FACT SHEETS

This section includes Fact Sheets highlighting EMSP Science Categories and associated Work Packages. These Fact Sheets were selected as part of an evaluation that focused primarily on the projects in the EMSP portfolio that were in more mature stages of development.

The Facts Sheets contained herein highlight 1999 EMSP-funded research projects; the original release date appears in the header of each individual Fact Sheet.

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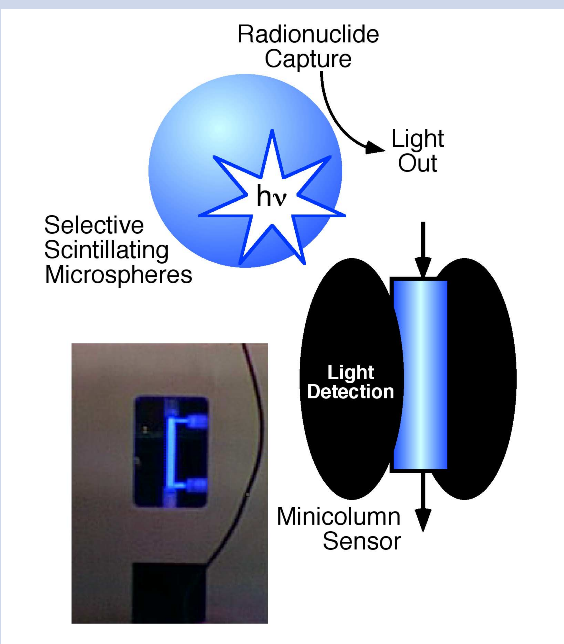
ANALYTICAL CHEMISTRY AND ACTINIDE CHEMISTRY

LEADING ACADEMIC AND NATIONAL LABORATORY SCIENTISTS IN THESE DISCIPLINES ARE PARTICIPANTS IN EMSP PROJECTS

Three 1999 EMSP projects have involved development of new analytical techniques for identification of contaminants in the field. Two other projects have focused on the chemistry of actinides in the environment.

Some of the leading groups researching analytical chemistry and instrumentation are involved in the three EMSP projects in this area. A novel system for detection of alpha- and beta-emitting radionuclides has received widespread notice in the analytical chemistry community, and continued development of the method is underway in one project. A second project involves a combination of selective surface coatings, electrochemistry, and spectroscopic detection to make a new, fieldable sensor for pertechnetate ions. A third project involves a diverse group of researchers from both universities and national laboratories who are working to develop a highly sensitive spectroscopic technique, i.e., resonant enhanced multiphoton ionization, into a field-deployable instrument for detection of organic compounds not easily determined by other means. If such a highly sensitive detector could be deployed with a cone penetrometer, the speed and accuracy for dense nonaqueous phase liquid (DNAPL) determinations could be improved by orders of magnitude over currently available techniques.

Both actinide chemistry projects are working to develop a more thorough understanding of the factors that could affect plutonium transport in the subsurface. One study has involved experimental determinations of plutonium species in the groundwater at Hanford and Savannah River and will illuminate the role that colloids play in plutonium transport. Another effort is directed toward understanding the role of manganese minerals in sequestering transuranics.



Selective Scintillating Microspheres for Analysis of Radionuclides

A Pacific Northwest National Laboratory/Clemson University group (70179) has developed a novel system for detecting radionuclides such as strontium-90, technetium-99, and actinides. The system is based on development of selective scintillating microspheres (SSMs).

PROBLEMS/SOLUTIONS

- As described in STCG Needs Statement OH-F004, laboratory analysis for technetium-99 in soil presently takes three days, and a need exists for an analyzer that can measure ^{99}Tc in the field and give results in a few hours. Two EMSP projects are directed toward solving this need, and one system has already been shown to detect ^{99}Tc in water at levels below the drinking water limits.
- Plutonium and actinides in groundwater can have widely varying transport properties that are dependent on distribution into colloid, particulate, and solution phases. One EMSP actinide chemistry project is providing detailed characterizations of the forms of plutonium present in Savannah River Site and Hanford groundwater so that more reliable predictions can be made about future migration patterns.

ANTICIPATED IMPACT

- The need for long-term monitoring at U.S. Department of Energy (DOE) waste sites was described in *Long-Term Institutional Management of U.S. Department of Energy Legacy Waste Sites* (National Academy of Science, 2000) where it was noted that relatively few sites will be cleaned up to the point where they can be released for unrestricted use. Conventional sampling followed by laboratory analyses could present very large cumulative expenses, so new techniques of the type being developed in several EMSP projects could have very large impacts on expenditures for long-term monitoring.
- There are known to be more than 5,000 DOE groundwater plumes, which have in total contaminated more than 600 billion gallons of water and 50 million cubic meters of soil. Because many of these sites will require long-term monitoring by sensitive analytical techniques, continued improvements in sensitivity and portability of monitoring instruments can result in large savings over the monitoring lifetime.

Technical Summary and Progress

Analytical Chemistry

A New Sensor for Pertechnetate Ions. A University of Cincinnati/PNNL group (70010) is developing a sensor for technetium based on the general concepts that they used in a previous project (54674). To be detected, a species must first be incorporated into a film that is coated onto an optically transparent electrode. Then it must be reduced under the conditions used for an electrochemical process. Finally, the species formed by the electrochemical reduction must form a complex that absorbs light at the wavelength used for the optical detection. The research effort for this project is directed at developing the surface coatings, electrochemical conditions, and complexing agents that will enable a sensitive detection of pertechnetate. The goal is to be able to detect pertechnetate ions in the vadose zone without the elaborate sampling and separation procedures used for conventional analyses.

Selective Scintillating Microspheres for Analysis of Radionuclides. A PNNL/Clemson University group (70179) has developed a novel system for detecting radionuclides such as strontium-90, technetium-99, and actinides. The system is based on development of selective scintillating microspheres (SSMs). Thus, a minicolumn containing the bead materials is used to selectively bind the analyte. The SSMs, however, also contain scintillating materials that emit light when an alpha- or beta-emitting substance is on a nearby location in the bead, and a photomultiplier or diode sensor can then be used to detect the emitted light. A system designed for detecting technetium-99 was described in a paper in *Analytical Chemistry* that shows that the detection limit was 10 picograms per milliliter (below the maximum permissible drinking water level). Development continues on systems for selective detection of strontium-90 and actinides.

A Fieldable, Sensitive Technique for Detection of Organic Compounds. High-intensity visible light can be used to drive a molecular system through intermediate electronic states to a final state in which the molecule is ionized. Because ions can be detected with very high efficiency, this resonant enhanced multiphoton ionization (REMPI) process provides a sensitive analytical method. The goal of a University of South Carolina/LLNL project (70050) is to develop the REMPI technique using visible lasers for determination of compounds not easily detected by other methods. An objective is to develop a system for measuring and identifying volatile organic compounds (such as carbon tetrachloride, trichloroethylene, toluene, etc.) at parts-per-billion (ppb) levels *in situ* in the subsurface using a fiber-optic REMPI probe in a cone penetrometer. They have already demonstrated measurements of toluene at 1.5 ppb with a linear calibration curve for concentrations over a three-orders-of-magnitude range.

Actinide Chemistry

Speciation and Mobility of Actinides in Groundwater. The objective of a Woods Hole Oceanographic Institute/PNNL project (70132) is to gather fundamental data essential for predicting the migration of plutonium in an aqueous environment. In a previous project (54683), they developed special procedures for groundwater sampling that made it possible to separate plutonium into particulate, colloids, and dissolved phases. They determined isotopic ratios using the high sensitivity of thermal ionization mass spectrometry and showed that Pu in Savannah River Site (SRS) groundwater originates from both weapons-grade Pu and from a more mobile curium precursor. Most of the Pu at SRS is in an oxidized form that is more mobile than most standard models predict. Current work involves extensive sampling at the Hanford site in order to assist in the prediction of the migration potential. The main focus remains on identifying the Pu species present at Hanford, the mobility of these species, and the role that colloidal materials play in Pu transport.

Reactions of Transuranics on Manganese Oxide/Hydroxide Minerals. Manganese oxides, which are minor phases in the vadose zone, may preferentially sequester transuranics over iron oxide minerals. Thus, the objective of a LBNL/PNNL project (70176) is to provide information about the interactions of plutonium and neptunium with manganese-containing minerals. Sorption experiments performed with dilute solutions of Pu(VI and V) on various manganese minerals found that these minerals have a very large sorption capacity for plutonium under neutral or slightly basic conditions. The thermodynamic and kinetic parameters for the sorption on various manganese minerals will be used as input for reactive transport modeling of transuranics in the vadose zone.

Project Teams

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  Pacific Northwest National Laboratory
- University of South Carolina
  PI: S. Michael Angel (70050)
  Lawrence Livermore National Laboratory
- Woods Hole Oceanographic Institute
  PI: Ken O. Buesseler (70132)
  Pacific Northwest National Laboratory
- Lawrence Berkeley National Laboratory
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  Pacific Northwest National Laboratory
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ENGINEERING SCIENCE AND PLANT SCIENCE

Basic research in environmental engineering and plant science can contribute to practical remediation techniques/procedures

This fact sheet summarizes three 1999 EMSP projects that involve engineering science and one project classified as plant science. One of the environmental engineering projects involves a study of a process for the immobilization of chromium and other metals. The process involves the injection of gaseous hydrogen sulfide into the subsurface where it can reduce the soluble and mobile form of chromium, Cr(VI), into an insoluble and therefore less hazardous form, Cr(III). Details of this reaction in the presence of all the complexities presented by subsurface minerals are being studied in this project.

Two other engineering science projects are related to remediation of dense nonaqueous phase liquids (DNAPLs) in the subsurface. Surface vapor extraction has been used at several sites for removal of DNAPLs, and one project aims to understand factors that limit DNAPL removal rates with the goal of improving the efficiency of this technique. The second project is exploring the role that biologically produced surfactants may have in DNAPL mobility. Although this issue has been raised before, the subject has not been well studied. Identification and characterization of the role of these surfactants may be needed to develop more reliable DNAPL fate and transport models.

The plant science project is a continuation of a previous project in which it was demonstrated that native trees, shrubs, and grasses could be bioengineered to convert mercury into less hazardous forms. These plants thrive under conditions that would kill normal plants and may provide a more efficient, less costly method for removing mercury from surface soils.

Role of Surface-Active Materials on DNAPL Migration
A Clarkson University/Westinghouse Savannah River Company project (70035) sampled DNAPL– contaminated soil to better understand interrelationships affecting accumulation of DNAPL as a function of grain size, moisture content, and microbial activity in the vadose zone.

Problems/Solutions

- An STCG Needs Statement (RL-SS25-S) notes that "additional information is…needed about the role of surfactants and other agents on the basic physical properties (solubility, interfacial tensions) of NAPLs or dissolved organics and how these relations can be exploited to mobilize such contaminants." The goal of one EMSP project is to provide this information using both laboratory studies and field studies using core samples from a DNAPL plume at Savannah River Site.
- The removal of low, but hazardous, levels of mercury and other heavy metals from soils by traditional physical and chemical procedures can be very expensive. An EMSP project has worked on incorporating bacterial genes into native plants and trees so that they can accumulate mercury. These plants are able to thrive on levels of mercury that would kill normal plants, and they may provide an inexpensive means to concentrate mercury from surface soils.

Anticipated Impact

- A report of the National Research Council, *Research Needs in Subsurface Science* (March 2000), had on its cover an image of the mercury contamination in soil at the Y-12 plant at Oak Ridge, illustrating the importance of this problem. That report also cited the need for basic research focused on reactions for immobilization of hazardous metals in the subsurface. Both of these issues are being addressed by EMSP projects.
- In *Accelerated Cleanup – Paths to Closure*, nine of the ten U.S. Department of Energy (DOE) Operations Offices cited DNAPL contamination as a major concern. More reliable predictions of DNAPL migration are essential for decision-making regarding remediation expenditures, and existing remediation strategies need to be improved. Both of these needs are addressed by EMSP projects.

Engineering Science

Immobilization of Metals by Reactions with Hydrogen Sulfide. Many metal ions form insoluble sulfides when exposed to hydrogen sulfide, H_2S, and the injection of gaseous H_2S into the subsurface has previously been suggested for immobilization of various hazardous metal ions. Chromium(VI) can also be reduced with H_2S to form chromium(III), which is not mobile, and a New Mexico Institute of Mining and Technology/PNNL project (70088) is focused on this process as a potential remediation technology. Some issues being addressed in laboratory studies include the effect of mineral surfaces on the rate of reduction of Cr(VI) as well as on the oxidation of H_2S by air, reactions of other soil minerals that could consume the H_2S, the long-term stability of Cr(III) species that are formed, and the effects of various soil water chemical compositions on the reduction reactions. Tests are also being conducted with Hanford soil samples to define reaction parameters for the Cr(VI)-H_2S-oxygen-soil system, and long-term oxidation tests will be conducted to ascertain the stability of the reduced chromium.

Project Teams

Lead Principal Investigator (Award Number)

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  Westinghouse Savannah River Company
- University of Illinois–Urbana-Champaign
  PI: Albert Valocchi (70045)
- University of Georgia
  PI: Richard B. Meagher (70054)
- New Mexico Institute of Mining & Technology
  PI: Baolin Deng (70088)
  Pacific Northwest National Laboratory

Factors that Limit the Effectiveness of Soil Vapor Extraction. Soil vapor extraction (SVE) is commonly used to remove DNAPLs from the vadose zone, but frequently a period of high recovery has been followed by a long period of low recovery. The research in a University of Illinois project (70045) aims to determine the processes that limit the removal of DNAPLs in heterogeneous porous media during SVE. Using magnetic resonance imaging, they can identify the location and size of individual pores containing DNAPLs, water, and vapor in flow-through columns filled with either model or natural sediments. Imaging results will be used along with modeling techniques to describe the transient distribution of phases as a function of time and location. These relationships will be used in a transport model to evaluate how different processes affect SVE performance in practical applications.

Role of Surface-Active Materials on DNAPL Migration. As anyone who has used a detergent knows, a small amount of a surfactant can have large effects on the interactions between dissimilar substances, i.e., oil and water. It would thus be reasonable to expect that surface-active chemicals present in the vadose zone could have a considerable effect on the migration of water-insoluble organic compounds, such as those classified as DNAPLs. Surface-active materials can be produced through microbial metabolic processes, and the goal of a Clarkson University/WSRC project (70035) is to understand the effects of various interfacial phenomena on the accessibility and migration of DNAPLs in the vadose zone. One objective is to identify the presence of surface-active materials and to quantify interfacial properties in an actual DNAPL plume at Savannah River Site. Other objectives include identifying how DNAPL–metabolizing cultures affect interfacial properties and quantifying the effects of DNAPL surface chemistry on flow in the vadose zone.

Plant Science

Phytoremediation of Mercury Pollution. A University of Georgia project (70054) is continuing work from a previous project (54837) to demonstrate that native trees, shrubs, and grasses can be engineered for remediation of mercury-contaminated sites. This group has engineered several plants to express two bacterial genes, *merB* and *merA*. Plants expressing *merA* extract and reduce ionic mercury to metallic mercury, which is transpired from the leaves. Those expressing *merB* extract highly-toxic methylmercury from the soil and degrade it to ionic mercury, and these plants are able to grow on concentrations of methylmercury that would kill normal plants. Plants expressing both *merA* and *merB* extract methylmercury and transpire metallic mercury. Current work is focused on obtaining a detailed understanding of the mechanisms by which these plants process the various forms of mercury in order to improve phytoremediation designs. In addition, attempts will be made to produce plants to accumulate mercury so that it can be removed by harvesting the plants rather than by vaporizing it into the environment.

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GEOCHEMISTRY AND BIOGEOCHEMISTRY

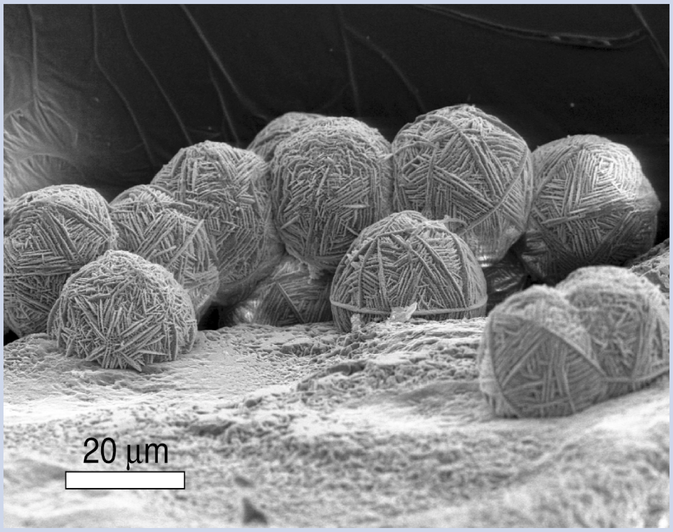
A THOROUGH UNDERSTANDING OF THE INTERACTION OF CONTAMINANTS WITH MINERALS IS ESSENTIAL FOR FATE AND TRANSPORT MODELING

Modeling of the fate and transport of radionuclides in the subsurface requires an understanding of the complex interactions among the numerous forms of radionuclides with the complex components of the vadose zone. Many 1999 EMSP projects are exploring issues related to contaminant transport. The subject of one study is how the migration of materials that leak from high-level storage tanks may be altered by changes caused by previous leaks, while the effects of subsurface reactions with highly alkaline solutions on immobilization of radionuclides is the focus of another project. Detailed characterizations of the interactions of radionuclides with calcium carbonate and with altered clay surfaces are the focus of several studies. Another is working on the thermodynamics of complexes formed by radionuclides in highly basic solutions. Technetium is of particular concern because it is easily oxidized to the highly soluble and mobile pertechnetate form, and another study is investigating reactions in the vadose zone that may reduce the pertechnetate to less mobile forms.

When precipitates are formed from solutions, they often trap other ions that would otherwise remain in solution. This method for removing radionuclides from solution has been employed since the earliest days of radiochemistry, and an EMSP project is investigating a process to form calcium carbonate precipitates in aquifers for *in situ* remediation of strontium-90 and other radionuclides.

One group is working on understanding the biological mechanisms involved in the reactions of a microorganism that can convert high concentrations of chlorinated hydrocarbons in the subsurface into less hazardous materials. The focus of another project is to develop an understanding of the vadose zone characteristics that encourage the growth of the same strain of bacteria.

Influence of Previous Tank Leaks on Migration of Subsequent Leaks



A University of Colorado/PNNL project (70070) is focused on obtaining a mechanistic understanding of how fluids that have leaked from Hanford single-shell tanks migrate through the vadose zone. Left: Nitrate cancrinite crystals formed on dissolving quartz grains after 13 days at 89°C from simulated waste tank solutions with pH 11.3, 2.1 molal sodium nitrate, and 0.01 molal aluminum. The ball-like precipitates cemented quartz grains together. Nitrate cancrinite is a zeolite-like phase that can incorporate cations such as cesium or strontium in its structure.

PROBLEMS/SOLUTIONS

- According to an STCG Need Statement (RL-WT053-S), “The current understanding of the mobility of contaminants from single-shell tank leaks…is inadequate to fully support cleanup, closure, or performance assessment-related decisions. Without knowledge about the distribution of contaminants beneath the tank farms, and without the ability to predict contaminant movement, it will be impossible to assure the public that the U.S. Department of Energy (DOE) can predict the impact of leaks during sluicing and the impact of leaving the tanks in place.” Seven projects are addressing issues directly related to this need.
- As stated in an STCG Need (ID-S.1.10), “Geochemistry of Contaminants in the Vadose Zone,” no correlation between substrate properties, solution chemistry, and the measured adsorption constant values has been determined for the vadose zone at most sites. Thus, the smallest available adsorption constants for binding radionuclides to minerals are used in predictive models to compensate for the lack of theoretical understanding. This may result in undertaking unnecessary remedial actions. Several EMSP studies are measuring binding constants of radionuclides to a variety of minerals relevant to this issue.

ANTICIPATED IMPACT

- Effective biodegradation of chlorinated hydrocarbons has advantages over physical removal methods in cost, speed, public acceptance, and final cleanup levels achieved. Several projects are focused on explorations of conditions that favor the use of biodegradation techniques.
- Sixty-seven of the single-shell tanks at Hanford are thought to have leaked a total of up to a million gallons of highly alkaline fluids containing substantial quantities of radionuclides into the subsurface. Most of the 1999 EMSP projects are exploring issues related to the migration of contaminants in the subsurface so that future remedial actions can be based on sound scientific knowledge.

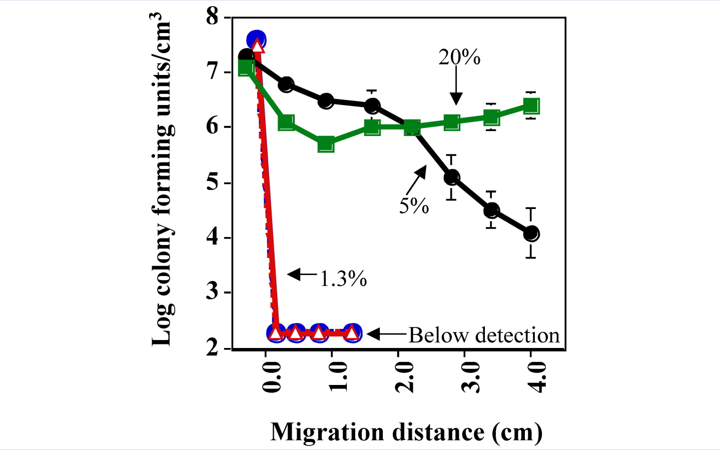
Characterization and Modeling of the Properties of the Vadose Zone

Influence of Previous Leaks from Tanks on Migration of Subsequent Leaks. Transport of the high ionic strength, high pH solutions through the vadose zone is dependent not only on the initial subsurface characteristics but also on chemical reactions from previous leaks that may have altered the properties of the subsurface. A University of Colorado/PNNL project (70070) is focused on obtaining a mechanistic understanding of how fluids that have leaked from the Hanford single-shell tanks migrate through the vadose zone. The first goal is to obtain kinetic rate laws for the dissolution of quartz and feldspar, as well as the precipitation of secondary phases, when tank liquids contact them. They will attempt to obtain an understanding of the nucleation mechanisms, nucleation sites on soil minerals, and the role of reactive surfaces on dissolution and precipitation reactions.

Transport of Radionuclides in Subsurface Solids Impacted by Alkaline Tank Fluids. An Ohio State University/PNNL/Stanford University project (70081) is directed toward understanding how the most common radionuclides might become immobilized in the subsurface solids that have been impacted by alkaline tank fluids. The effect of aging on the stability of complexes on solids formed from neutralization and nucleation of alkaline aluminate solutions is being investigated, and the sorption or co-precipitation of various radionuclides in the solids formed by reactions of alkaline aluminate solutions with various minerals and with Hanford sediments is being studied. They also plan to use a variety of modern instrumental methods to characterize the chemical forms of the species present in actual core samples taken from underneath the SX-108 tank.

Sorption of Cesium and Strontium on Altered Clay Surfaces. The focus of a Pennsylvania State University/BNL/PNNL (70126) project is on the extent of sorption and release of cesium and strontium on purified clays (illite, vermiculite, montmorillonite, and kaolinite) during the reaction with solutions similar to those encountered beneath leaking high-level storage tanks. Sorption studies on clays have shown that the extent of Sr sorption is higher than for Cs, except in the case of illite. Kinetic studies show that Cs/Sr uptake on clays is strongly controlled by secondary mineral formation, with the types of phases formed being dependent on each clay system and initial contaminant concentrations. Nuclear magnetic resonance, X-ray diffraction, and X-ray absorption spectroscopy techniques are being used to characterize the coordination environment of the sorbed ions. Their results are intended to be applied in equilibrium and transport models for radionuclide distribution between solid, colloidal, and dissolved phases.

Role of Calcium Carbonate Grain Coatings on Contaminant Migration. Calcium carbonate exists as grain coatings and intergrain fill in the vadose zone at Hanford. The goal of a PNNL/Stanford University/University of Wyoming project (70121) is to understand the interaction of some contaminants (strontium-90, cobalt-60, chromate, and pertechnetate) with these materials in order to improve forecasts of contaminant migration. Questions being addressed include: (1) Do carbonate coatings form preferentially on particular mineral surfaces? (2) Do carbonate coatings inhibit electron transfer reactions at otherwise reactive surfaces? and (3) Do carbonate coatings enhance the binding of species such as ^{90}Sr and ^{60}Co?



Impact of Vadose Zone Properties on Microorganism Colonization A PNNL/Oregon State University project (70165) is focusing on the ability of strain KC to colonize sediment from a single inoculation point as a function of vadose zone characteristics. Above: Migration of bacteria after 120 hours in static (no flow) unsaturated columns containing 1.1 mm sand; bacteria were inoculated at 0.0 cm. Migration decreased with decreasing volumetric water contents (green, black, red) when nutrients were not supplied in the column. Water content of 1.3% prevented movement of bacteria even in the presence of nutrients (blue).

Characterization of Metal Ions Bound to Calcium Carbonate Surfaces. A State University of New York–Stony Brook/PNNL project (70146) is designed to assess the role of calcium carbonate in the uptake and retention of inorganic contaminants, such as cobalt, cesium, lead, strontium, and chromium. Their work has made extensive use of the National Synchrotron Light Source at Brookhaven and the Advanced Photon Source at Argonne for detailed microscopic and spectroscopic characterization of the interactions of various metal ions with carbonate surfaces. Early work showed that the detailed structure of the carbonate surface controls the extent to which chromate is removed from vadose-zone fluids, and similar work is exploring uranyl uptake on carbonate surfaces. They have also shown that only a small fraction of a natural caliche surface offers favorable reaction sites for lead uptake. X-ray absorption fine structure spectroscopy and X-ray fluorescence techniques are being used to characterize the binding of various metal ions to carbonate surfaces.

Thermodynamics Parameters for Radionuclide Species in Highly Basic Solutions. Highly basic solutions can dissolve large concentrations of silica from minerals present in the subsurface, and the resulting solutions can form stable complexes with radionuclides and hence enhance the transport of radionuclides. A PNNL/Florida State University project (70163) is working on the thermodynamics of the species formed by radionuclides in highly basic solutions, particularly those with high silica concentrations. Their work includes experimental determinations of the species present in solution, molecular simulations to help identify species structures, and physical chemistry measurements to obtain the thermodynamic data necessary for predicting contaminant complexation and waste neutralization reactions.

Mobility of Technetium in the Vadose Zone. A PNNL/LANL project (70177) is focused on reactions in the vadose zone that may decrease the mobility of the technetium that has been released at Hanford. Technetium is easily oxidized to form the highly soluble and mobile pertechnetate species, but reduction reactions on iron(II)-containing mineral surfaces could result in forming technetium dioxide and other reduced species with much lower mobility. Their first goal is to develop a description of the reduction of pertechnetate ions on iron(II)-containing minerals, and they have characterized the amorphous technetium dioxide formed by both hydrazine and reduction with an iron-reducing bacterium. They plan to determine the stability of the reduced technetium solids and to use contaminated Hanford sediments to validate their models of technetium mobility in the vadose zone.

Chemical Treatment of the Saturated Zone

In Situ Formation of Calcium Carbonate to Immobilize Radionuclides. An INEEL/Portland State University/University of Toronto project (70206) is directed toward a remediation technique that uses the formation of calcium carbonate precipitates to trap radionuclide contaminants. The idea is to inject urea into a contaminated aquifer. If urease-containing organisms are present, the urea will be hydrolyzed to form ammonium carbonate, which will react with low concentrations of calcium to form calcium carbonate and trap other metal ions in the precipitate. Early results indicated that the potential for using urea hydrolysis as the basis for an *in situ* remediation technique for strontium-90 and other divalent metal ions is promising. Urea-hydrolyzing bacteria were found in the Snake River Plain Aquifer at INEEL, and it was found that these bacteria can catalyze formation of calcite in the presence of urea.

Bioremediation in the Subsurface

Biodegradation of DNAPLs. Biodegradation of concentrated chlorinated solvents was previously thought not to be possible because these solvents are toxic to microorganisms, but a Stanford University project (70063–a renewal of 54666) is exploring use of anaerobic biodegradation in regions near DNAPL plumes. They demonstrated the potential of certain microorganisms to reductively dehalogenate tetrachloroethylene and other chlorinated ethenes at high concentrations, and their work demonstrated the advantage that can be achieved by carrying out *in situ* dehalogenation directly on DNAPL rather than on more dilute solutions. The group is attempting to provide a molecular understanding of the biological mechanisms involved in the reactions and to determine the cellular components involved in carbon tetrachloride transformation by a *Pseudomonas stutzeri* strain KC without the formation of chloroform.

Impact of Vadose Zone Properties on Microorganism Colonization. Injection of non-engineered microorganisms and aqueous-based nutrient delivery are potentially acceptable technologies at DOE sites, and a PNNL/Oregon State University project (70165) is also exploring use of the same *Pseudomonas* strain for DNAPL remediation. However, the focus of their work is on the ability of strain KC to colonize sediment from a single inoculation point as a function of vadose zone characteristics, such as water-filled porosity, pore throat size, aqueous nutrient concentration, and distance from a nutrient injection point. Researchers in this project are also modifying a widely used computer program for vadose zone flow and transport modeling to include coupled biological and hydrologic processes.

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  Pacific Northwest National Laboratory
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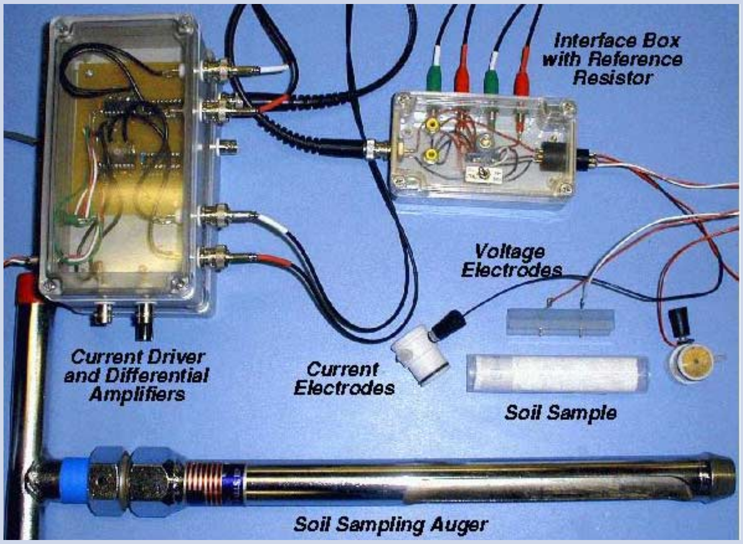
GEOPHYSICS

Geophysical methods are essential for large-scale characterization of subsurface properties

Dense nonaqueous phase liquids (DNAPLs), mostly chlorinated hydrocarbons, were widely used in the U.S. Department of Energy (DOE) complex, and thousands of gallons were released into the subsurface. Thus, a high-priority need at many sites is a reliable method to locate DNAPLs in the subsurface without direct sampling via boreholes. One 1999 EMSP project is developing use of complex electrical resistivity measurements for monitoring DNAPL contamination in the subsurface, while another project is focused on use of ground-penetrating radar for direct detection of DNAPLs.

Predictions of contaminant transport in the subsurface require an understanding of the properties of the region between the surface and the groundwater, i.e., the vadose zone. Major efforts by many subsurface scientists are directed toward use of geophysical tools for more precise determinations of subsurface properties. EMSP projects in this area include an effort to develop relationships between measured geophysical properties and porosity, saturation, and fluid distributions in the vadose zone. Another study is focused on expanding the usefulness of ground-penetrating radar methods for the determination of moisture content in the vadose zone, while another project is designed to improve the usefulness of high-frequency electrical impedance methods for determinations of the amount and composition of fluid present in porous media. A diverse group of researchers is working on a project to develop a hydrologic-geophysical method for characterizing flow and transport in the vadose zone. Their work involves electrical resistance tomography, ground-penetrating radar measurements, and new computational codes to analyze flow during a hydrologic field experiment. The hybrid hydrologic-geophysical inverse technique uses work done in a previous EMSP project.



Complex Electrical Resistivity Measurements
A New England Research project (70012) is working on use of complex electrical resistivity measurements for monitoring DNAPL contamination in the subsurface. Above: Principal components for laboratory measurement of frequency-dependent electrical resistivity of soils. Samples obtained in the field with the hand auger can be studied immediately with minimal disturbance to the soil structure.

Problems/Solutions

- As noted in *Research Needs in Subsurface Science* (National Research Council, 2000), “currently available indirect methods…are inadequate for locating most types of contaminants in the subsurface, and direct methods such as drilling are both expensive and limited in effectiveness.” The report suggested that there is a high-priority need for research on improved indirect methods for measuring contaminant and subsurface properties, and EMSP projects are focused on this goal.
- Similar needs have been cited in many STCG Needs Statements. For example, RL-SS31 notes that only a low percentage of subsurface contaminants has been located in the vadose zone and that “characterization methods are needed to define the *in situ* physical and chemical aspects of the vadose zone, and average field-scale properties describing fluid flow and reaction. These methods need to have the sensitivity to characterize subsurface geohydrologic and geochemical properties with sufficient accuracy to permit prediction of contaminant fate and transport.” Many EMSP projects are not only working on innovative characterization tools, they are also testing them in the field at contaminated DOE sites.

Anticipated Impact

- DOE waste sites are found over a wide range of hydrogeologic settings, so the containment, removal, or treatment of subsurface contaminants at one site may involve quite different challenges than those encountered at other sites. Contamination occurs in thick unsaturated zones, in high- and low-permeability soils, in aquifers, and in fractured basalt and karst bedrock. Therefore, many different geophysical techniques are being explored by EMSP projects in order to maximize the widespread applicability of the results to problems faced by the full range of DOE sites.

PROJECT TEAMS

LEAD PRINCIPAL INVESTIGATOR (AWARD NUMBER)

- New England Research, Inc.
  PI: Stephen R. Brown (70012)
- University of Wyoming
  PI: John Bradford (70052)
- Lawrence Livermore National Laboratory
  PI: Patricia A. Berge (70108)
- Stanford University
  PI: Rosemary Knight (70115)
  University of British Columbia
- Sandia National Laboratories–Albuquerque
  PI: Gregory A. Newman (70220)
  ElectroMagnetic Instruments, Inc.
- University of Wisconsin–Madison
  PI: David L. Alumbaugh (70267)
  Sandia National Laboratories–Albuquerque

Monitoring DNAPLs in the Subsurface

Complex Electrical Resistivity Measurements. Researchers in a New England Research project (70012) are working on use of complex electrical resistivity measurements for monitoring DNAPL contamination in the subsurface. The work is based on a four-electrode electrical resistivity measurement, where two electrodes are used to impose a sinusoidal current and the remaining two sense the response voltage of the sample. The phase lag between the source and response signals at low frequencies is the measured parameter thought to be characteristic of certain organic solvents in clay-bearing soils. Early work involved developing a system to resolve complex resistivity phase angles of a milliradian over a wide frequency range.

Ground-Penetrating Radar. A University of Wyoming project (70052) is directed toward use of ground-penetrating radar for direct detection of DNAPLs. Most organic liquids have lower dielectric permittivity and conductivity than does water, so a contrast in properties is induced when DNAPLs displace water. This project focuses on three aspects of reflected wave behavior: propagation velocity, frequency dependent attenuation, and amplitude variation with offset. The objectives are to develop a suite of methodologies for direct detection of DNAPLs, to perform field verifications at well-characterized, contaminated sites, and to do contaminant detection in a field setting with subsequent verification through direct sampling.

Characterization of Properties of the Vadose Zone

Improved Geophysical Imaging Techniques. An LLNL project (70108) is developing relationships between measured geophysical properties and porosity, saturation, and fluid distribution for partially saturated soils, such as those found in the vadose zone. This work is a continuation of a previous project (55411) aimed at improving geophysical imaging techniques. An ultrasonic apparatus for simultaneously measuring compressional and shear wave velocities was modified to enable measurements on partially saturated soil samples. Other work has involved X-ray computed tomography imaging of moisture distribution in sands, using the Advanced Photon Source at Argonne. Future work will focus on developing algorithms for relationships between composition, saturation, and geophysical measurements.

Determination of Moisture Content in the Subsurface. The objective of a Stanford University/University of British Columbia project (70115) is to develop the usefulness of radar methods for the determination of moisture content because contaminant transport in the vadose zone is very dependent on moisture content. Their work is focused on (a) the relationship between the dielectric constant of a subsurface volume and the moisture content of that volume and (b) the use of radar data to obtain information about the spatial variation of moisture content. They plan to develop a model for the joint inversion of geophysical and hydrological data to obtain hydrological parameters.

High Frequency Impedance Methods. Electromagnetic methods are sensitive to the amount and composition of fluid present in porous media. High-frequency impedance methods are particularly useful for situations in which ground-penetrating radar cannot explore sufficient depths. A SNL/ElectroMagnetic Instruments project (70220) is designed to improve the usefulness of this method. Their work involves the development of nonlinear 2D/3D inversion solutions and the use of these solutions to improve image resolution. The goal is to collect impedance measurements at the Hanford site and to interpret the field data with the newly developed inversion techniques along with independent information from other sources.

A Hydrologic-Geophysical Method. A University of Wisconsin/SNL project (70267) is working on a hydrologic-geophysical method for characterizing flow and transport processes within the vadose zone. The method uses electrical conductivity information from electric resistivity tomography, dielectric constants obtained from cross-borehole ground-penetrating radar, statistical information about heterogeneity and hydrologic processes, and sparse hydrologic data to provide maps of hydrogeological heterogeneity and extent of contamination. This work uses some methods developed by another project (55332). The geophysical imaging techniques will be used to image the changes produced by transport experiments as they occur, and the data will provide checks for the numerical flow and transport simulations.

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HYDROGEOLOGY

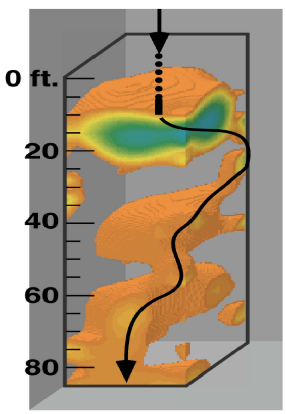
Understanding how water flows through diverse geologic structures is essential for understanding contaminant migration

Several 1999 EMSP projects are working on various aspects of flow and transport in the vadose zone, which is the region between the soil surface and the groundwater. The physics of fast flow processes in coarse-textured media is fundamentally different from that of flow in finer-textured media, and one project is attempting to improve understanding of this phenomenon because it may be important at several U.S. Department of Energy (DOE) sites. Another project is conducting both experimental and modeling studies of subsurface structures that may allow preferential vertical flow paths, because even small concentrations of such structures could have a profound influence on the total downward migration of contaminants.

The “Vadose Zone Observatory” at Lawrence Livermore is a facility with numerous geophysical and hydraulic observational instruments throughout the 70-foot vadose zone. This facility is being used by one research group to show how vadose zone characteristics influence the transport of contaminants down to the water table. Another diverse group of researchers is using small-scale direct measurements of soil properties along with geophysical techniques to develop large-scale predictions of transport properties. The fate and transport of radionuclides beneath the Hanford tank farm are the subject of a project in which the researchers have obtained both horizontal and vertical undisturbed core samples to enable realistic laboratory studies of the transport properties of materials similar to those beneath the tanks.

In recent years it has become clear that some radionuclides can become suspended in colloids that will result in much greater mobility than anticipated on the basis of the solubility of the radionuclide species. One project is investigating such colloid-facilitated transport.

Vadose Zone Observatory
Salt Water Infiltration



Saturation changes at bottom of VZ in less than 6 hours

Vadose Zone Observatory

An LLNL project (70149) is using infiltration experiments at a Vadose Zone Observatory to show how vadose zone characteristics influence transport of contaminants to the water table. Left: An ERT image showing the electrical conductivity distribution less than 6 hours after a 1,500-liter infiltration event using very saline water. The water table is normally below 65-70 feet, but the salt water signal appears to have actually penetrated below the water table owing to its greater density. This result, in conjunction with a related tracer study, strongly suggests that fast paths can carry at least part of the “contaminated” water rapidly to the water table.

Problems/Solutions

- As described in an STCG Science Need Statement (RL-SS29-S), “The science needed to elucidate the role of physical and chemical heterogeneities on subsurface transport of solutes and colloids can be focused on both (1) developing a more thorough understanding of the relative contributions of these heterogeneities to contaminant transport through controlled experimentation, and (2) rapidly and accurately characterizing the presence of these heterogeneities.” These are precisely the subjects being addressed by EMSP projects in this area.
- As noted in an STCG Science Needs Statement (RL-SS29-S), “knowledge of how heterogeneous physical and chemical properties affect chemical solute and colloidal transport is important to the design of appropriate remedial technologies. Key science issues related to how physical properties affect transport include determining the effect of multidomain pore structures on contaminant transport rates, determining the role of pore structure on the movement of water in unsaturated porous media, and relating this information to convective and diffusive transport of contaminants.” These are some of the areas being pursued by researchers on EMSP hydrogeology projects.

Anticipated Impact

- Only a low percentage of the total radionuclide and hazardous materials in the subsurface at DOE sites has been thoroughly located and characterized. Even if the entire inventory of contaminants was located, most sites with low levels of contamination could not be treated to remove the contaminants because of the high cost-to-benefit ratios. Thus, it is especially important that reliable hydrogeology information is available to enable sound scientific predictions of the fate and transport of contaminants so that remediation resources can be used where the benefits will be the greatest.

Technical Summary and Progress

Hydraulic Properties of Coarse Sediments. An LBNL project (70069) is designed to improve understanding of flow in coarse-textured media such as those at Hanford. The objectives are to quantify the macroscopic hydraulic properties of very coarse sediments and to determine the microscale basis for fast unsaturated flow. Macroscopic studies have used several column methods. The microscopic tests of film flow have used the National Synchrotron Light Source at Brookhaven to determine average water film thicknesses on Hanford gravel samples. The combined results of macroscopic and microscopic experiments will be used to develop a physical model of unsaturated flow in coarse sediments.

Preferential Flow in Vertical Paths. Most flow and transport models of the vadose zone have assumed horizontally layered sediments with no preferential vertical flow paths. But preferential flow through vertically oriented, more highly permeable structures may enhance movement of moisture and contaminants through the vadose zone. A PNNL/New Mexico Institute project (70193) is exploring field and modeling studies of these clastic dikes. They have used a detailed ground-penetrating radar survey to identify dike spacing and thickness, and are measuring the distribution of hydraulic properties within dikes using infiltration experiments.

Project Teams

Lead Principal Investigator (Award Number)

- Lawrence Berkeley National Laboratory
  •PI: Tetsu K. Tokunaga (70069)
- Washington State University
  PI: Markus Flury (70135)
- Lawrence Livermore National Laboratory
  PI: Charles R. Carrigan (70149)
- Pacific Northwest National Laboratory
  PI: Philip D. Meyer (70187)
- Pacific Northwest National Laboratory
  PI: Christopher J. Murray (70193)
  New Mexico Institute of Mining & Technology
- Oak Ridge National Laboratory
  PI: Philip M. Jardine (70219)
  Pacific Northwest National Laboratory
  Stanford University

A Vadose Zone Observatory. An LLNL project (70149), which is a continuation of project 54950, is using infiltration experiments at a “Vadose Zone Observatory” to show how vadose zone characteristics influence the transport of contaminants to the water table. The LLNL facility contains wells with geophysical instruments, tensiometers, lysimeters, and other sensors throughout the vadose zone. One experiment involved infiltrating water and tracking the downward transport of tracers previously added to the soil. This mimics a cleaning of Hanford tanks when leakage of uncontaminated water might mobilize existing soil contamination. Electrical imaging tracks the development of a groundwater plume as the injected water moves to the water table.

Modeling Flow and Transport in the Heterogeneous Vadose Zone. A PNNL project (70187) is using small-scale direct measurements of soil physical and hydraulic properties (hard data) along with indirect geophysical measurements (soft data) to develop a systematic approach for parameterization of numerical models for simulation of field-scale flow and transport problems. Data from controlled field experiments at Hanford are being used to evaluate the parameterization methods. Neural network analyses are also being applied to develop pedo-transfer functions for relating soil texture and bulk density data to hydraulic properties. The prediction uncertainty associated with using sparse and/or surrogate data for model parameterization is being addressed.

Migration of Radionuclides beneath the Hanford Tanks. The fate and transport of radionuclides beneath the Hanford tank farms are the subject of an ORNL/PNNL/Stanford University project (70219). They obtained both horizontal and vertical undisturbed core samples from a Hanford location. The transport of several tracers will be investigated at a variety of water contents reflective of the range of recharge rates at Hanford. Preliminary results suggest that lateral flow beneath the tank farms is a strong contributor to the spread of contaminants. In addition to the macroscopic fate and transport experiments, interfacial molecular techniques will be used to quantify the distribution and chemical environments of the sorbed contaminant species. The goal is to provide an improved understanding and predictive capability for the fate of the radionuclides that have leaked from the Hanford tanks.

Colloid-Facilitated Transport of Radionuclides. A Washington State University project (70135) is designed to study colloid-facilitated transport of radionuclides. The first objective is to determine the characteristics of the colloidal particles that form under conditions similar to those found beneath the Hanford tanks. Next, the interactions between colloids, contaminants, and the soil matrix will be studied under various ionic strength and pH conditions, and the mobility of colloids through the soil will be evaluated. Preliminary experiments have shown that a considerable amount of colloidal particles can be mobilized when a concentrated salt solution infiltrates the Hanford sediments and is subsequently diluted.

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LOW-DOSE RADIATION

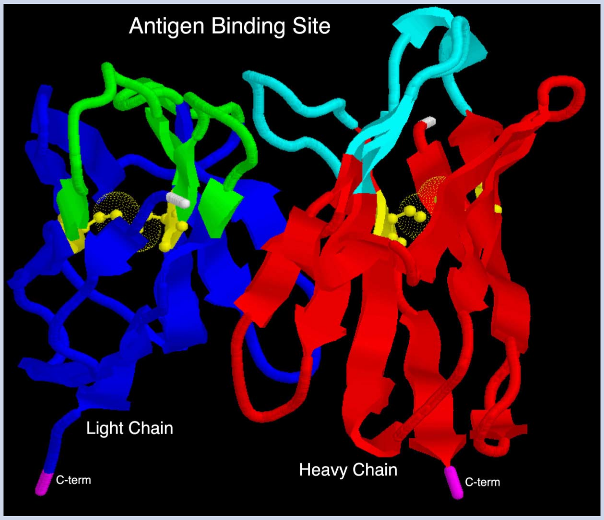
IS THE BIOLOGICAL DAMAGE INDUCED BY LOW DOSES OF RADIATION REPAIRED WITH THE SAME EFFICIENCY AS NORMAL OXIDATIVE DAMAGE?

The Notice Inviting Grant Applications for the EMSP projects described here suggested that research was needed to understand the normal cellular processes responsible for repairing oxidative damage and radiation-induced damage. If it could be proved that there is no enhanced cancer risk with radiation exposures up to some threshold, the end point for remediation activities could be defined more precisely and wasteful remediation activities that would provide no benefit could be avoided.

Radiation damage in DNA is caused by free-radical reactions initiated by ionization events, and one EMSP project is attempting to determine if conventional laboratory results overestimate *in vivo* cellular responses because of higher oxygen concentrations. A unique focused X-ray facility is being used by another group to study the effects of low-dose radiation on single cells that absorb the radiation as well as on neighboring cells that are not directly exposed.

One EMSP project was designed to determine whether there is an adaptive response against neoplastic transformation by ionizing radiation, and another is investigating why low-dose exposures induce resistance to damage from subsequent exposures. Another effort is directed toward development of tools to allow more sensitive visualization of double-stranded DNA break repair complexes so that the formation of repair complexes can be studied at lower exposure levels. The detection of changes in certain molecular events in cells due to radiation exposures may provide a sensitive method for detecting effects of radiation exposure, and another project includes a determination of whether the use of such methods *in vitro* can be used to reliably predict *in vivo* processes.

Variations in DNA repair mechanisms could make some individuals more susceptible to radiation-induced cancers than normal, and an EMSP project is studying the effect of one hereditary disorder on risk due to low-level radiation. Finally, a social science project is directed toward understanding individual, group, and community responses to perceived radiation risks.



Better Determinations of Health Risks
A Medical College of Georgia project (69906) is developing tools to allow direct *in situ* visualization of double-strand DNA break repair complexes. The project uses genetically engineered single chain antibody and digital image processing technologies. Left: Recombinant single chain antibody directed against the DNA repair protein, DNA-PKcs. Ribbon diagram shows model of antibody heavy and light chain domains (red and blue), each stabilized by a disulfide bond (yellow), with antigen binding site marked.

PROBLEMS/SOLUTIONS

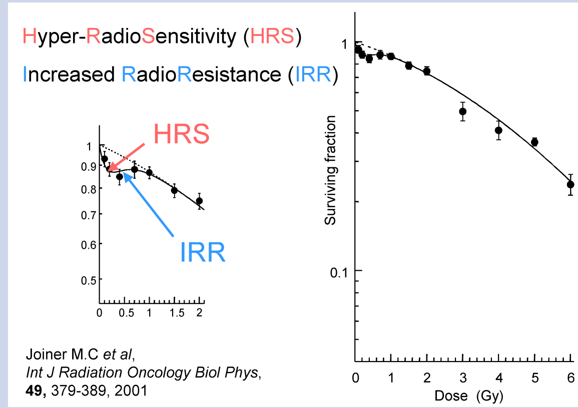
- More than 100,000 single-strand DNA breaks per day occur in each cell in our bodies due to normal processes, and the additional breaks due to low-level radiation are a tiny fraction of the total. Thus, the fundamental issue is whether the amount and kinds of DNA damage produced at low doses of radiation are different from those normally produced within cells. Several EMSP research efforts are contributing to a basic understanding of the molecular processes that follow the absorption of ionizing radiation.
- Despite the fact that the frequency of double strand breaks is much lower than that of other types of damage, double strand breaks may be the major determinant that distinguishes normal oxidative damage from low-dose radiation induced damage to DNA. The goal of an EMSP project is to develop tools to allow a two-orders-of-magnitude increase in sensitivity over existing methods for measuring double-strand breaks.

ANTICIPATED IMPACT

- The goal of all remediation work with radioactive waste is to minimize impacts on the health of living species. If it can be proved that there are dose thresholds below which no biological responses or increases in radiation risk occur, then the endpoint of remediation can be clearly defined. If it is assumed that no radiation exposure is risk free, then it is difficult to define standards for free release of any site.
- All the information for radiation-induced DNA damage is from data obtained at high doses; there are no data at the low doses that could occur at formerly contaminated sites after remediation. It is essentially impossible to determine by direct observation in animals increased cancer risks due to acute exposures to 10 rem or 0.1 Sv, so several EMSP projects are working on development of techniques that may be able to detect changes in certain molecular events that are prerequisites to the development of observable cellular abnormalities.

Comparisons of the Effects of Low-Dose Radiation and Normal Oxidative Damage

Gamma radiation (for example) produces most of its effects through the generation of reactive oxygen species, which are also produced by normal metabolic processes. Most *in vitro* experiments are conducted in air where oxygen is present at six times its *in vivo* physiological concentration, so the unnaturally high levels of oxygen may distort the true cellular response to low-level ionizing radiation. A LANL project (69938) will compare the consequences of inducing genetic damage either by radiation or by temporary exposure to elevated oxygen concentrations. Their "oxidative stress laboratory" will also be used to investigate whether the reported beneficial effects of low-radiation doses result from triggering an antioxidant defense mechanism.

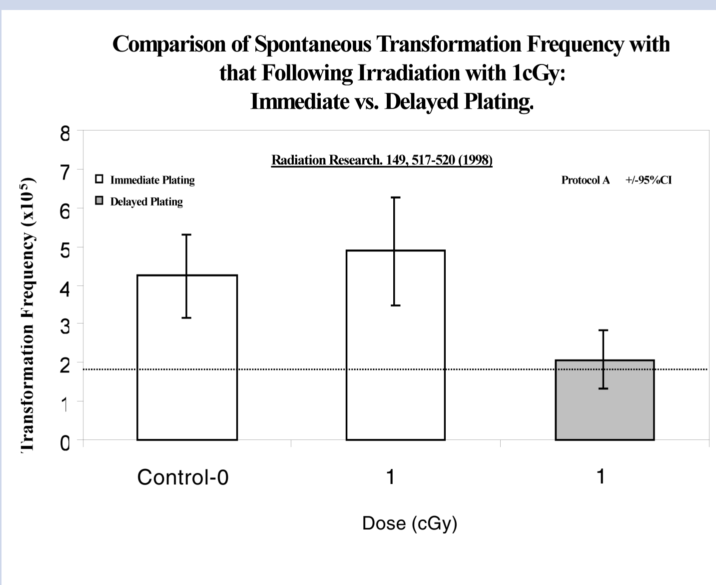


Low-dose hyper-radiosensitivity (HRS) and increased radioresistance (IRR)
The overall aim of a Gray Laboratory Cancer Research Trust project (69981) is to acquire an understanding of the mechanisms underlying low-dose HRS and IRR. Above: Sub-structure in the survival response of cells to low-LET ionizing radiation at less than 1 Gy, shows the HRS region of low-dose HRS below 20 cGy. Above 20 cGy, IRR occurs. Thus the low-dose response is considerably greater than predicted by the high-dose response, and has to be measured separately.

The objective of the Gray Cancer Research Trust (UK)/ Massachusetts General Hospital project (69980) is to increase understanding of the responses of cells to the low doses of ionizing radiation typically encountered in environmental exposures. The researchers use a unique focused X-ray facility for irradiation of individual cells or even subcellular regions. Prior single-cell irradiation studies with this facility gave evidence for bystander responses in unirradiated cells and a dose-effect relationship that indicated a low-dose threshold. The goals for this project include determinations of the responses of individual cells to low doses of X-rays as well as determinations of the response of cells to reactive oxygen species generated by chemical agents in a fashion similar to normal cellular processes. Other objectives include investigations of the interactions between oxidative processes and ionizing radiation and determinations of the effects that reactive species or radiation in an individual cell can cause in surrounding, untreated cells.

Better Determinations of Health Risks Due to Exposures to Low-Dose Radiation

How much do low doses of radiation protect against subsequent low doses of ionizing radiation? The experiments being undertaken by a University of California–Irvine project (69848) are designed to address this question. They will measure the neoplastic transformation frequency in a skin fibroblast human hybrid cell system as a function of exposures to gamma and X-rays. Total doses will be 0, 0.1, 1.0 and 10 centiGrays (1 rad) and will include single and multiple exposures to reach the total dose. These experiments are designed to provide information required to determine whether there is an adaptive response against neoplastic transformation by ionizing radiation. Earlier studies (*Radiation Research* 149: 517-520, 1998) demonstrated the induction of a significant adaptive response against spontaneous neoplastic transformation by a dose of 1 cGy of ^{137}Cs gamma radiation. Preliminary data from the current project indicate a similar adaptive response at single doses as low as 0.1 cGy and as high as 10.0 cGy.



Adaptive Response
A University of California–Irvine project (69848) is investigating to what degree low doses of radiation protect against subsequent low doses of ionizing radiation. Above: Adaptive response against spontaneous neoplastic transformation induced by 1 cGy of ^{137}Cs gamma radiation.

Without radiation exposure, single strand breaks in DNA occur at a rate of 150,000 per day per cell, and exposures at the upper limit of low-level radiation cause about 200 per cell. But perhaps the double-strand DNA breaks (DSBs) induced by radiation are more important, and a Medical College of Georgia project (69906) is directed toward developing tools to allow direct *in situ* visualization of DSB repair complexes. This work may provide an improvement of two orders of magnitude in sensitivity over existing methods of measuring double-strand breaks. The project uses genetically engineered single chain antibody and digital image processing technologies. If the approach proves successful, it will be used to compare the formation of repair complexes at various dose levels and to study the effect of low doses on the response to subsequent higher doses.

The most conservative cancer risk assessments are based on linear extrapolations of high dose data to low doses, but the existence of repair mechanisms would suggest that linear extrapolations to low doses are not reasonable. A PNNL study (69941) is developing the molecular tools necessary to define thresholds in cell signaling pathways that are required for cellular transformation and that may be affected by low-dose radiation. They are investigating the effects of low-dose radiation exposures on certain molecular events in a well-characterized system of mouse cells, and they plan to determine whether the low-dose radiation responses demonstrated *in vitro* are relevant to *in vivo* processes using a standard mouse skin initiation-promotion strategy.

The overall aim of a Gray Laboratory Cancer Research Trust (UK) project (69981) is to acquire an understanding of the mechanisms underlying low-dose hyper-radiosensitivity (HRS) and increased radioresistance (IRR). They have shown that cell lethality measured after low-dose exposure to gamma- or X-rays is markedly enhanced relative to that expected by extrapolation of the high-dose response. This may compensate for processes that would lead to cancer formation at low doses and suggests that the adverse effects of small radiation doses could be overestimated. Specific goals of the project are to identify which aspects of DNA repair determine HRS and IRR, to investigate changes in DNA structure and conformation that may change the DNA repair rate, and to determine whether the adaptive response and HRS/IRR are separate or interlinked phenomena.

Project Teams

Lead Principal Investigator (Award Number)

- University of California–Irvine
  PI: J. Leslie Redpath (69848)
- Decision Science Research Institute
  PI: James Flynn (69904)
- Medical College of Georgia
  PI: William S. Dynan (69906)
- Los Alamos National Laboratory
  PI: Edwin H. Goodwin (69938)
- Pacific Northwest National Laboratory
  PI: Jim Morris (69939)
- Pacific Northwest National Laboratory
  PI: Jeffrey D. Saffer (69941)
- Gray Laboratory Cancer Research Trust (UK)
  PI: Barry D. Michael (69980)
  Massachusetts General Hospital
- Gray Laboratory Cancer Research Trust (UK)
  PI: Michael Joiner (69981)

Genetic Factors that Affect Susceptibility to Low-Dose Radiation

Are there genetic differences that make some individuals more susceptible to radiation-induced cancers than normal? Variations in DNA repair mechanisms or conditions that provide a differential growth advantage for mutated cells could provide enhanced susceptibility. The goal of a PNNL project (69939) is to determine whether persons with hereditary hemochromatosis (HH) would have an increased susceptibility to cancer induced by low-dose radiation. HH is a fairly common inherited disorder that causes the body to absorb and store too much iron, and strains of mice with the same genetic defect are being used in this study. Two objectives are to determine whether these mice have greater sensitivity to radiation-induced cancers and to determine whether this sensitivity depends on the accumulation of iron. If higher sensitivities are detected at high-radiation exposure levels, an effort will be made to identify thresholds in the dose-response relationships at low exposure levels.

Communication of Research Results

A goal of the Decision Science Research Institute project (69904) is to establish risk communication as an integral part of the decision process involved in establishing public policies related to cleanup of sources of low-dose radiation. The focus of their research will be understanding individual, group, and community responses to radiation risks. A set of questionnaires was designed to examine attitudes about radiation exposure, the relationship between respondent worldviews and risk perceptions, the role of emotions, and how media stories influence perceptions. Ongoing work will examine the community level context for radiation risk perceptions using the framework of the Social Geography of Risk Communication. Community studies address the social, political, and economic context and the resulting influence on societal responses to low-dose radiation exposures. Other studies will attempt to understand how science information is viewed, evaluated, understood, and applied to low-dose radiation conditions.

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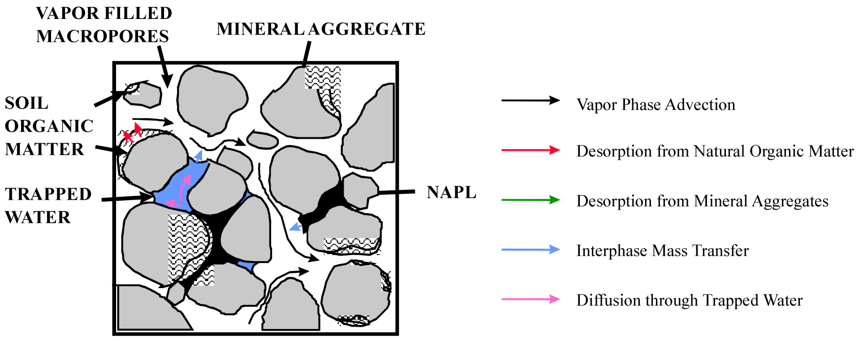
SUBSURFACE CONTAMINATION – DENSE NONAQUEOUS PHASE LIQUIDS

SIGNIFICANT NONAQUEOUS PHASE LIQUID CONTAMINATION IS PRESENT AT ALMOST EVERY MAJOR U.S. DEPARTMENT OF ENERGY SITE

Chlorinated solvents were released into the environment in massive quantities between 1950 and the early 1980s. A small pool of dense nonaqueous phase liquids (DNAPLs) can contaminate a very large volume of water while being difficult to locate, so there is widespread interest in finding geophysical techniques for locating DNAPLs without using numerous boreholes. One EMSP investigation is based on the hypothesis that the complex electrical resistivity of the subsurface will change as the DNAPL concentration changes, so the method is being studied for use as a monitor for remediation activities. Another study is investigating the applicability of ground-penetrating radar for detection of organic liquids in the subsurface, and researchers are conducting field experiments at U.S. Department of Energy (DOE) and U.S. Department of Defense (DOD) sites with known contamination. Another effort is directed toward taking a highly sensitive analytical technique from the research laboratory into a practical, fieldable instrument that could be deployed down-well or in a cone penetrometer for the detection of traces of organic contaminants.

Two studies are working on factors that affect the migration of nonaqueous organic materials in the subsurface. One is exploring the role that naturally produced surfactants may play in the migration of these materials, and another is exploring the vadose zone factors that limit the effectiveness of soil vapor extraction for removing DNAPL contamination from the subsurface.

Factors related to the use of a *Pseudomonas* strain for bioremediation of chlorinated hydrocarbons are being studied in two projects. One group is exploring use of anaerobic biodegradation in regions near DNAPL plumes, and they are also investigating the molecular biology involved in the reactions. Another group is working with the same microorganism, but the focus of their study is on the vadose zone characteristics that are important for the ability of the strain to colonize a region from a single injection point.



Factors that Limit the Effectiveness of Soil Vapor Extraction
This schematic, provided by a University of Illinois project (70045), illustrates the various processes that control the removal of volatile organic chemicals from the vadose zone during soil vapor extraction (SVE). The researchers hypothesize that at sites like Hanford, dry vapor can be pulled into the ground and affect the soil water content during SVE. Consequently, the controlling processes may change with time.

PROBLEMS/SOLUTIONS

- An STCG Needs Statement (SR00-3017) reflects a need that could be stated for every major DOE site: "Technologies, that are non-invasive and prevent cross-contamination, are being sought to determine the concentration of specific contaminants present at the SRS." Two EMSP projects are working on noninvasive methods to satisfy this need.
- An STCG need (OK99-22) stated for a site at Lawrence Livermore National Laboratory is also applicable to every site with DNAPL contamination: "An increased understanding of chlorinated volatile organic compound plume behavior in various hydrogeologic settings is needed to support remediation strategy decision-making." Among many relevant EMSP projects, one is working on unraveling the effects of surface-active materials on DNAPL migration.

ANTICIPATED IMPACT

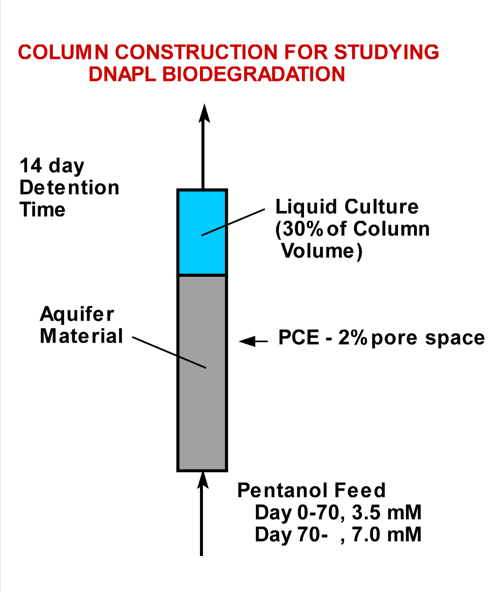
- At current drinking water standards of five parts per billion, one gallon of tetrachloroethylene can contaminate 300 million gallons of water. Thus, techniques for location and remediation of concentrated DNAPLs in the subsurface can save years of pump-and-treat operations.
- Fundamental research in geophysical techniques for locating DNAPLs in the subsurface could lead to substantial long-term savings because every well that does not have to be drilled to locate contaminants saves up to $20,000.
- Microorganisms that can convert chlorinated organic compounds to inorganic chloride and nonhazardous organic materials are known, but large-scale, practical bioremediation of contaminated sites requires a thorough understanding of the factors that enable these organisms to thrive. Successful application of bioremediation procedures would offer very great reductions in cost for remediation of DNAPL plumes as compared to existing removal methods.

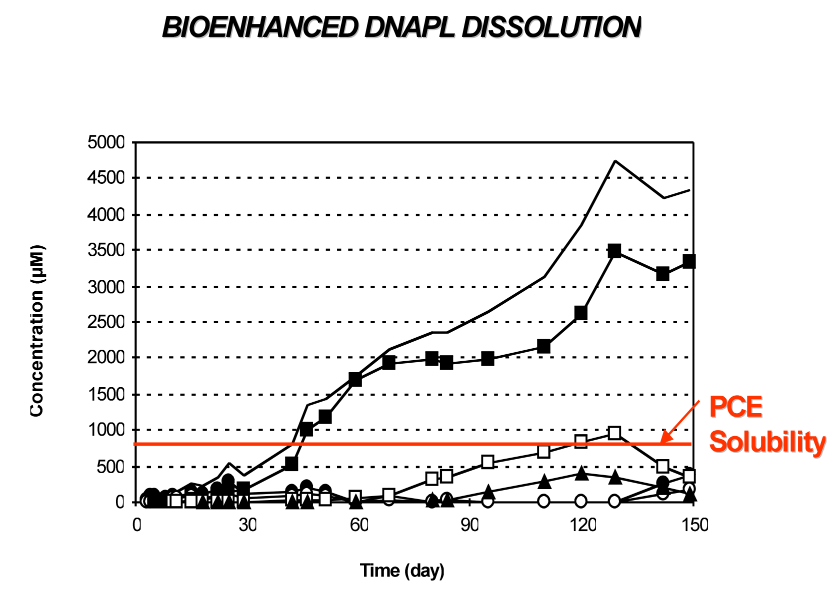
Characterization and Monitoring of DNAPLs in the Vadose Zone

Complex Electrical Resistivity Measurements. Researchers in a New England Research project (70012) are working on the use of complex electrical resistivity measurements for monitoring DNAPL contamination in the subsurface. The work is based on the hypothesis that as organic compounds are removed from the subsurface, the complex resistivity will change. The measured quantity is the phase angle between the applied sinusoidal current applied with two electrodes and the voltage produced in two other electrodes mounted in the sample. Early work on this project involved developing a system that could resolve complex resistivity phase angles of a milliradian over the frequency range of 0.001 to 100,000 Hertz. Because of variable moisture levels, a challenge for field measurements will be to distinguish changes in DNAPL concentrations from other changes in the system.

Ground-Penetrating Radar for Detection of DNAPLs. A University of Wyoming project (70052) is directed toward the use of ground-penetrating radar (GPR) for direct detection of DNAPLs. This project focuses on three aspects of reflected wave behavior—propagation velocity, frequency dependent attenuation, and amplitude variation with offset. Field experiments are being conducted at the Savannah River and Hanford sites as well as at five DOD sites. The first survey was conducted at a shallow DNAPL zone at Savannah River, and extensive efforts were being made to correlate the GPR data with information available from direct measurements made using a cone penetrometer. Other field experiments either in progress or completed include a controlled tetrachloroethylene injection experiment at Dover AFB, an experiment to detect jet fuel at Hill AFB in Utah, and DNAPL detection in the vicinity of a carbon tetrachloride crib at Hanford. Other experiments over known contaminated sites will occur at three additional air force bases in Michigan and California.

Sensitive REMPI Methods for Detection of Organic Vapors. There are currently no *in situ* methods for measuring low levels of organic vapors of the type that would be indicative of subsurface contamination in the vadose zone. High concentrations of organic compounds can be detected with Raman spectroscopy, for example, and a few compounds can be detected by their fluorescence properties. The goal of a University of South Carolina/LLNL project (70050) is to develop a resonant enhanced multiphoton ionization (REMPI) system that can be deployed in a cone penetrometer for the sensitive detection of species such as carbon tetrachloride that cannot be detected by fluorescence techniques. Their team includes persons with expertise in analytical spectroscopy, hydraulic measurements and cone penetrometers, electrical engineering with expertise in optical parametric oscillator design, and fiber optics. They have demonstrated measurements of low parts-per-billion levels of toluene, and they are designing new REMPI probes that use visible lasers to reduce the cost and complexity of the instrumentation.





Anaerobic Biodegradation near DNAPL Plumes

A Stanford University project (70063) exploring use of anaerobic biodegradation in regions near DNAPL plumes has found that certain dehalogenating microorganisms can decompose tetrachloroethylene, trichloroethylene, and other chlorinated ethenes at concentrations near saturation in water. Above: Biological enhancement of tetrachloroethene (PCE) dissolution shown in a soil column with 2% residual PCE saturation and fed a solution containing up to 7 mM pentanol as electron donor. Effluent concentration of PCE (•), TCE (∘), cDCE (■), VC (□), ethene (♦), and the total (without marker).

Effects of Surface-Active Materials on DNAPL Migration. The distribution of DNAPLs within the vadose zone is affected by heterogeneities in the porous matrix and by the interfacial properties that determine the interactions among different solid and liquid phases. Small amounts of surfactants can have large impacts on the interactions of immiscible fluids, such as oil and water, so it would be reasonable to expect that surface-active chemicals present in the vadose zone could have a considerable effect on the migration of DNAPLs. Surface-active materials can be produced through microbial metabolic processes, and the goal of a Clarkson University/WSRC project (70035) is to understand the effects of various interfacial phenomena on the accessibility and migration of DNAPLs in the vadose zone. One objective is to identify the presence of surface-active materials and to quantify interfacial properties in an actual DNAPL plume at Savannah River Site. Other objectives include identifying how DNAPL-metabolizing cultures affect interfacial properties and quantifying the effects associated with DNAPL surface chemistry on flow in the vadose zone.

Factors that Limit the Effectiveness of Soil Vapor Extraction. The aim of a University of Illinois project (70045) is to gain a better understanding of the processes that limit the effectiveness of soil vapor extraction (SVE) for the removal of DNAPLs from heterogeneous porous media typical of the vadose zone. Sorption isotherms and desorption kinetic profiles will be measured for silica gel and sand at various humidities, incubation times, and DNAPL concentrations. The location and size of individual pores containing DNAPLs, water, and vapor in flow-through columns filled with either model or natural sediments will be determined using magnetic resonance imaging. Imaging results will be used along with modeling techniques to describe the transient distribution of phases as a function of time and location. These relationships will be used in a transport model to evaluate how different processes affect SVE performance in practical applications.

Project Teams

Lead Principal Investigator (Award Number)

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  PI: S. Michael Angel (70050)
  Lawrence Livermore National Laboratory
- University of Wyoming
  PI: John Bradford (70052)
- Stanford University
  PI: Perry L. McCarty (70063)
- Pacific Northwest National Laboratory
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  Oregon State University

Bioremediation

Anaerobic Biodegradation near DNAPL Plumes. Solvents such as carbon tetrachloride or trichloroethylene have low mutual solubilities with water, so these materials tend to remain segregated as concentrated liquids in the subsurface. Biodegradation of these DNAPLs was previously thought not to be possible because of toxicity to microorganisms, but a Stanford University project (70063–a renewal of 54666) is exploring the use of anaerobic biodegradation in regions near DNAPL plumes. They have found that certain dehalogenating microorganisms can decompose tetrachloroethylene, trichloroethylene and other chlorinated ethenes at concentrations near saturation in water. These solutions are inhibitory to other naturally occurring organisms so they did not compete for the electron donor required for the reaction. The group is attempting to provide a molecular understanding of the biological mechanisms involved in the reactions and to determine the cellular components involved in carbon tetrachloride transformation by a *Pseudomonas* strain without the formation of chloroform.

Factors that Affect Microorganism Colonization in the Subsurface. The lack of knowledge about how physical and hydrologic features of the vadose zone control the spatial distribution of microbial activity and the potential for microorganisms to colonize this region create uncertainties about the practicality of deep vadose zone bioremediation. A PNNL/Oregon State University project (70165) is also exploring the use of the same *Pseudomonas* strain for DNAPL remediation as described in the previous project, but the focus of this project is on the ability of strain KC to colonize sediment from a single inoculation point as a function of vadose zone characteristics, such as water-filled porosity, pore throat size, aqueous nutrient concentration, and distance from a nutrient injection point. The impact of several other vadose zone hydrological processes on colonization will also be studied. In addition, researchers in this project are modifying a widely used computer program for vadose zone flow and transport modeling to include coupled biological and hydrologic processes.

EMSP
Environmental Management Science Program

Office of Science & Technology
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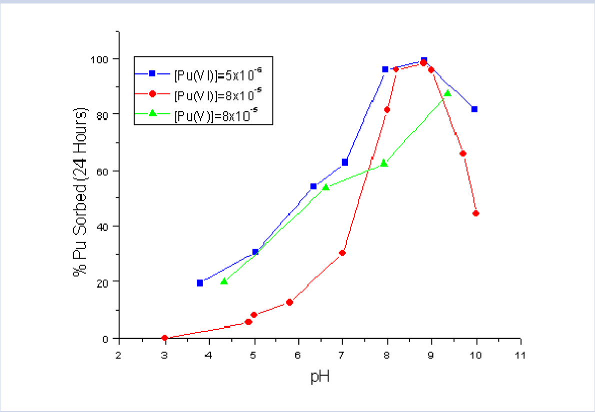
LOCATION AND TRANSPORT OF METALS AND RADIONUCLIDES IN THE SUBSURFACE

DISCOVERY OF MORE RAPID MIGRATION OF RADIONUCLIDES THAN EXPECTED HAS LED TO A GREATER EFFORT TO INTEGRATE SUBSURFACE SCIENCE INTO CLEANUP ACTIVITIES

The projects described here involve either analytical determinations of radionuclides or studies related to the mechanisms by which metal ions migrate away from the original site of contamination.

An innovative analytical technique was developed by one EMSP research group to incorporate scintillating materials into extraction chromatographic separation materials so that alpha- and beta-emitting radionuclides could be both separated and detected with high sensitivity. Another project was directed toward developing a selective sensor for detection of pertechnetate ions in complex mixtures.

Understanding the fate and transport of radionuclides is essential for rational design of remediation efforts. Two projects are exploring how the formation of colloids affects the transport of plutonium and other radionuclides in the subsurface, and one of these has developed ways to determine the colloidal species actually present in groundwater with very low levels of contamination. Several studies are investigating the effects the highly alkaline fluids that have leaked from the Hanford tanks may have on radionuclide transport. One project has obtained core samples like those under the tanks, and these samples are being used for transport experiments. Another group has studied the sorption of radionuclides on clays that have been in contact with highly alkaline solutions, while another is focused on a mechanistic understanding of how tank fluids migrate through the vadose zone.



Transuranic Interfacial Reactions on Manganese Oxide/Hydroxide Minerals
The objective of a LBNL/PNNL project (70176) is to provide information about the interactions of plutonium and neptunium with manganese-containing minerals. Above: Sorption of Pu(VI) and Pu(V) on manganite (MnOOH) as a function of plutonium concentration and pH. The point of zero charge of manganite (the point where the mineral surface is electrically neutral) occurs at a pH of 6.4. At pH values greater than this, the surface has a net negative charge, resulting in a larger amount of Pu sorbed onto the surface.

Studies of interactions of radionuclides with specific components of the subsurface include two studies of the interaction of various radionuclides with carbonate coatings on minerals and how these interactions may affect transport. Another project is making a detailed study of the silica oligomers that can form in highly basic solutions and the complexes they can form with various radionuclides. Another study is directed toward understanding interactions of plutonium and neptunium with manganese minerals that are present at low levels at some U.S. Department of Energy (DOE) sites.

PROBLEMS/SOLUTIONS

- STCG Need RL-SS14 points out that radioactive contaminants requiring improved field detection sensitivities include uranium, plutonium, strontium-90, and technetium-99. A novel system based on the incorporation of scintillating materials into extraction chromatographic separation beads has already been demonstrated to have sufficient sensitivity for technetium-99 groundwater monitoring, and similar work is underway to develop systems for strontium-90 and actinide determinations.
- Although many radionuclide contaminants are present at very low levels at various DOE sites, some common contaminants include plutonium, strontium-90, cesium-137, various isotopes of uranium and rare earths, tritium, thorium, technetium-99, radium, and potassium-40. Either the detection or migration of most of these species is being investigated in EMSP projects awarded in 1999.

ANTICIPATED IMPACT

- As described in an STCG Need Statement (ID-S.1.10), "migration of plutonium to sedimentary interbeds underlying buried waste at some Idaho sites has apparently occurred at a rate much faster than could be predicted by solute transport processes. Plutonium has been determined in laboratory studies and field sampling programs to form colloids in water. These colloids are not reactive with exchange sites on rocks and minerals and have the potential to migrate at essentially the same rate as the water moving through the vadose zone." Two EMSP projects are working on understanding how these colloids can form and which are present at some DOE sites.
- About 350 billion gallons of radionuclide-contaminated water were intentionally discharged into the ground over the years of weapons production, and at least a million gallons of much more concentrated solutions have leaked from high-level storage tanks. Recent detection of radionuclides in the groundwater beneath some high-level tanks has made more reliable predictions of transport a high priority.

Analytical Determinations of Metals and Radionuclides in the Subsurface

Scintillating Microspheres for Radionuclide Detection. Alpha- and beta-emitting substances in water are difficult to detect because of the short ranges of the emitted particles in water. A PNNL/Clemson University group (70179) has developed a novel system for the detection of radionuclides such as strontium-90, technetium-99, and actinides. The system is based on the development of selective scintillating microspheres (SSMs). Thus, the ion of interest is selectively bound to the microspheres. The SSMs, however, also contain scintillating materials that emit light when an alpha- or beta-emitting substance is on a nearby location in the bead, and a photomultiplier or diode sensor can then be used to detect the emitted light. This system has been used to detect technetium in water at concentrations below the maximum permissible drinking water level, and work continues on developing systems for the selective detection of strontium-90 and actinides.

Pertechnetate Sensor. Analysis of any substance in a complex mixture is difficult because most sensors will respond to many species. A University of Cincinnati/PNNL group (70010) is developing a sensor for technetium based on the same general concepts that they used in a previous project (54674) to develop a sensor for ferrocyanide. A chemically selective film is coated onto an optically transparent electrode. Even though the film cannot bind a particular ion exclusively, it can be chosen to show selectivity for pertechnetate ions. Then the pertechnetate ion will be reduced electrochemically and converted into a technetium coordination compound that gives a strong optical signal. Therefore, to be detected, a species must be incorporated into the film, be reduced at the potential used for the electrochemical process, and then form an absorbing substance at the wavelength used for the optical detection. This threefold selectivity may enable reliable detection of pertechnetate without the usual elaborate separation procedures required for conventional analyses.

Transport of Metals and Radionuclides in the Vadose Zone

Colloid Facilitated Transport of Radionuclides. Radionuclides, such as plutonium and cesium, have been detected under the Hanford tanks at much greater depth than predicted by current theories of vadose zone contaminant transport. It has been suggested that the mobility may be higher than expected because of colloid-facilitated transport through the vadose zone, and a Washington State University project (70135) is designed to investigate this possibility. The first objective is to determine the characteristics of the colloidal particles that form under conditions similar to those found when Hanford tank liquids leak into the vadose zone beneath the tanks. Next, the interactions between colloids, contaminants, and the soil matrix will be studied under various ionic strength and pH conditions, and the mobility of colloids through the soil will be evaluated. Preliminary experiments have shown that a considerable amount of colloidal particles can be mobilized when a concentrated salt solution infiltrates the Hanford sediments and is subsequently diluted.

Studies with Core Samples from Hanford
The goal of an ORNL/PNNL/Stanford University project (70219) is to provide an improved understanding and predictive capability for the fate of the radionuclides that have leaked from the Hanford tanks. In their work, as illustrated here, undisturbed sediment cores of material similar to that beneath the Hanford tank farms were acquired with a rotary coring apparatus that could obtain cores at any angle within the formation. Both horizontal and vertical cores were obtained, and the fate and transport of radionuclides at different water contents were investigated.

Speciation, Mobility, and Fate of Actinides in Groundwater. A Woods Hole Oceanographic Institute/PNNL project (70132) is designed to gather fundamental data essential for predicting the migration of plutonium in an aqueous environment and is a continuation of a previous project (54683) that also addressed this issue. The researchers collect samples using a technique that allows them to separate species in solution from colloids. Samples for ascertaining redox properties are separated immediately in the field. They determine the isotopic ratios using the high sensitivity of thermal ionization mass spectrometry, with subfemtogram detection limits. They used these techniques to show that Pu in the groundwater at Savannah River Site (SRS) originates from both weapons grade Pu and from a more mobile curium precursor. Most of the Pu at SRS is in an oxidized form that is more mobile than most standard models predict. Current work involves extensive sampling at Hanford to assist in the prediction of the migration potential. The main focus remains on identifying the Pu species present at Hanford, the mobility of these species, and the role that colloidal materials play in Pu transport.

Studies with Core Samples from Hanford. The fate and transport of radionuclides beneath the Hanford tank farms are also the subject of an ORNL/PNNL/Stanford University project (70219). They obtained undisturbed 0.3 meter x 0.3 meter cores by both horizontal and vertical sampling in a Hanford location similar to those under the tank farms, so they can duplicate field conditions. Preliminary results suggest that lateral flow beneath the tank farms is a strong contributor to the spread of contaminants and that uranium is strongly bound to the various sediments beneath the tank farms. The transport of cesium, technetium, and uranium radionuclides will be studied in a manner that will isolate hydrological and geochemical mechanisms that are important at different water contents. In addition to the macroscopic fate and transport experiments, interfacial molecular techniques will be used to quantify the distribution and chemical environments of the sorbed contaminant species. The goal is to provide an improved understanding and predictive capability for the fate of the radionuclides that have leaked from the Hanford tanks.

Sorption of Radionuclides on Altered Clay Surfaces. Few studies have been conducted to study the sorption of radionuclides on clays at the extreme conditions expected when highly concentrated basic solutions leak from high-level storage tanks into the subsurface. The focus of a Pennsylvania State University/BNL/PNNL study (70126) is on the sorption and release of cesium and strontium on clay surfaces that have been altered by exposure to solutions similar to those in the high-level tanks. They have studied the extent of the sorption of Cs and Sr on a variety of purified clay samples, both before and after exposure to a synthetic tank waste simulant solution. Sorption studies on a variety of clays have shown that the extent of Sr sorption is higher than for Cs, as expected, and strongly controlled by secondary mineral formation and short-range-ordered phases that evolve with increasing reaction time. Major efforts are being made to characterize the coordination environment of the sorbed ions. Their results are intended to be applied in equilibrium and transport models for radionuclide distribution between solid, colloidal, and dissolved phases.

Effects of Tank Leaks on Subsequent Flow and Transport. A University of Colorado/PNNL project (70070) is focused on obtaining a mechanistic understanding of how tank fluids migrate through the vadose zone, and they are particularly interested in how leaks of tank liquids will cause changes in porosity and permeability that will affect flow paths of subsequent leaks. The tank solutions have high concentrations of various salts, high pH, and high aluminum concentrations, which can significantly alter the vadose zone sediments by dissolution of primary minerals and precipitation of new minerals. Their first goal is to obtain kinetic rate laws for the dissolution of quartz and feldspar, as well as the precipitation of secondary phases, when tank liquids contact them. They will attempt to obtain an understanding of the nucleation mechanisms, nucleation sites on soil minerals, and the role of reactive surfaces on dissolution and precipitation reactions.

Project Teams

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  Pacific Northwest National Laboratory
- Washington State University
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- Oak Ridge National Laboratory
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  Pacific Northwest National Laboratory
  Stanford University

Interactions of Radionuclides with Carbonate Coatings. Carbonate grain coatings are more abundant in some vadose zone locations than are the oxyhydroxide grain coatings that are usually thought to control the sorption of inorganic ions. The goal of a PNNL/Stanford University/University of Wyoming project (70121) is to understand the interaction of some contaminants (strontium-90, cobalt-60, chromate, and pertechnetate) with carbonate coatings in order to improve forecasts of contaminant migration. Questions being addressed include: (1) Do carbonate coatings form preferentially on particular mineral surfaces? (2) Do carbonate coatings inhibit electron transfer reactions at otherwise reactive surfaces? (3) Do carbonate coatings enhance the binding of species such as ^{90}Sr and ^{60}Co? The rate of dissolution of carbonate coatings has been shown to be enhanced by the presence of certain impurities, and this could be important for understanding the stability of contaminant-containing carbonate surfaces.

Factors that Affect Carbonate Uptake of Contaminants. The objective of a State University of New York–Stony Brook/ PNNL project (70146) is to assess the role of calcium carbonate in the uptake and retention of inorganic contaminants, such as cobalt, cesium, lead, strontium, and chromium. Their work includes detailed microscopic and spectroscopic characterization of carbonate coatings and caliche along with studies of the factors that influence uptake behavior and retention behavior. Early work showed that the detailed structure of the carbonate surface controls the extent to which chromate is removed from vadose-zone fluids. Similar work is exploring uranyl uptake on carbonate surfaces. They have also studied the interaction of lead and strontium ions with natural caliche samples, and they have shown that only a small fraction of the caliche surface offers favorable reaction sites for lead uptake. X-ray absorption fine structure spectroscopy and X-ray fluorescence techniques are being used to characterize the binding of various metal ions to carbonate surfaces.

Thermodynamics of Radionuclides in Highly Basic Solutions. A PNNL/Florida State University project (70163) is working on the thermodynamics of the species formed by radionuclides in highly basic solutions, particularly those with high silica concentrations. Silica can form monomers, dimers, and higher oligomers in highly basic solutions, and each of these species has unique binding capabilities with different radionuclides. These complexes may result in more highly soluble and mobile species of radionuclides than would be anticipated from the initial composition of the vadose zone minerals. Their work includes experimental determinations of the species present in solution, molecular simulations to help identify species structures, and physical chemistry measurements to obtain the thermodynamic data necessary for predicting contaminant complexation and waste neutralization reactions. Their efforts are particularly directed toward reactions of strontium, cobalt, americium, uranium, technetium, and thorium ions in these complex solutions.

Transuranic Interfacial Reactions on Manganese Oxide/Hydroxide Minerals. The objective of a LBNL/PNNL project (70176) is to provide information about the interactions of plutonium and neptunium with manganese-containing minerals. Even though these minerals are typically minor phases in the vadose zone, they may preferentially sorb plutonium and other transuranics over the much more prevalent iron oxide minerals. Sorption experiments have been performed on several manganese-containing minerals to determine both the rate and the extent of the sorption. The data for plutonium sorption on manganite (MnOOH) show that independent of the initial oxidation state (VI or V) the plutonium is completely taken up by the mineral at pH 8.6, thus immobilizing the radionuclide contaminant. Above and below this pH, the uptake decreases steadily to 0% at pH 3 and about 40% at pH 10. Hausmannite (Mn_3O_4) shows even better plutonium uptake under the same conditions. A combination of X-ray absorption fine structure spectroscopy and optical absorption spectroscopy showed that the plutonium sorbed onto the minerals is present as Pu(IV). This implies that the minerals reduce the high oxidation state plutonium in solution (VI and V) to insoluble tetravalent plutonium, which then sorbs onto the mineral surfaces. The plutonium remaining in solution at the pH values where incomplete uptake occurred was present as Pu(V). The thermodynamic and kinetic parameters obtained from these experiments will be used as input data for reactive transport modeling in the vadose zone.

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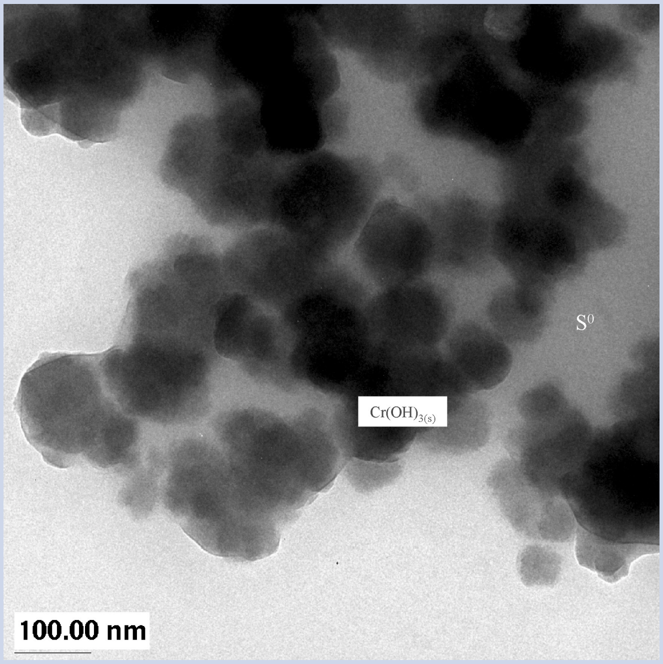
STABILIZATION AND TREATMENT OF METALS AND RADIONUCLIDES IN THE SUBSURFACE

CONVERSION OF METALS AND RADIONUCLIDES TO LESS MOBILE SPECIES IS THE ONLY PRACTICAL REMEDIATION STRATEGY AT MANY SITES

This fact sheet is the second of two that summarize 1999 EMSP projects that are related to the U.S. Department of Energy (DOE) Subsurface Contaminants Focus Area (SCFA) Metals and Radionuclides Product Line. Two of these projects are closely related to the fate and transport issues considered in the first fact sheet, but they deal more directly with specific interactions that can result in immobilization of species in the subsurface. One is exploring reactions of pertechnetate ions that can occur on certain iron-containing minerals, while the other is focused on understanding the interactions of various radionuclides with the new materials that are formed by reactions of highly alkaline fluids with minerals under the Hanford tanks.

Two other projects involve methods for inducing chemical reactions in the subsurface that convert a more mobile metal species in solution into a less mobile solid form. One of these is exploring the injection of urea into aquifers that contain organisms that will hydrolyze it to form ammonium carbonate, which will form calcium carbonate precipitates that can trap low concentrations of other radionuclides that were in solution. The injection of hydrogen sulfide gas into the subsurface to form insoluble sulfides with more mobile metal species has been explored by projects in the SCFA, and an EMSP project is investigating fundamental issues related to this potential method for chromate remediation.

A study of the use of genetically engineered plants to remove mercury from soils is being continued from a previous project, with current work focused on understanding the molecular biology of this phytoremediation process. Similar techniques could perhaps be used to develop plants to accumulate other heavy metals.



***In Situ* Gaseous Reduction**
A New Mexico Institute of Mining and Technology/PNNL project (70088) is exploring the potential use of gaseous hydrogen sulfide, H_2S, to convert chromium(VI) and other hazardous metal ion species into insoluble compounds with low mobility. Chromate reduction by hydrogen sulfide produces less mobile $Cr(OH)_{3(s)}$ (dark area) and S^0 (bright area), as analyzed by Transmission Electron Microscopy (TEM) and associated Energy-Dispersive X-ray Spectroscopy (EDS).

PROBLEMS/SOLUTIONS

- "The primary technical gap associated with describing and quantifying the solubility of contaminants is that there is an insufficient understanding of solubility of selected contaminants in various waste matrices (e.g., technetium in tank waste) and how this solubility then changes as the waste interacts with the vadose zone sediments at the interface" (STCG Need RL-SS14). One project is focused on developing an understanding of the solubility of technetium in contact with iron-containing minerals in the vadose zone.
- An STCG Need, Transport of Contaminants (RL-SS26-S), cites a need for "geochemical models for the incorporation of trace contaminants (metals, radionuclides) into secondary phases via co-precipitation." A project that is exploring potential methods to induce calcium carbonate precipitation for removing certain radionuclides from groundwater may also contribute information useful for understanding natural processes that stabilize radionuclides.

ANTICIPATED IMPACT

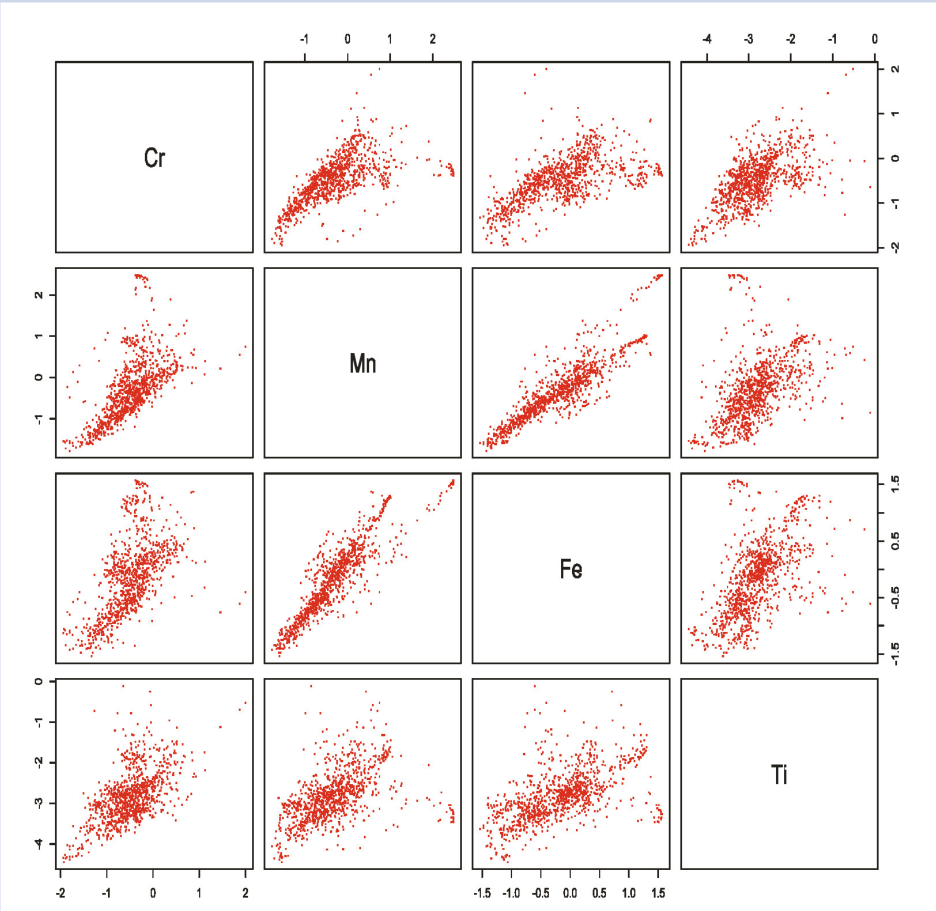
- An estimated 240,000 to 470,000 pounds of elemental mercury were discharged at the East Fork Poplar Creek site at Oak Ridge as a result of a lithium separation process at the Y-12 Plant, and several other DOE sites have substantial mercury pollution problems. Although direct physical and chemical remediation processes may be useful at sites with very high mercury levels, genetically engineered plants produced in an EMSP project may provide a less expensive means for remediating lower levels of mercury from contaminated soils.
- To illustrate the magnitude of the cleanup problem, there are 35 Project Baseline Summaries for the Hanford site alone, and one of these (300 Area Remedial Action) cites 240 waste sites, many of which have radionuclide contamination. Retrieval of the contaminants from all contaminated sites is not feasible, so methods to stabilize radionuclides in their current location may offer the best solution for most sites.

Technetium Mobility in the Vadose Zone. More than 900 curies of technetium were discharged into the ground at Hanford. Technetium is easily oxidized to form the highly soluble and mobile pertechnetate species, but reduction reactions on iron(II)-containing mineral surfaces could result in forming technetium dioxide and other reduced species with much lower mobility. These processes are the focus of a PNNL/LANL project (70177). Their strategy is to develop a description of the reduction of pertechnetate ions on iron(II)-containing minerals, to determine the stability of the resulting reduced technetium solids, and to use contaminated Hanford sediments to validate their models of technetium mobility in the vadose zone. The goal is to be able to ascertain which sites pose the greatest environmental threat.

Impact of Alkaline Tank Fluids on Radionuclide Immobilization. The Ohio State University/PNNL/Stanford University project (70081) is directed toward understanding how the most common radionuclides might become immobilized in the subsurface solids that have been impacted by alkaline tank fluids. The effect of aging on the stability of complexes on solids formed from neutralization and nucleation of alkaline aluminate solutions is being investigated, and the sorption or co-precipitation of various radionuclides in the solids formed by reactions of alkaline aluminate solutions with various minerals and with Hanford sediments is being studied. They have shown that addition of amorphous silica to alkaline sodium aluminate solutions forms solids that are much more effective at removing cesium from solution than were the solids formed in the absence of the silica. They also plan to use a variety of modern instrumental methods to characterize the chemical forms of the species present in actual core samples taken from underneath the SX-108 tank.

Chemical Treatment of Metals and Radionuclides in the Subsurface

In Situ Formation of Calcium Carbonate for Radionuclide Immobilization. An INEEL/Portland State University/University of Toronto project (70206) is directed toward development of an *in situ* formation of calcium carbonate to remove certain radionuclides from solution. The idea is to inject urea into a contaminated aquifer. If urease-containing organisms are present, the urea will be hydrolyzed to form ammonium carbonate, which will react with low concentrations of calcium to form calcium carbonate and trap other metal ions in the precipitate. Urea is inexpensive and poses no environmental



Impact of Alkaline Tank Fluids on Radionuclide Immobilization

An Ohio State University/PNNL/Stanford University project (70081) is directed toward understanding how the most common radionuclides might become immobilized in subsurface solids that have been impacted by alkaline tank fluids.

This graph shows correlations of the spatial distributions between Cr, Mn, Fe, and Ti for a borehole sample under tank SX-108. Data were collected on the undulator beam line at GSECARS Sector 13 (Advanced Photon Source, Argonne National Laboratory) using X-ray micro-fluorescence elemental mapping technique. The x-axis represents the logarithm of the normalized fluorescence intensity of the element in each column. The y-axis corresponds to the log intensity of each element.

X-ray absorption spectra (XAS) collected at beam line 11-2 of the Stanford Synchrotron Research Laboratory indicate that most of the Cr in the sediments beneath SX-108 remains as the more mobile Cr(VI). However, sediments samples with pH values in excess of 9 did show a dominance of Cr as Cr(III). Companion laboratory studies suggest that some Cr(VI) was reduced to Cr(III) *in situ*, by reactions with Fe(II) present in alumino-silicate clays, magnetites, and illmenites.

hazard, so it could be injected into aquifers. Early results indicated that the potential for using urea hydrolysis as the basis for an *in situ* remediation technique for strontium-90 and other divalent metal ions is promising. Urea-hydrolyzing bacteria were found in the Snake River Plain Aquifer at INEEL, and it was found that these bacteria can catalyze the formation of calcite. An experiment to test this procedure in a groundwater well at INEEL is being planned, and the group is also exploring the feasibility of this technique to remediate a strontium plume at the Hanford 100 area.

In Situ Gaseous Reduction. Unlike organic chemicals, metal ions in the subsurface cannot be destroyed. However, more soluble and mobile species, such as chromate, can be converted into insoluble, less mobile, and therefore less hazardous forms. A New Mexico Institute of Mining and Technology/PNNL project (70088) is exploring the potential use of gaseous hydrogen sulfide, H_2S, to convert chromium(VI) and other hazardous metal ion species into insoluble compounds with low mobility. If H_2S is injected into the soil, what will be the effect of mineral surfaces on the rate of reduction of chromate or on the rate of oxidation of H_2S by air? What other minerals in the subsurface will also react with the H_2S, making it unavailable for the desired reaction? If chromium(VI) is reduced to chromium(III) by H_2S in the subsurface, what is the long-term resistance to reoxidation to the more mobile Cr(VI)? What variables in soil water chemistry can affect the reduction reaction? These and other related questions are being addressed in laboratory studies, and tests are being conducted with Hanford soil samples to define reaction parameters for the Cr(VI)-H_2S-oxygen-soil system.

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Phytoremediation of Heavy Metals from Soils

Use of Plants for Removal of Mercury from Soils. Several DOE sites, particularly the Oak Ridge National Laboratory, have areas with significant levels of mercury contamination. A University of Georgia project (70054) is continuing work from a previous project (54837) to demonstrate that native trees, shrubs, and grasses can be engineered for remediation of mercury-contaminated sites. This group has engineered several plants to express two bacterial genes, *merB* and *merA*. Plants expressing *merA* extract and reduce ionic mercury to metallic mercury which is transpired from the leaves, and those expressing *merB* extract highly-toxic methylmercury from the soil and degrade it to ionic mercury. Current work is focused on obtaining a detailed understanding of the mechanisms by which these plants process the various forms of mercury in order to improve the phytoremediation designs. In addition, attempts will be made to produce plants to accumulate mercury so that it can be removed by harvesting the plants rather than by vaporizing it into the environment. Presumably, similar techniques could be used to design plants to hyperaccumulate other heavy metal pollutants.

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SUBSURFACE CONTAMINATION – SUBSURFACE SCIENCE AND SOURCE TERM CONTAINMENT

A MAJOR OBJECTIVE OF THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM IS TO GENERATE NEW KNOWLEDGE TO SUPPORT CLEANUP OF SUBSURFACE CONTAMINATION

The Source Term Containment and Remediation product line in the Subsurface Contaminants Focus Area (SCFA) addresses the development of containment and stabilization methods to prevent the spread of contaminant plumes, particularly from former landfills, disposal areas, and trenches. Most of the EMSP projects summarized here are applicable to this area because knowledge of the characteristics of the subsurface is a prerequisite for the treatment, confinement, and stabilization of subsurface contamination. Many of these projects, however, involve investigations of fundamental subsurface science and so are of general interest to all areas of the SCFA.

It is not possible for the most sophisticated modeling programs to make reliable predictions of contaminant migration in the subsurface without detailed information about characteristics such as porosity, permeability, and moisture level. Geophysical techniques being explored to provide some of this information include seismic methods, cross-borehole and ground-penetrating radar, high-frequency electrical impedance methods, electrical resistance tomography, and others in combination with hydrogeological measurements. Several of these projects involve controlled laboratory experiments, while others have set up large-scale experiments in well-characterized, heavily instrumented facilities to provide better understanding of how measured geophysical parameters are related to known changes in subsurface parameters.

The heterogeneity of the subsurface characteristics at many of the arid sites with major contaminant problems presents severe problems for fate and transport modeling. EMSP projects include efforts to improve experimental and modeling studies of flow in coarse media, and another effort is directed at combining small-scale direct measurements of soil properties along with geophysical measurements to infer soil properties at unsampled locations. Another project is using an extensively instrumented, large-scale test facility to correlate geophysical and hydrogeological measurements with known contaminant infiltrations. Vertically oriented, permeable structures may provide the most significant pathways for contaminant transport, so another project involves a detailed survey to identify the spacing and thickness of such vertical structures at Hanford.

Vertical Structures and Contaminant Migration
A PNNL project (70193) has conducted a ground-penetrating radar survey to identify spacing and thickness of clastic dikes. Above: Vertical clastic dike cutting layered sediments of the Hanford formation. Measurements are providing data for reactive flow and transport modeling to determine if clastic dikes provide fast paths for fluid transport through the vadose zone.

Problems/Solutions

- As stated in an STCG Science Need (ID-S.1.09), “a method or model is needed that will address the effects of space, time, and scale on the mass transport of the solute through differing media.” The vadose zone at several major U.S. Department of Energy (DOE) sites contains gravel and gravelly sands, and flow through such materials is not described well by classical models. Both macroscopic and microscopic studies of fluid flow in Hanford sediments are being conducted by an EMSP project to improve predictions for the fate of contaminants in such media.
- As described in *Research Needs in Subsurface Science* (National Research Council, March 2000), “the subsurface characteristics at a site place fundamental controls on contaminant fate and transport behavior. Knowledge gaps include understanding which characteristics control fate and transport behavior in the subsurface and also understanding how those characteristics can be measured at the appropriate scales over large subsurface volumes, using both indirect and direct techniques.” Most of the projects described here are directed at closing precisely these gaps in understanding subsurface characteristics.

Anticipated Impact

- “The primary technical gap associated with delineating contaminant plumes in the vadose zone is insufficient soil, geophysical, geochemical, and hydrological data or methods to resolve subsurface heterogeneities, characterize geohydrologic properties, and map contaminant distributions at different scales in the vadose zone,” (STCG Science Need RL-SS31). A wise use of resources requires that remediation activities occur where the most significant risks occur and that resources not be wasted on sites that do not present tangible risks. Thus, the ability to tell the difference is prerequisite to an effective environmental remediation program.

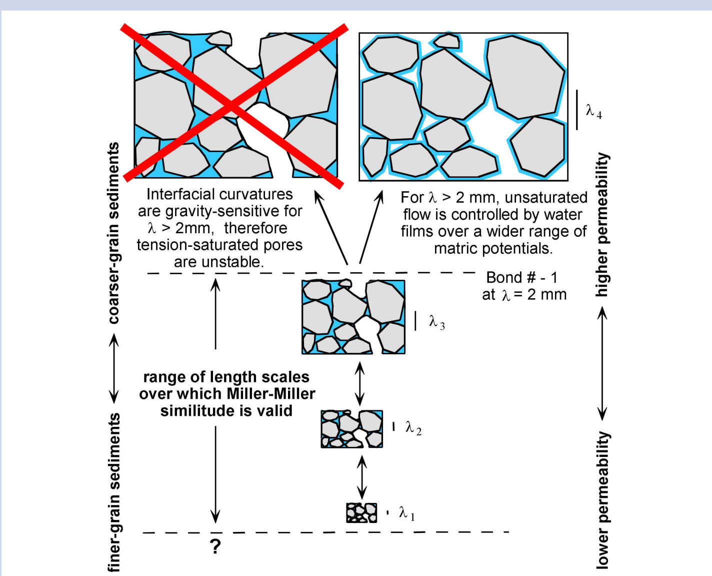
Geophysical Techniques

Improved Geophysical Imaging. In situ remediation requires information about subsurface porosity, permeability, and fluid saturation, and an LLNL project (70108) is designed to determine the effects of fluid distribution on measured geophysical properties for partially saturated, shallow subsurface conditions. The project is a continuation of a previous project (55411) with the goal of improving geophysical imaging without using expensive, slow-core drilling methods. An ultrasonic apparatus for simultaneous measurement of compressional and shear wave velocities has been modified to enable measurements on partially saturated soil samples, and researchers are continuing testing of a new data analysis method for seismic data that shows how partial saturation affects seismic properties. Thus, controlled laboratory experiments are being used to measure geophysical properties as functions of saturation, pressure, and soil composition, and then rock physics theories will be used to relate these measurements to hydrogeologic properties and to generalize results to the field scale.

Ground-Penetrating Radar for Determining Moisture Content. Contaminant transport in the vadose zone is very dependent on moisture content, so accurate estimates of moisture content are essential for the design of containment or treatment processes. The objective of a Stanford University/University of British Columbia project (70115) is to develop the usefulness of both cross-borehole and ground-penetrating radar methods for the determination of moisture content. Their work is focused on answering two questions: (1) Can a measure of the dielectric constant of a volume of the subsurface be used to determine the moisture content of that volume? and (2) Can the spatial distribution of radar reflections be used to characterize the spatial distribution of moisture content in the subsurface? This work is a combination of laboratory, field, and theoretical studies, all of which are related to improved use of radar methods to characterize moisture content in the vadose zone.

High-Frequency Impedance Methods. High-frequency impedance methods in the 10-Hertz to 1-Megahertz range are sensitive to the amount and composition of fluids present in porous media and are particularly useful for situations in which ground-penetrating radar cannot penetrate to sufficient depths. A SNL/ElectroMagnetic Instruments project (70220) is designed to improve the usefulness of this method. The goal of their work is to produce a combined measurement and interpretation package for noninvasive, high-resolution characterization of larger transport pathways, certain types of contamination, and heterogeneity within the vadose zone. Early work has involved measurements at a well-characterized site in order to test the instruments and methods; future work will be conducted at Hanford site.

A Hydrologic-Geophysical Method for Characterizing Flow and Transport. A University of Wisconsin/SNL project (70267) is using some of the techniques developed by another project (55332) to develop a hydrologic-geophysical method for characterizing flow and transport processes within the vadose zone. The method uses electrical conductivity information from electric resistivity tomography, dielectric constants obtained from cross-borehole ground-penetrating radar, statistical information about heterogeneity and hydrologic processes, and sparse hydrologic data to provide maps of hydrogeological heterogeneity and the extent of contamination. The objectives are to provide better models of flow and transport mechanisms within heterogeneous vadose zone deposits, a data base to assess the performance of the models, and a validated experimental method that could be applied to DOE sites to determine flow and transport rates.



Flow and Transport in Coarse Media
An LBNL project (70069) is designed to improve understanding of the flow and transport of contaminants because some aspects of the flow in coarse media are not predictable with classical modeling techniques. Above: Scaling of unsaturated flow in porous media has an upper grain-size limit. For gravel-dominated sediments (> 2-mm grains), a much broader range of flow is determined by water films rather than by interconnected pathways of saturated pores. Studies are being conducted to determine how grain topography and water films control unsaturated flow in gravel.

Hydrogeology

Flow and Transport in Coarse Media. Some of the most badly contaminated DOE sites are at the Hanford site, where much of the vadose zone consists of coarse-textured materials with grain sizes greater than 1 millimeter. An LBNL project (70069) is designed to improve understanding of the flow and transport of contaminants in such sediments because some aspects of the flow in coarse media are not predictable with classical modeling techniques. Their objectives are to quantify the macroscopic hydraulic properties of very coarse sediments and to determine the microscale basis for fast unsaturated flow. Macroscopic studies have used several different column methods. The microscopic tests of film flow have used the National Synchrotron Light Source at Brookhaven for the X-ray beam used to determine average water film thicknesses on Hanford gravel samples. The combined results of macroscopic and microscopic experiments will be used to develop a physical model of unsaturated flow in coarse sediments.

A Vadose Zone Observatory for Exploring Contaminant Transport. An LLNL project (70149), which is a continuation of a previous project (54950), is investigating details of contaminant transport in the vadose zone using the "Vadose Zone Observatory" at LLNL. The observatory has been designed to be particularly relevant for understanding contaminant transport issues at Hanford. The facility contains instrumented boreholes with electric resistance tomography arrays, wells for electromagnetic induction tomography, and tensiometers, lysimeters, and other sensors throughout the 70-foot zone between the surface and groundwater. Thus, infiltration events can be monitored using both geophysical imaging techniques as well as more conventional hydrologic measurements at discrete points. The infiltration studies involve releases of water at the surface, some with chemical tracers and some without added tracers for evaluating the effect of new infiltration on the downward movement of tracers remaining from previous releases. A computer modeling program is used to develop infiltration models for interpreting the wide variety of observations obtained during an infiltration experiment.

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Flow and Transport in Heterogeneous Porous Media. Accurate predictions of water flow and contaminant transport in the vadose zone are made more difficult because of the spatial variability of soils and sediments. This variability is difficult to characterize on a sufficiently small scale, so most models assume more uniform subsurface conditions than are actually present. A PNNL project (70187) is developing methods for combining small-scale direct measurements of soil physical and hydraulic properties with indirect geophysical measurements made at a larger scale to infer soil hydraulic properties at unsampled locations. These data are being used for model parameterization and numerical simulation of a large-scale, field injection experiment conducted at Hanford Site. The issue of parameter upscaling is being addressed as part of this research. The project is also investigating use of so-called pedo-transfer functions derived from neural network analyses to estimate model parameters. One of the key components of the research involves quantification of the prediction uncertainty associated with using sparse and/or surrogate data for model parameterization.

Role of Permeable, Vertical Structures in Contaminant Migration. Most flow and transport models of the vadose zone used in the past at the Hanford site assume horizontally layered sediments with no preferential vertical flow paths. But vertically oriented, more highly permeable structures occur at many locations in both the 200 West and 200 East areas, and these structures may enhance the vertical movement of moisture and contaminants through the vadose zone. A PNNL/New Mexico Institute of Mining and Technology project (70193) has involved a detailed ground-penetrating radar survey to identify the spacing and thickness of these vertical structures or clastic dikes. The distribution of hydraulic properties within clastic dikes is being measured using infiltration experiments. Geostatistical methods will then be used to provide numerical three-dimensional grids of the infiltration site for flow and transport modeling, and the resulting transport models will be compared with the actual observations.

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