTAMINATED GROUNDWATER**

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Methyl-tert-butyl ether (MtBE) is a commonly used gasoline additive as an octane enhancer. Leaking underground storage tank systems and pipelines for gasoline products are the causes of reported groundwater contamination with MtBE. The role of vegetation in limiting MtBE plume transport in groundwater was experimentally examined. The experimental system consists of six channels, five of them are planted with alfalfa plants and one is unplanted to allow an investigation of the impact of vegetation. MtBE solution of 0.844mM was continuously fed into each channel at 1 L/day for two months, then the feeding was switched back to distilled water. The channel groundwater effluent MtBE concentration and the soil gas MtBE fluxes were monitored. Alfalfa plants appear to help control the MtBE plume. The experimental results from planted channels and the unplanted channel will be compared.

*Key words: MtBE, groundwater, vegetation*

## Posters

### Golden Cliff

#### Metals/Radionuclides/Inorganics

## P45 HERS SUPPORTS CONNECTION BETWEEN TECHNOLOGY AND NATIVE AMERICAN COMMUNITIES

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The Haskell Environmental Research Center works to facilitate the exploration of environmental issues and technology relevant to American Indian communities. HERS, based at Haskell Indian Nations University (HINU), administers several programs to stimulate the involvement of American Indians in these areas. Two of these programs are the Haskell Environmental Seminar Series and the Technical Outreach Services for Native American Communities (TOSNAC) Program. The goal of the Haskell Environmental Seminar Series is to produce a series of seminars primarily for audiences at Haskell Indian Nations University (HINU) and other American Indian Higher Education Consortium (AIHEC) colleges and universities. This project provides technical information to students, faculty, and tribal environmental professionals throughout the U.S. using quality videotaped seminars and to students and faculty at HINU through traditional seminars on campus. The TOSNAC Program works to provide university educational resources to individuals, community groups and environmental programs in tribal communities affected by hazardous substance contamination issues. The TOSNAC program provides tribal nations with access to technical information via informational brochures, fact sheets, and technical summaries. In addition, TOSNAC personnel travel to tribal nations to provide Native American communities with workshops, hands-on assistance and personal, expert assistance. The TOSNAC program

draws upon resources at HERS, HINU, and the HSRC Consortium when providing technical assistance and education to tribal nations. In addition, the incorporation and support of AIHEC science and technical resources is utilized when possible.

*Key words: Native American, minority, research, technology transfer, hazardous substances*

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