



**WESTERN REGION
HAZARDOUS SUBSTANCE RESEARCH CENTER**

1993 ANNUAL REPORT

Stanford University
Oregon State University

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WESTERN REGION HAZARDOUS SUBSTANCE RESEARCH CENTER

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THE CENTER AT A GLANCE

The Western Region Hazardous Substance Research Center (WRHSRC) is a cooperative activity between Stanford University and Oregon State University that was established in February 1989 to address critical hazardous substance problems in EPA Regions 9 and 10. The Regions include the states of Alaska, Arizona, California, Hawaii, Idaho, Nevada, Oregon, and Washington, and Guam. The Center receives its base financial support from the U.S. Environmental Protection Agency, but also is supported through grants, contracts, and gifts from other federal agencies, states, municipalities, consultants, and industry.

The objectives of the Center are:

1. To promote through fundamental and applied research the development of alternative and advanced physical, chemical, and biological processes for treatment of hazardous substances in the surface and subsurface environments.
2. To disseminate the results of research to the industrial and regulatory communities, to foster exchange of information with these communities, and to promote a better understanding of the scientific capability to detect, assess, and mitigate risks associated with hazardous substance usage and disposal.

Groundwater cleanup and site remediation, with a strong emphasis on biological approaches, represent the major focus of Center activities. The research and training functions of the Center address the major hazardous substance problems in EPA Regions 9 and 10, including chlorinated and nonchlorinated solvents, petroleum products, pesticides, and toxic inorganic compounds including heavy metals. Environmental problems from these substances, which often occur in mixtures, result largely from the production of electronic equipment, chemicals, forestry products, and food, as well as mining and military activities, all of which are important in the region pair.

This past year, the Center faculty and research staff were engaged in 21 separate research projects. One project concerning biodegradation of chlorinated solvents was completed, 15 projects represent continuation of research begun during previous years, and five represent new starts. As in the past, these projects have a focus on groundwater cleanup and remediation of sites contaminated with chlorinated solvents, halogenated aromatic compounds such as pentachlorophenol, nonhalogenated aromatics, including petroleum derivatives such as gasoline,

and heavy metals. Other projects specifically address the evaluation of factors affecting movement and fate of the above contaminants in the environment and design and management issues for site cleanup in general. All of the five new projects were at least partially support by agencies other than the U.S. EPA. Two of the five new projects were concerned with heavy metals and received partial support from the Department of Energy; one project, concerned with modeling strategies for optimizing in-situ bioremediation, was fully supported by the Department of Energy, as was a new project for determining the potential of using substituted porphyrins for degradation of chlorinated solvents. The fifth new project is receiving support from the U.S. Air Force to conduct additional evaluations at the Moffett Field test site of aerobic cometabolic in-situ bioremediation of chlorinated solvents, as a preliminary step towards full-scale implementation.

Technology transfer and training activities are broad and include sponsorship of sessions at several major conferences, technical workshops directed toward technology transfer, development of a major training program in Oregon, and numerous presentations of research information and technology transfer at conferences, workshops, and seminars for regulators, industry, consulting firms, and university faculty and students. Technology transfer has become a major focus of activity at the WRHSRC, with four new initiatives, all directed towards field demonstrations of technologies developed through WRHSRC research.

The faculty and staff who are directing the Center's research, training, and technology transfer activities are listed in Table 1. They collectively represent an integrated research team representing five different schools (engineering, science, earth sciences, medicine, and veterinary medicine), and many different disciplines (microbiology, chemistry, hydrogeology, hydrology, chemical engineering, civil engineering, and medicine). Perry L. McCarty is Director of the overall Center and of the research program. Kenneth J. Williamson serves as Associate Director in charge of training and technology transfer and coordinates the Center's overall activities in Oregon. Lewis Semprini completed his term this year as Assistant Director for coordination of technology transfer and research activities in California. While leaving Stanford, he has not left the WRHSRC as he accepted a position as Associate Professor at Oregon State University, where he continues his activities in hazardous substance research. Mark N. Goltz is the new Assistant Director, who is taking over the responsibilities formerly handled by Semprini. He received a Ph.D. degree from Stanford in 1986, and recently retired as a Lieutenant Colonel from the U.S. Air Force. Assistant Director Martin Reinhard remains in charge of the Center's analytical program. Marilyn C. King is the Center's Administrative Assistant.

Table 1. KEY PERSONNEL AT THE CENTER

<u>Stanford University</u>	<u>Oregon State University</u>
Prof. David L. Freyberg	Prof. Daniel J. Arp
Prof. Mark N. Goltz	Prof. A. Morrie Craig
Prof. Steven M. Gorelick	Dr. Michael R. Hyman
Prof. Dunja Grbić -Galić	Prof. James D. Ingle
Prof. Lynn M. Hildemann	Prof. Jonathan D. Istok
Mr. Gary D. Hopkins	Prof. Peter O. Nelson
Mrs. Marilyn C. King	Prof. Lewis Semprini
Prof. Peter K. Kitanidis	Prof. John C. Westall

Prof. James O. Leckie
Prof. Abdul Matin
Prof. Perry L. McCarty
Prof. Martin Reinhard
Prof. Paul V. Roberts

Prof. Kenneth J. Williamson
Prof. Sandra L. Woods

The Center has two major advisory groups to guide its activities. The Science Advisory Committee (SAC) has oversight for all Center research activities, and the Training and Technology Transfer Advisory Committee (TTTAC) oversees the Center's training and technology transfer activities. The members of SAC and TTTAC during this past year are listed in Tables 2A and 2B, respectively. They represent federal and state governments, industry, consulting firms, and universities. The budgets for the past year and the total since the Center's inception are summarized in Table 3. The education of students interested in careers directed toward finding solutions to environmental problems is another important goal. The number of students supported through WRHSRC funds is also listed in Table 3.

Table 2A. SCIENCE ADVISORY COMMITTEE

<u>Member</u>	<u>Affiliation</u>	<u>Expertise</u>
Douglas R. Christensen	Consulting Engineering	Treatment Processes
John Conomos	Govt/USGS	Hydrology
David E. Ellis	Industry	Biological Processes
David Frank	Govt/EPA	Hydrogeology
John Glaser	Govt/EPA	Physical/Chemical Processes
Ronald Hoeppel	Govt/DOD	Microbiology
Michael C. Kavanaugh*	Consulting Engineer	Physical/Chemical Processes
Rilchard G. Luthy	University	Process Engineering
James M. Tiedje	University	Microbiology
John L. Wilson†	University	Hydrology
John Wise	Govt/EPA	Planning

*Chairman

†Vice Chairman

Table 2B. TRAINING AND TECHNOLOGY TRANSFER ADVISORY COMMITTEE

<u>Member</u>	<u>Affiliation</u>	<u>Expertise</u>
James T. Allen	Govt/ California	Treatment Technology
John J. Barich	Govt/EPA	Regulations
Kenneth Bigos	Govt/EPA	Air Pollution
Lynn Coleman	Govt/Washington	Regulations
Sandy Gurkewitz	Govt/Oregon	Environmental Quality
David Kennedy†	Consulting Engineer	Treatment Technology
Jon Kindschy	University	Hazardous Substances Training
Gregory Peterson	Consulting Engineer	Treatment Technology
Mary E. Peterson	Govt/DOE-Industry	Treatment Technology
M. R. Scalf	Govt/EPA	Groundwater Remediation
Kenneth Sutherland*	Industry	Treatment Technology
Winona Victory	Govt/EPA	Training/Tech Transfer

*Chairman

†Vice Chairman

Table 3. CENTER FUNDING

<u>Funding Sources</u>	<u>FY 1993*</u>	<u>Funds to Date</u>
EPA: Centers Program	\$922,000	\$5,956,015
EPA: Other	\$48,000	\$635,816
Other Govt: Federal†	\$2,122,216	\$3,192,216
Other Govt: State	\$0	\$0
Consortium	\$548,054	\$1,361,322
Private Sector#	\$225,000	\$1,669,741
TOTAL	\$3,865,270	\$12,815,110

*Oct. 1, 1992 - Dec. 31, 1993

†Department of Energy; Department of Defense

#Allied Signal Corporation; Brown and Caldwell; CH2M HILL; DuPont Corporation; Electric Power Research Institute; Gas Research Institute; Hewlett-Packard Company; Montgomery-Watson, Inc.; Kennedy/Jenks; Kleinfelder, Inc.; MBT Environmental Engineering, Ltd.; McLaren/Hart; Monsanto; Orange County Water District; Schlumberger Technologies; Shell Development Corporation

<u>Student Support</u>	<u>Number*</u>	<u>Funds to Date†</u>
M.S.	18	\$472,676
Ph.D.	52	\$3,038,237
Post Doctoral	13	\$756,677
TOTAL	83	\$4,267,590

*Total person-years working on Center Projects

†Includes tuition, travel, supplies, etc.

CENTER DIRECTOR'S REPORT

The WRHSRC has 18 faculty members representing two universities and five disciplines (chemistry, engineering, hydrogeology, medicine, and microbiology). Since its inception, the Center has completed 20 research projects, and during 1993 had 21 active projects. These active projects continue to emphasize the theme that the Center began with. That is to focus the Center's limited resources on the major hazardous problems resulting from subsurface contamination. The Center's main focus is on groundwater, and the most prevalent and difficult chemical contaminants in groundwater, which include chlorinated solvents and their transformation products, aromatic hydrocarbons, halogenated hydrocarbons, and heavy metals. A major focus with the organic contaminants is on chemical and biological transformations. The interest here is in determining whether or not natural processes can reduce the hazards associated with subsurface contamination, and whether through engineering approaches the transformation processes can be enhanced in a way that will more rapidly reduce or eliminate the hazards posed in a cost effective manner.

The results of the Center's research over the past three and one-half years have been disseminated broadly. To date there have been 122 publications from work supported by the WRHSRC. These include 49 journal publications, with 12 more submitted and under review; one bound proceedings; 29 chapters in books or articles in bound conference proceedings, 13 project reports, seven Ph.D. dissertations, and 10 M.S. theses. There have been numerous oral or poster presentations on research findings at international, national, and regional conferences, and many more that represent broad summaries of research for technology transfer. The WRHSRC has sponsored or cosponsored 21 conferences, seminars, or workshops on subjects as diverse as research findings, environmental engineering education, hazardous substance chemistry and management, and the training and technology transfer process.

One of the significant outcomes of a Five Centers' Conference on Technology Transfer hosted by the WRHSRC through the efforts of Prof. Kenneth Williamson, Director of Training and Technology Transfer, was a realization that true transfer of technology to a user community does not result from oral and written presentations alone. There is a need to work closely with organizations interested in implementing new technology so that the knowledge gained through research can be better communicated and put into practice. In addition, there is much to be learned from the act of implementation itself. Areas where implementation would benefit from additional research can thus be better identified, providing a highly beneficial feedback into the research process itself. Such feedback from the Center's activities with several field pilot and full-scale investigations has resulted in four new technology transfer projects for the WRHSRC this year.

Most of the WRHSRC's budget is represented by core funding from EPA. However, other federal funds have come to the Center from other branches within EPA, and from the Department of Defense and the Department of Energy, because of the interest these agencies have in the Center's research. In addition, several industrial organizations and consulting engineering firms have contributed support as well in research contracts and gifts. The latter are important to the Center, not only because they represent financial support and cooperative activity with the users of the Center's research, but they also help achieve the minimum of 20 percent non-federal support that is required for the EPA-sponsored HSRCs.

One of the major findings of recent years is that chlorinated solvents are transformed in groundwater by both chemical and biological processes. The thrust group associated with this problem is directing its efforts toward finding engineering methods for the subsurface mixing of chemicals that can help enhance these natural processes with the contaminants of concern. The desire is to produce harmless end products. This is closely associated with the related effort to determine how best to remove polluted groundwater and contaminants from the subsurface environment. The major efforts underway here will continue both through active involvement with those applying technologies pioneered through Center activity, and through additional research to improve the understanding of the processes involved.

Research by the thrust group studying aromatic compounds and a portion of the research by the thrust group studying chlorinated solvents has focused on anaerobic processes. A great deal of evidence has been obtained that aromatic compounds and chlorinated solvents are often transformed in groundwater naturally by microorganisms living under anaerobic conditions. The anaerobic conditions result when the quantity of contaminants present exceed the available oxygen supply, which is often the case. The basic research ongoing here is directed toward predictions of transformation rates, the determination of transformation products, and the development of engineering methods that might enhance the rates of desired anaerobic transformations. It may be that in some cases, the most environmentally sound and least expensive alternative is the no-treatment alternative. However, in order to justify this, we must first learn how to make sound judgments about transformation potential at any given location. Research on these major issues is continuing.

A third associated thrust area is the modeling of transport and fate processes and groundwater-management strategies. In order to remove polluted groundwater and associated contaminants, improved mathematical models are desirable that consider the great uncertainties in the hydrogeological structure of a contaminated site, and the relative chemical and physical properties of both the contaminant and the aquifer materials that impact on contaminant distribution and movement. An additional highly complex need is for methods to introduce nutrients or other chemicals required to enhance biological or chemical transformation, and to mix these chemicals with groundwater contaminants as noted above. The absence of good methods for this is one of the major barriers to in-situ treatment. The models and engineering methods being developed here have direct impact on the activities of the other two thrust groups described above so that good interactions between the three thrust groups is necessary.

A fourth thrust area of the WRHSRC is concerned with heavy metals. Chromium and lead are among the most frequently found hazardous substances at contaminated sites. The WRHSRC has been conducting research both on improved procedures for removing heavy metals from groundwater, and also on surface treatment of heavy-metal-contaminated groundwater. Research here is being conducted by Center faculty partly through Center funding, but perhaps on a larger scale with direct support from other federal and private sources.

Highlights of accomplishments this past year in our research thrust groups and our training and technology transfer program are given in the following.

HIGHLIGHTS FOR 1993

RESEARCH AND TECHNOLOGY TRANSFER

With entrance into the fifth year of research activity this past year, the WRHSRC not only continued to conduct laboratory and field-scale research, but also began a major effort to apply its research results to full scale application. The latter, which is part of the Center's decision to make a major commitment to technology transfer, was instrumental in the Center's seeking of four major technology transfer projects. During previous efforts to implement full-scale application of methanotrophic cometabolic biodegradation of chlorinated solvents at the St. Joseph, Michigan, Superfund site, the Center investigators found that they were challenged by many new questions that required new research. Among these were how to insure that indigenous microorganisms at the St. Joseph site would perform similarly to those present in groundwater at our Moffett field research station, where the pilot scale field studies were conducted. How can the chemicals of interest, for example methane and oxygen, be introduced into the groundwater in such a way that they would mix with the contaminants of interest and the bacteria that would effect their biodegradation? What chemical introduction strategies would be optimal for bringing about efficient biodegradation of contaminants? How would microbial growth and biodegradation activity be distributed within the treatment zone? What type of monitoring protocol should be used to evaluate the possible effectiveness of in-situ bioremediation? These questions are being addressed within several of the ongoing WRHSRC research projects. But, in addition, we realized that new questions of importance are likely to arise when full-scale implementation itself was carried out, and partially for this reason, efforts to undertake full-scale implementation were begun.

Two of the technology transfer projects are being implemented at the Department of Energy's Hanford site in Richland, Washington, through cooperative studies with the Batelle Pacific Northwest Research Laboratory (PNL). One study is concerned with in-situ biodegradation of carbon tetrachloride in groundwater by denitrifying bacteria that grow on acetate. The potential for carbon tetrachloride biodegradation was demonstrated through several laboratory studies and Moffett Field pilot studies conducted by WRHSRC investigators at Stanford University. These studies indicated that the consortia of microorganisms that resulted from acetate introduction and denitrification could convert carbon tetrachloride, for the most part, to carbon dioxide. However, a fraction was converted to chloroform. In order to implement in-situ bioremediation, the WRHSRC researchers have proposed chemical introduction through wells screened at two levels and containing a pump that draws water in through one screen, adding chemicals to the water within the well, and pumping the water through the other screen back into the aquifer for in-situ biodegradation. Mathematical models are being developed by Professors Peter Kitanidis and Paul Roberts at Stanford University and Lewis Semprini at Oregon State University, and their students, to simulate the effectiveness of different operational strategies at the site. PNL and their contractors are addressing other questions of importance, and will design and implement the full-scale system.

A second study, also at Hanford and conducted through cooperative studies with PNL, is for the use of in-situ vapor stripping to remove volatile organic compounds, particularly carbon tetrachloride. The theoretical studies for this project are being conducted by Professor Steven Gorelick and his students and research staff. The groundwater table at Hanford is deep. The

advantages of either in-situ bioremediation or vapor stripping is that the water does not need to be pumped all the way to the surface for treatment and subsequent disposal. In addition, at Hanford, the groundwater contains tritium, which would be difficult to remove through surface treatment, but can be left in the groundwater to decay sufficiently over 20 years or so.

The third study is funded by the U.S. Air Force for a full-scale demonstration of in-situ aerobic cometabolic biodegradation of trichloroethylene (TCE). The Moffett Field site was developed in Mountain View, California, at the Moffett Naval Air Station in 1985 specifically to evaluate this process in the field. Since then, there have been numerous laboratory research studies at Stanford University and elsewhere to evaluate the potential of this process. Originally, methane and oxygen were introduced into groundwater to stimulate methanotrophic bacteria, which cometabolize TCE, a process based upon observations originally provided by John and Barbara Wilson at the U.S. EPA Robert S. Kerr Environmental Research Laboratory. This process has now seen full scale implementation over the last few years at DOE's Savannah River Laboratory. However, over the past three years, the WRHSRC has demonstrated at Moffett Field that the injection of phenol provides much more efficient cometabolism of TCE in groundwater than does methane. The use of phenol as an alternative to methane was first demonstrated by scientists at U.S. EPA's Environmental Research Laboratory at Gulf Breeze, Florida. In preparation for the full-scale effort, toluene was studied in research at Moffett Field funded by the U.S. Air Force, and found to be as effective as phenol for TCE biodegradation. These processes are also effective at biodegradation of 1,2-dichloroethylenes and vinyl chloride, but not 1,1-dichloroethylene. Indeed, the presence of a significant concentration of the latter compound was found to render the process ineffective even for TCE biodegradation. Thus, potential applications should be conducted only where 1,1-dichloroethylene is not significant in concentration. Groundwater microorganisms were found to degrade both the injected phenol and toluene to below detection at 1 µg/l, well below possible toxicity or taste and odor thresholds. Funds are now available to the WRHSRC for full scale implementation of this process, and an appropriate U.S. Air Force base for the study is being sought.

The fourth project is concerned with biodegradation of soils contaminated with a mixture of chlorinated aromatic and aliphatic compounds through a combination of anaerobic followed by aerobic treatment. The anaerobic portion of the study is to achieve dechlorination so that the remaining organic products can be degraded aerobically. This technology transfer project is being funded by the Oregon Department of Transportation.

RESEARCH ACTIVITIES

Groundwater Management

One major difficulty in the remediation of contaminated groundwaters is the presence of nonaqueous phase liquids (NAPLs), such as chlorinated solvents and gasoline, that are relatively insoluble, and are the major source of continued contamination of groundwater over time. Unless NAPLs can be located, it is difficult to eliminate their contaminating influence by containing them or removing them from the subsurface environment. One potential method to locate NAPLs is to measure the concentration of radon in groundwater in the vicinity of the NAPLs. This approach was developed by Prof. Lewis Semprini of Oregon State University

through his project title, "Radon-222 Method for Locating and Quantifying Contamination by Residual Non-Aqueous Phase Liquids in the Subsurface." Radon is produced in essentially all subsurface material from the decay of radium-226 and decays with a half-life of 3.83 days. Radon also preferentially absorbs into NAPLs so that its concentration near NAPLs is less than its normal steady-state concentration in groundwater. The practical use of radon measurements for locating NAPLs was demonstrated in controlled field studies at the CFB Borden test site in Ontario, Canada. The research was performed as a collaborative effort with the Waterloo Centre for Groundwater Research "University Consortium Solvents-in-Groundwater Research Programme." The radon method located the presence of NAPL over short spatial scales in the aquifer, and indicated the direction the NAPL plume spread. The results indicate the radon deficit method has potential for both locating and quantifying subsurface NAPL contamination, and monitoring the progress of remediation.

The Pump and Treat strategy is often used for removing contaminants from aquifers. Important insights into this process were gained through a study titled, "Aquifer Remediation Design in the Presence of Kinetic Limitations," that was supervised by Prof. Steven Gorelick of Stanford University. The study was concerned with pump-and-treat remediation involving multiple contaminant plumes and removal of these contaminants from groundwater when rate-limited mass transfer occurs. One insight is that remediation requires a minimum amount of time, which cannot be improved upon by changing pumping rates, number of wells, or well locations. The minimum remediation time may be approximated by:

$$t_{\min} = - \frac{1}{k_2} \ln\left(\frac{s^*}{s'}\right)$$

where t_{\min} [T] is the minimum remediation time for the site; k_2 is the linear reverse mass transfer coefficient; s^* [M/L³] is the concentration to which the immobile phase must be reduced; s' [M/L³] is the maximum initial immobile concentration found at the site.

A key limitation on the efficiency of pump-and-treat aquifer remediation is due to slow mass transfer from an immobile domain to a mobile domain. A method was developed for estimating forward and backward linear mass transfer rate coefficients from field data. After a well has pumped or injected water into a contaminated aquifer, the changes in observed concentrations provide information about the rate of transfer of mass from the immobile to the mobile domain. Measurements of concentration are superimposed on a type curve, and the rate coefficients can be calculated. Use of this approach requires knowledge of two of the following three items: (1) the total mass per unit volume of contaminant; (2) the distribution coefficient; and/or (3) the concentration of the mobile phase at equilibrium.

With contamination of the unsaturated or "vadose" zone above the groundwater table, vapor extraction is commonly used to remove volatile contaminants such as gasoline and chlorinated solvents. In a study directed by Profs. Martin Reinhard and Paul Roberts entitled, "Gaseous Stripping of Nonaqueous Liquids from the Vadose Zone," sorption equilibrium and kinetics were found to be major determinants of the effectiveness of vapor stripping as a remediation technique. Sorption isotherms and rates of volatile organics removal were measured using

different aquifer materials, soils, clays and model solids and a novel batch-column desorption technique. Desorption isotherm shape was the only correlating parameter with rates of vapor stripping. Rates did not correlate as expected with the soil properties commonly implicated for slow contaminant removal. Soil properties, including organic matter content, internal porosity, and particle size, were not useful for predicting rates of volatile organic compound removal. Significant hysteresis was observed even after 6 month equilibration periods. The amount of slow desorbing residual on a soil was found to depend not on the equilibrium vapor concentration, nor on the initial solids concentration, but on the highest contaminant concentration to which the solids were exposed. Pore diffusion models were not entirely adequate to describe the rates of organic removal. Desorption was found to proceed at two widely different rates. The majority of sorbed contaminant was removed within ten minutes, but on some soils, periods greater than two years are required to reach solid concentrations below 1 mg/g.

Chlorinated Solvents

Several of the Center's projects are concerned with chlorinated solvents, the most common chemicals at contaminated sites. Of interest here are the major solvents: carbon tetrachloride (CT), tetrachloroethylene (PCE), trichloroethylene (TCE), and 1,1,1-trichloroethane (TCA). Other CAHs of interest include natural degradation products of these major solvents, including the three isomers of dichloroethylene (1,1-DCE, c-DCE, t-DCE), 1,1-dichloroethane (DCA), and vinyl chloride (VC). The research on CAHs range from basic studies on the kinetics and reaction products from both chemical and biological transformations as well as methods for introduction and mixing of remediation chemicals with groundwater contaminants, to pilot studies at the Center's Moffett Naval Air Station field site (Moffett Field), to studies directed towards full-scale application at Superfund and other sites with groundwater contamination. Of particular interest for highlighting this year are the results of new Moffett Field studies that were conducted by a new grant from the U.S. Air Force in preparation for a full-scale demonstration.

The first controlled field demonstration of in-situ cometabolic bioremediation of chlorinated aliphatic compounds by methane-oxidizing microorganisms was conducted at the Moffett Field Naval Air Station in Mountain View, California by WRHSRC staff [P. V. Roberts et al., *In-Situ Aquifer Restoration of Chlorinated Aliphatics by Methanotrophic Bacteria*, EPA/600/2-89/033, U.S. EPA Center for Environmental Information, Cincinnati, OH (July 1989)]. While this system was found to be effective for biodegradation of TCE, cis-DCE, trans-DCE, and VC, the efficiency for TCE and 1,2-DCE were not felt to be sufficiently high for practical application. During the past two year, studies with a new enzyme system that can be induced with either phenol or toluene has been evaluated. The potential for this system was first demonstrated by M. J. K. Nelson et al., *Applied and Environmental Microbiology*, 53, 949-954 (1987). During the first two years of this study, phenol was injected into the Moffett Field aquifer in order to stimulate growth of bacteria containing toluene oxygenase. The thickness of the confined aquifer used is about 1.5 m, and lies at a depth below ground surface of 4.5 to 6 m. The test site consists of an injection well, where phenol, oxygen, and the chlorinated aliphatic hydrocarbons were introduced, and an extraction well located 7 m away. In line between the injection and extraction wells are three monitoring wells. The time of water travel between the injection and extraction wells is about two days. An automated data acquisition system permitted semi-

continuous concentration measurements for bromide tracer, dissolved oxygen, phenol, pH, TCE, cis-DCE, and trans-DCE.

With the methane-oxidizing bacteria in the past, CAH degradation at Moffett Field was approximately: TCE, 20%; cis-DCE, 45%; trans-DCE, 90%; and VC, 95%. However, in the newer studies with phenol addition, transformations found were quite different: TCE, 90%; cis-DCE-95%; trans-DCE, 40-60%, and VC, 95%. The 90% removal efficiency for TCE was found with concentrations of TCE up to 0.5 mg/l with the addition of 12 mg/l phenol and 30 mg/l dissolved oxygen. In continuation studies this past year, using more sensitive analytical techniques, the concentration of phenol remaining in the aquifer after bioremediation was less than 1 µg/l. An additional important finding was that the presence of 1,1-DCE at concentrations between 65 and 130 µg/l had a significant adverse effect on biodegradation of 250µg/l of TCE, reducing the efficiency from 95% to about 40%. Thus, the presence of 1,1-DCE is likely to impose a significant limitation on the use of this technology.

In additional studies, toluene was substituted as a primary energy source and toluene monooxygenase inducer. There was no decrease in TCE removal efficiency with the changeover from 12 mg/l phenol to 9 mg/l toluene, indicating the stimulated microorganisms could use both of these substrates. TCE removal efficiency was not changed. Bioremediation resulted in reducing the injected toluene concentration down to a level below 1 µg/l, well below the U.S. EPA Drinking water MCL and MCLG values of 1000 µg/l. These results indicate that the use of phenol or toluene has great promise for in-situ remediation of TCE. The WRHSRC now has a grant from the U.S. Air Force for a full-scale demonstration of this technology at an Air Force base.

Aromatic Compounds

One of the major interests of the WRHSRC thrust group, who are studying biotransformations of halogenated and nonhalogenated aromatic compounds, is on anaerobic transformations. Aquifers heavily contaminated with organic materials tend to be anaerobic, and transformations, if they are to occur, must thereafter be through the action of anaerobic consortia of microorganisms. Research in this area has been pioneered by WRHSRC staff. Studies are being conducted on anaerobic transformations of PCBs, pentachlorophenol (PCP), the soluble components of gasoline (benzene, ethylbenzene, toluene, and xylenes, which are collectively termed BTEX), polycyclic aromatic hydrocarbons (PAHs), and heterocyclic compounds containing oxygen, sulfur and nitrogen.

Intrinsic in-situ anaerobic biodegradation of BTEX is suspected to occur at many sites. However, there is a major need for methods to quantify the rates of such biotransformation. In a grant from the U.S. Navy titled, "In-Situ Biological Treatment of Aromatics in Groundwater," Prof. Martin Reinhard of Stanford University and his research group have begun this year to develop a controlled injection procedure for quantifying at the U.S. Navy's Seal Beach site both intrinsic biodegradation and engineered biodegradation. Laboratory microcosm studies have indicated the indigenous bacteria at this site can transform benzene, toluene, p-xylene, and o-xylene under sulfate reducing conditions, and toluene, ethylbenzene, and m-xylene have been biotransformed under anoxic denitrifying conditions. With the preliminary experiments of controlled injection of nitrate in the field, significant reduction in all the BTEX aromatic compounds has also been observed, confirming the results of the microcosm experiments. An

experiment will soon take place with the controlled injection of BTEX into the groundwater at Seal Beach in further developments of the field protocol. The methods being developed offer great promise for evaluating anaerobic bacterial activity at a site.

RESEARCH AND TRAINING AND TECHNOLOGY TRANSFER PROGRAM SUMMARY

RESEARCH PROGRAM SUMMARY

Chemical Movement, Fate, and Treatment

Hildemann, 1990-1994
Roberts
(\$118k total/\$36k current year) Dispersion Modeling of Volatile Organic Emissions from Ground-Level Treatment Systems

Gorelick 1992-1995
(\$207k total/\$69k current year) Aquifer Remediation Design in the Presence of Kinetic Limitations

Kitanidis 1992-1995
(\$201k total/\$67k current year) Determination of Macroscopic Transport Parameters for Biologically Reacting Solutes in Aquifers

Semprini 1992-1994
(\$114k total/\$59k current year) Radon-222 Method for Locating and Quantifying Contamination by Residual Non-Aqueous Phase Liquids in the Subsurface

Westall, 1992-1995
Ingle
(\$164k total/\$55k current year) Redox Transformations of Inorganic Pollutants: Coupling to the Biogeochemical Matrix

Roberts, 1992-1994
Semprini
(\$160k total/\$80k current year) Process Submodel Formulation and Parameter Estimation for Simulation of Bioremediation

Kitanidis, 1993-1994
Roberts,
Semprini
(\$180k total/\$180k current year) Modeling Strategies for Optimizing In-Situ Bioremediation

Reinhard, 1989-1992
Roberts
(\$191k total/\$63k current year) Gaseous Stripping of Nonaqueous Phase Liquids from the Vadose Zone

Reinhard, 1989-1992
Roberts
(\$274k total/\$93k current year) Treatment of Complex Mixtures

Chlorinated Solvents

Reinhard, 1989-1993
McCarty
(\$109k total/\$24k current year) Long-Term Chemical Transformation of 1,1,1-Trichloroethane (TCA) and Freon 113 Under Aquifer Conditions

McCarty 1989-1993 Oxidation of Chlorinated Solvents by Methanotrophs
(\$345k total/\$80k current year)

Chlorinated Solvents (Continued)

McCarty, 1990-94 Test-Bed Evaluation of In-Situ Bioremediation of
Hopkins, Chlorinated Aliphatic Compounds by Toluene Oxygenase
Semprini Microorganisms
(\$584k total/\$384k current year)

Reinhard 1992-1995 Transformation of Chlorinated Hydrocarbons by Reduced
Metallocoenzymes—Kinetic Model Development and
Applications to Environmental Systems

McCarty 1992-1994 Transformation of TCE by Methanotrophic Biofilms
(\$124k total/\$64k current year)

Arp, 1992-1995 Degradation of Chlorinated Aliphatic Compounds by
Williamson Nitrifying Bacteria
(\$197k total/\$65k current year)

McCarty 1992-1995 In-Situ Treatment of Chlorinated Solvents
(\$215k total/\$215k current year)

McCarty 1992-1994 Anaerobic Treatment of Chlorinated Solvent
Contaminated Groundwater
(\$100k total/\$100k current year)

Reinhard, 1993-1995 Enhancement of Biodegradation Through the Use of
Sublette Substituted Porphyrins to Treat Groundwater
Contaminated with Halogenated Aliphatics
(\$240k total/\$240k current year)

McCarty, 1993-1995 Moffett Field In-Situ Bioremediation Study in Support of
Goltz Full-Scale Application
(\$316k total/\$163k current year)

Aromatic Compounds

Reinhard 1991-1993 In-Situ Biological Treatment of Aromatics in
Groundwater
(\$428k total/\$188k current year)

Grbić -Galić, 1992-1995 Microbial Degradation of Toluene Under Sulfate
Reinhard Reducing Conditions--The Role of Iron
(\$205k total/\$73k current year)

Craig 1990-1992
(\$120k total/\$120k current year)

Biotransformation of Ordnance Wastes Using Unique
Consortia of Anaerobic Bacteria

Woods 1992-1993
(\$146k total/\$45k current year)

The Effect of Environmental Conditions on Reductive
Dechlorination Rates

Heavy Metals

Leckie 1993-1995
(\$263k total/\$82k current year)

Heavy Metals in Ceramic Matrix: Heavy Metal/Clay
Interactions in Ceramic Processing

Nelson 1993-1995
(\$75k total/\$75k current year)

Lead Sorption, Transport, and Remediation in Natural
Soils and Subsoils

TRAINING AND TECHNOLOGY TRANSFER PROGRAM SUMMARY

Williamson, Nelson 1989-1993 (\$60k total/\$15k current year)	Hazardous Waste Training
Williamson, Semprini 1989-1993 (\$60k total/\$15k current year)	Advanced Topic Workshops
Williamson, Olcott 1989-1993 (\$60k total/\$15k current year)	Continuing Education Program
Williamson, Semprini 1989-1993 (\$45k total/\$15k current year)	Conference Sponsorship
McCarty, Williamson 1992-1993 (\$10k total/\$10k current year)	Field Application of Remediation Technologies
Gorelick 1993-1995 (\$645k total/\$235k current year)	Field Test of In-Situ Vapor Stripping for Removal of VOCs from Groundwater
Kitanidis, Roberts, Semprini 1993-1995 (\$255k total/\$255k current year)	System Design for Enhanced In-Situ Biotransformation of Carbon Tetrachloride: Application to DOE's Arid Site Integrated Demonstration
McCarty, Goltz 1993-1995 (\$489k total/\$316k current year)	Full-Scale Evaluation of In-Situ Bioremediation of Chlorinated Solvent Groundwater Contamination
Williamson, Woods 1993-1994 (\$40k total/\$30k current year)	Remediation of Contaminated Soil from the Baldoc Station Maintenance Facility

RESEARCH PROJECT DESCRIPTIONS

CHEMICAL MOVEMENT, FATE, AND TREATMENT

Dispersion Modeling of Volatile Organic Emissions from Ground-Level Treatment Systems: Lynn M. Hildemann and Paul V. Roberts, Stanford University (Partially Supported by the U. S. Department of Energy)

Goal: Treatment of contaminated groundwater can result in the emission of hazardous volatile organics into the atmosphere. The goal of this project is to develop a detailed model for the dispersion of emissions from a ground-level area source into the atmosphere that will accurately predict concentration levels in the vicinity of the source as well as further downwind.

Rationale: The potential toxicity of air emissions resulting from the treatment of wastewater and groundwater has been the focus of increasing concern over the past decade. However, published attempts at estimating the potential impact of such treatment processes on the local atmosphere have utilized simple dispersion models which are only reliable at significant distances downwind for an elevated point source. A more accurate approach is needed to evaluate the risk posed to humans in the near vicinity of a ground-level treatment process due to atmospheric emissions.

Approach: A detailed model capable of predicting the near-source dispersion of emissions from a ground-level area source has been developed. In order to accurately model dispersion in the surface layer regime, this model incorporates accurate expressions for the variation of wind speed and eddy diffusivity with vertical height, and also includes dry deposition as a removal mechanism. The dispersion model has been linked to an existing volatilization model which predicts emission rates resulting from aerobic biological treatment based on the influent concentrations and the operating parameters of the system. The predictions of this combined modeling system have been compared with predictions obtained using simpler, more commonly-used models.

Status: This project was completed in August of 1993. A dispersion model was developed which accurately represents conditions near groundlevel, and the model was linked to a second model used to estimate VOC emission rates from a surface aerobic treatment unit based on influent concentrations and operating conditions. The predictions of the dispersion model were compared with those obtained using other "popular" models under various conditions, revealing that these popular models often are under-predicting downwind concentrations by as much as an order of magnitude. The model has been refined to better reflect the interaction between the type of terrain and the variation of turbulence with height. The literature also has been examined to characterize emission rates from landfill sites, in the interests of utilizing this source emission data as input to the model.

Client/Users: Industries and regulators involved in the treatment of contaminated groundwater and/or the characterization of airborne concentrations of toxics downwind of a contaminated site, as well as researchers concerned with assessing the risks associated with such site emissions.

Aquifer Remediation Design in the Presence of Kinetic Limitations: Steven M. Gorelick, Stanford University

Goal: The objectives of this study are (1) to recognize and quantify field-scale rate limitations on pump-and-treat aquifer remediation; (2) to predict the effects of contaminant mass transfer rate limitations during remediation; and (3) to develop practical guidelines for conventional and unconventional remediation strategies, such as pulsed-pumping, that efficiently remove contaminants whose removal is controlled by rate limited mass transfer.

Rationale: In recent years, it has become clear that the cleanup of contaminated groundwater has been less successful than originally anticipated. Conventional pump-and-treat methods have failed to remove the amount of contaminant mass that was once predicted. Although pumping tends first to remove high concentrations from an aquifer, concentrations soon diminish. Unfortunately, during pumping the concentrations remain far above water quality standards, and can remain so for decades. In some cases this behavior is explained by slow desorption and diffusion of immobile contaminants into the groundwater being remediated. Although slow diffusion and desorption processes have been extensively documented and are frequently cited as reasons for the failure of conventional remediation strategies, these processes have not been incorporated into the design of aquifer remediation systems. At a fundamental level, the parameters governing mass transfer have not been estimated at the field-scale.

Approach: This study involves five stages: (1) development of a two-dimensional, advective-dispersive groundwater contaminant transport model that includes linear and nonlinear rate-limited mass transfer; (2) comparison of contaminant removal by continuous- and pulsed-pumping; (3) sensitivity analysis with different nonequilibrium models and rate parameters to develop efficient pump/rest cycles for pulsed-pumping; (4) development of a nonequilibrium rate parameter estimation method from standard field observations; and (5) formulation and development of an optimization procedure for design of pulsed-pumping remediation.

Status: Within the past year two manuscripts were completed and several new ideas on aquifer remediation in the presence of rate-limited mass transfer were developed. The main new results are: First, aquifer remediation requires a minimum amount of time that depends on mass transfer, and can be estimated using a rule-of-thumb. Second, a semi-analytic solution for advective-dispersive transport with rate-limited mass transfer was developed. Using this solution it was shown, for a limited set of flow and transport conditions, that pulsed pumping can be as efficient as, but not more efficient than, continuous pumping. Guidelines for designing efficient pump/rest cycles were presented. Third, a simple type-curve method for estimating mass transfer rate coefficients was developed. Current research is aimed at testing the efficiency of pulsed pumping in more complicated and realistic settings. Specifically, the plan is to include the effects of nonlinear mass transfer and a regional hydraulic gradient. In addition, an approach to estimate field-scale mass transfer rate coefficients is being developed.

Client/Users: Engineers, hydrogeologists, and regulators involved in remediation design and contaminant transport modeling where rate-limited transport is of concern, will be interested in this technology.

Determination of Macroscopic Transport Parameters for Biologically Reacting Solutes in Aquifers: Peter K. Kitanidis, Stanford University

Goal: This research aims to improve the understanding of scale effects on the transport and fate of biologically reacting chemicals in heterogeneous formations. Research objectives include:

(a) to develop guidelines on how to relate field and laboratory data; (b) to explain how heterogeneity and diffusional rate limitations at a sub-scale may determine the observed rates of transport and transformation; and to suggest reasonable macroscopic models.

Rationale: Soils and aquifers are composed of materials that are heterogeneous at all scales. Several studies have indicated the need for a quantitative understanding of the effect of spatial variability and sub-scale processes on the mechanism and the parameters that describe the transport and fate of reactive solutes at a certain scale. For example, it has been found that the dispersion coefficient obtained from a conservative nonreacting tracer test in the field can be considerably larger than the dispersion coefficient that applies to the transport of reacting solutes.

Approach: Macroscopic parameters are computed from microscopic ones using a volume averaging approach based on the Taylor-Aris-Brenner method of moments. We intend to examine some cases of upscaling from the pore scale to the laboratory scale and from the laboratory scale to the field.

Status: The equations which govern the transport of a reactive solute at the macroscale have been derived using the Taylor-Aris-Brenner method of moments. The analysis provides the macroscopic coefficients of reaction, velocity, and dispersion which describe the transport of the volume averaged concentration. The results are not limited to any particular scale, but can be used to move between a small and large domain whenever there exists a disparity in spatial scales, such as from pore to Darcy scales, or from laboratory to field scales. As a particular application of the method, a two-dimensional pore scale model of a porous medium was created. The model captures some of the essential features of pore scale flow by having converging and diverging flow in pore throats and chambers. A numerical solution scheme was developed which solves for all the relevant macroscopic parameters. The solution technique is based on a new iterative solver and is reasonable fast and efficient allowing for many trial runs. Graphs have been made which show how the macroscale parameters are controlled by the underlying microscale mechanisms.

Clients/Users: Environmental modelers; developers of in-situ bioremediation methods.

Radon-222 Method for Locating and Quantifying Contamination by Residual Non-Aqueous Phase Liquids in the Subsurface: L. Semprini, Oregon State University (Partially Supported by the U. S. Department of Energy)

Goal: The goal of this project is to develop a geochemical method for locating and quantifying Non-Aqueous Phase Liquid (NAPL) contamination in the subsurface. The method is based on the concentration of radon-222 in subsurface fluids.

Rationale: Locating and describing quantitatively the residual or pools associated with source areas of NAPL contamination in the subsurface remains as one of the major obstacles to implementing through site monitoring and effective remediation programs. Geochemical methods may provide an inexpensive means of locating and quantifying NAPL contamination, and monitoring the progress of remediation.

Approach: Radon-222 concentrations in subsurface fluids may provide a means of locating and quantifying NAPL contamination in the subsurface. The method is based on radon's unique properties including: its production from the decay of radium-226 in subsurface materials, its radioactive decay with a half-life of 3.83 days, and its preferential partitioning into organics compared to water. Equilibrium model calculations indicate that radon would become depleted in the aqueous phase during transport through a NAPL zone. Thus, changes in the radon concentration in an aquifer might be used to locate and quantify NAPL contamination.

Status: The method was tested in two controlled field studies at the CFB Borden test site in Ontario, Canada. In the first study a fairly uniform NAPL source composed of a mixture of chloroform, trichloroethylene, and tetrachloroethylene, was emplaced in the shallow sand aquifer and permitted to slowly dissolve under natural gradient conditions. Groundwater radon concentrations decreased by a factor of 2 to 3 in the NAPL zone. Radon concentrations downgradient of the source reequilibrated within a few meters to upgradient background values. A NAPL residual saturation of 3 % was estimated using the radon method, compared to 3.8 % based on mass balances. In the second study 5 liters of the same NAPL mixture were released from a well creating a non uniform source in the aquifer. Radon concentration deficits were observed at shallow depths in the immediate area of the spill, with spatial changes occurring over vertical distances of up to 10 cm. Upon leaving the NAPL source area radon concentrations gradually increased consistent with transport model estimates. The radon observations predicted that the NAPLs had spread laterally upon release. This lateral spreading was confirmed when the test cell was excavated. The results indicate the radon deficit method has potential for both locating and quantifying subsurface NAPL contamination. WRHSRC funding for this project terminates in June, 1994.

Clients\Users: Consultants, industries, regulators, and researchers interested in locating and quantifying NAPL contamination, and monitoring the remediation process.

**Redox Transformations of Inorganic Pollutants: Coupling to the Biogeochemical Matrix:
John C. Westall and James D. Ingle, Oregon State University**

Goal: The long-range goals of this project are: (i) to understand under what conditions redox transformations of inorganic pollutant species will take place and (ii) to develop sensors that can be deployed in situ to indicate when these conditions prevail.

Rationale: A clear understanding of the redox state and speciation of chemicals is required in virtually all aspects of hazardous waste management: (i) evaluation of disposal options, (ii) risk assessments of contaminated sites, and (iii) evaluation of clean-up options for contaminated sites. Specifically, the redox state of an inorganic pollutant affects its speciation and thereby its transport, fate and biological effects.

Approach: In characterizing redox transformations of inorganic pollutants, three components are considered: the redox-active inorganic pollutant, the geochemical matrix, and the redox sensor. Coupling of redox processes must be understood at three linkages -- pollutant and matrix, sensor and matrix, and pollutant and sensor. Each linkage is being investigated on a species-by-species basis, without the a priori assumption of equilibrium. The initial focus of this study is on transformations of Cr(III) / Cr(VI) in geochemical matrices of Fe(II), Fe(II)-minerals, Mn(IV)-minerals, natural organic matter, and aquifer material from a Cr-contaminated site. In parallel

experiments, transformations of redox indicators will be investigated spectrochemically and electrochemically, towards the goal of developing optrodes and electrodes that can be deployed in-situ.

Status: This project began in March, 1992. Thermodynamic models for redox conditions in geochemical matrices have been developed to establish equilibrium boundary conditions. A reactor (chemostat) for maintaining or systematically varying experimental redox conditions and in-situ monitoring of platinum electrode potential and pH has been developed. Provision is made for on-line filtering prior to on-line spectrophotometric measurement to minimize scattering. Electrochemical and spectrochemical studies to characterize the reactions of redox indicators have been completed. Coupling of ten reversible redox indicators with the inorganic pollutant Cr(VI) and geochemical matrices of Fe(II) and Ti(III) have been studied. The indicators selected also couple with a platinum electrode to "poise" the redox potential of the system over the E_H range -450 to +300 mV at pH 7. The absorbance of the oxidized form of most indicators can be used to estimate the "redox" potential and predict the prevalent redox forms of Fe and Cr. With solid matrix components such as Fe(II) minerals adsorption of the indicators on the surface of the solids precludes spectrophotometric measurements. To alleviate this problem, several methods of immobilizing the indicators are being investigated.

Client/User: Consultants, regulators, geochemists, and modelers concerned with all aspects of the speciation of redox-active pollutants.

Process Submodel Formulation and Parameter Estimation for Simulation of Bioremediation: Paul Roberts, Stanford University and Lewis Semprini, Oregon State University

Goal: To improve mathematical simulation and parameter estimation methods for bioremediation based on aerobic cometabolic transformation.

Rationale: Previous and ongoing work sponsored by the Center has demonstrated the efficacy of aerobic cometabolic transformations in degrading halogenated aliphatic contaminants such as vinyl chloride. However, our ability to design such systems is limited by gaps in understanding the effects of complications such as aquifer heterogeneity, mass transfer rate limitations, and toxicity or inhibition. To evaluate and circumvent these difficulties, advanced control methods are needed.

Approach: Previous work encompassed 1) review of field and laboratory data, 2) quantification of vertical variations in velocity, 3) assessment of model dimensionality, and 4) incorporation of sorption and competitive inhibition phenomena. Our current work is assessing the applicability of adaptive control engineering to in situ bioremediation systems.

Status: This two year project was initiated in September 1992. Progress in 1993 includes continued exploration of the dependence of contaminant removal by methanotrophic bacteria on oxygen and methane delivery schedules, evaluation of different system configurations, and an exploration of adaptive control technologies. Simulation experiments of full-scale in situ bioremediation systems using methanotrophic organisms revealed that the contaminant removal rates varied greatly with the delivery schedule of oxygen and methane. These simulation

experiments also show that steady-state oxygen and methane delivery schedules did not perform well and in some cases caused system failure. Consequently, methods of adapting oxygen and methane delivery based on the state and performance of the system are currently being explored.

Clients/Users: Researchers, regulatory agencies, and consultants who evaluate, optimize, and design bioremediation technologies.

Modeling Strategies for Optimizing In-Situ Bioremediation: Peter K. Kitanidis and Paul V. Roberts, Stanford University, and Lewis Semprini, Oregon State University (Supported by U. S. Department of Energy)

Goal: First, to develop, calibrate, and apply mathematical models of subsurface flow and transport and fate of halogenated aliphatic compounds. Second, to develop conceptual designs for enhanced in-situ bioremediation. The research is guided by our understanding of conditions at two DOE sites: the Hanford site and the Rocky Flats site. The primary objectives are (a) to improve the understanding of in-situ mixing of nonreactive and reactive solutes, and (b) to recommend effective designs for in-situ mixing and strategies for improving the conditions for bioremediation.

Rationale: In-situ bioremediation typically requires the injection into the formation and mixing of electron acceptors, donors, or nutrients. Other innovative remediation methods, such as chemically enhance pump-and treat remediation, require controlled mixing of chemicals. It is important to improve the grasp of dilution and mixing processes in the subsurface and to devise effective methods for their control.

Approach: The hydrodynamic parts of the model(s) account for three-dimensional flow and transport. The effects of heterogeneity on dilution and mixing are being studied. The biochemical parts (kinetics of biotransformation) incorporate current understanding of processes based on recent laboratory and field experiments. The research focuses on the incorporation of appropriate kinetic formulations for the cometabolic transformations that account for toxicity effects and deactivation of the microbial population.

Status: During the first year, the processes of in-situ dilution and mixing were studied at a more fundamental level; a report is being prepared that describes these processes and provides guidelines for practitioners of in-situ bioremediation. Different ways to represent cometabolic transformations are being evaluated. Preliminary simulations of the transient in-situ experiments at the Moffett field site, using microbes grown on phenol, indicate that a deactivation cometabolic transformation model yields results consistent with the field observations.

Client/Users: Practitioners of enhanced in-situ bioremediation; industry, and regulators.

Gaseous Stripping of Nonaqueous Phase Liquids from the Vadose Zone: Martin Reinhard and Paul V. Roberts, Stanford University

Goal: The objective of this research was to investigate the rates of organic contaminant desorption from soils and sediments and elucidate the mechanisms responsible for slow desorption rates.

Rationale: Because soil-air-venting, pump-and-treat, and bioremediation are all predicated on desorption of sorbed contaminants, remediation of soils and sediments contaminated by organic solvents is often limited by the release of contaminants sorbed within porous soil or sediment grains. Assessment of desorption rates and an understanding the mechanisms responsible for contaminant release will yield: better appraisals of when conditions are favorable for a particular remediation strategy, better estimates of remediation times, and the development of strategies for enhancing desorption rates

Approach: The methods used in this study allowed both early and late time measurement of desorption rates. The improved methodology was capable of resolving desorption rates over more than seven orders of magnitude, and was used to measure both desorption isotherms and desorption kinetics for chloroform, trichloroethylene, and tetrachloroethylene from model solids, aquifer sediments, and soil. The use of model solids with selected and controlled properties facilitated investigation of both the mechanisms responsible for organic vapor sorption, and those controlling desorption rates.

Status: The study resulted in the following major conclusions. The improved experimental techniques revealed that, contrary to prior investigations over more limited concentration ranges, the pore diffusion model was not adequate to describe both the fast and slow desorbing fractions. For the experiments with contaminant vapor concentrations near saturation, the pore diffusion model was able to describe desorption of the fast desorbing fraction, but was not able to describe the secondary, slowly released fraction. Experiments performed at different initial concentrations showed that the pore diffusion model may be erroneously fit to desorption rate data over limited concentration ranges. Consequently, the pore diffusion model is severely limited for predictive purposes beyond measured concentration ranges, or for extrapolation to other systems. Measurable solid properties including internal porosity, organic matter content, internal surface area, and pore and particle size showed no correlation with the fraction of slow desorbing contaminant. Only the slopes of the desorption isotherms correlated with the fractions of slowly released contaminants. However, decreasing pore diffusion rates resulting from isotherm nonlinearity were not sufficient to account for the decreasing desorption rates. The kinetic and isotherm data implicate intragranular micropores of mineral solids as responsible for both the isotherm nonlinearity, and the slowly released fraction. This is in contrast to previous investigations implicating soil organic matter as responsible for the slow release of sorbed contaminants. Results from this research indicate that current models for predicting desorption rates are not adequate over large concentration ranges, or for assessing rates *a priori* based on the measured solid and contaminant physical properties. Without an adequate mechanistic model for contaminant desorption, it appears that actual measurements of desorption rates must be made to provide engineers and regulators with the decontamination rates to be expected under environmental conditions.

Client/Users: Researchers, educators and the engineering community concerned with aquifer remediation and soil cleanup.

Treatment of Complex Mixtures: Martin Reinhard and Paul V. Roberts, Stanford University

Goal: A computer-aided information system was developed for estimating physico-chemical properties of organic compounds needed for the design of treatment processes and assigning the risk of hazardous waste sites.

Rationale: Relevant physico-chemical properties are unknown for many waste constituents. In some cases, such properties can be estimated using estimation techniques.

Approach: A structure-based data evaluation system for organic compounds (DESOC) has been developed for storage, evaluation, retrieval, and estimation of physico-chemical properties, including octanol-water partition coefficient, aqueous solubility, vapor pressure, the acid dissociation constant, molar volume and refraction, cohesion parameters (Hildebrand values, HBA), Henry's coefficient, and connectivity indices.

Status: With the completion of a user interface and a manual, DESOC will be released. The capabilities and applicability of DESOC for air water partitioning (Drefahl et al. in preparation) complex treatment problems (Reinhard et al., in preparation) has been demonstrated. A novel algorithm (GIMOC) for estimating compound properties was developed and is incorporated in DESOC. GIMOC is a combination of the group contribution model and similarity based approaches (Drefahl and Reinhard, J. Chem. Info. Comp. Sci., 1993).

Client/Users: The software package will be made available to a the educational, research and engineering community at large.

CHLORINATED SOLVENTS

Long-term Chemical Transformation of 1,1,1-Trichloroethane (TCA) and Freon 113 under Aquifer Conditions: Martin Reinhard and Perry McCarty, Stanford University (Supported by Schlumberger)

Goal: The goals of this project are to (1) determine the rates and pathways of chemical transformation of 1,1,1-trichloroethane (TCA) and CFC 113 under conditions representative of those encountered in an aerobic aquifer, and (2) determine the extent to which sorbing aquifer materials and different solution composition influence the rates and pathways of TCA.

Rationale: Previous data obtained at high temperature has demonstrated that TCA undergoes abiotic dehalogenation in aqueous solution. However, extrapolation to groundwater temperature is fraught with uncertainty and the influences exerted by the presence of aquifer solids and groundwater solutes are not well understood.

Approach: Transformation rates of 1,1,1-trichloroethane (TCA) and 1,1,2-trichloro-1,2,2-trifluoroethane (CFC 113) were determined at ambient temperature for three aerobic systems: 0.2 µm-filtered groundwater, autoclaved and non-autoclaved sediment slurries for four years.

Status: The experimental part of the study has been completed and the final report is in preparation. The 95% confidence intervals for the half-lives of TCA (753 days for filtered groundwater, 603 days for autoclaved sediment slurries, and 770 days for non-autoclaved sediment slurries) overlapped, suggesting that there were no effects of sorption or microbial

activity on initial TCA transformation in aerobic systems. Products of TCA transformation in all systems were 1,1-dichloroethylene (DCE), carbon dioxide (CO₂), and acetate. Because CO₂ was produced in all three systems, microbial contamination of supposedly sterile systems was measured. Sorption of TCA and transformation products was measured in non autoclaved sediment slurries. A TCA transformation experiment was also run at 50°. The half-lives from the 50°C TCA transformation study were not significantly different (9.32 days for Milli-Q water, 9.19 days for groundwater alone, 9.50 days for groundwater and ground ampoule glass, and 9.21 for groundwater spiked with ¹⁴C-labeled TCA). Products of TCA transformation at 50°C were DCE (40%) and acetate (57-60%). ¹⁴CO₂ accounted for 4% of ¹⁴C-labeled TCA transformation products at 50°C. The percentage of DCE formation appeared to increase with temperature. CFC 113 did not transform during the four-year study.

Client/Users: Engineers, regulators and researchers interested in the rates and pathways of dehalogenation reactions of TCA and Freon at hazardous waste sites and in ground water.

Oxidation of Chlorinated Solvents by Methanotrophs: Perry L. McCarty, Stanford University (Supported by the Gas Research Institute)

Goal: Methanotrophic bacteria, which oxidize methane for energy, have been found capable of oxidizing chlorinated solvents such as TCE by cometabolism. The goals of this project are: (1) to evaluate the effect of competitive inhibition between methane and chlorinated compounds on the overall chlorinated solvent degradation rate; (2) to assess the importance of mass transfer limitations on treatment-reactor design; and (3) to use the knowledge gained to optimize the design for an above-ground treatment system for chlorinated solvent destruction.

Rationale: There have been several studies of treatment systems for degrading chlorinated solvents and related compounds. However, the knowledge of reaction kinetics associated with cometabolism are poorly understood so that little scientific basis currently exists for optimizing treatment reactor design. In addition, since the primary substrate, methane, the required electron acceptor, oxygen, and the chlorinated contaminants are all poorly soluble in water, mass transfer properties of treatment systems become of great significance and must be considered.

Approach: It is hypothesized that oxidation rates for methane and chlorinated contaminants can be described by a competitive inhibition model. Here, the rate-limiting step is the oxidation of either methane or TCE by methane monooxygenase (MMO). To evaluate this hypothesis, reaction coefficients for methane and TCE alone are being evaluated using a mixed methanotrophic culture derived from the Moffett Field aquifer. Reaction rates when they are used in combination are then being predicted and measured in order to test the hypothesis. The effect of reactor operational parameters such as detention time and nitrogen supply on the quantity of methane required to effect a given amount of TCE transformation are being evaluated. In mass transfer studies, model calculations are being made for a variety of reactor configurations in order to determine flow patterns that are realistic and optimal for given treatment objectives. These calculations consider mass transfer effects and biological reaction kinetics. The model results are expected to guide reactor design as well as help to determine important knowledge gaps that may be in need of further research.

Status: Laboratory studies have indicated basic reaction coefficients for methane and trichloroethylene utilization alone by methanotrophs. Initial studies with the two compounds together in various combinations have been conducted. Model calculations have been carried out. The effects of reactor detention time and nitrogen nutrient concentration on transformation capacities and yields have been evaluated. These studies have indicated that the presence of methane at high concentration enhances rather than retards TCE degradation, but at low concentrations competitive inhibition becomes significant. Thus competitive inhibition kinetics alone does not appear appropriate in models for predicting transformation rates. Also, reduced detention time and reduced nitrogen supply changes culture characteristics, but does not result in significant changes in the transformation yield (ratio of TCE transformed to methane consumed). Transformation yield was found to change more radically with time for a given mixed culture than with the variables explored. This study is now completed.

Client/Users: Researchers interested in cometabolism for halogenated aliphatic compounds; and industry, consulting engineers, and state and EPA regulators who are evaluating treatment options for chlorinated solvents.

Test-Bed Evaluation of In-Situ Bioremediation of Chlorinated Aliphatic Compounds by Toluene Oxygenase Microorganisms: P.L. McCarty, G.D. Hopkins, L. Semprini, Stanford University (Partially Supported by the U. S. Department of Energy and the U. S. EPA Biosystems Program)

Goal: The goal is to evaluate in the field and the laboratory the rate and extent of degradation of chlorinated aliphatic hydrocarbons (CAHs) through cometabolism using phenol as a primary substrate.

Rationale: Recent research has indicated that microorganisms that oxidize phenol can oxidize CAHs such as trichloroethylene (TCE) by cometabolism, similar to biodegradation by methanotrophs with methane monooxygenase (MMO). In order to obtain a comparison between the relative advantages and disadvantages of phenol- and methane-oxidizing microorganisms, a field evaluation is being conducted at the Moffett Naval Air Station in Mountain View California.

Approach: The field study with phenol oxidizing bacteria is being conducted similar to the previous study in which methane was used as a primary substrate so that the results can be directly compared. Here phenol and oxygen are dissolved in the recycled groundwater along with TCE, cis-and-trans-1,2-dichloroethylene (DCE), and vinyl chloride for introduction into a 1 meter thick confined aquifer located four meters below the ground surface. The growth of a native phenol degrading population and the rate and extent to which the introduced chlorinated compounds are removed is being monitored and compared with conservative tracers as a reference to determine the extent of transformation. In conjunction with the field studies laboratory microcosm studies are being performed under conditions that mimic the field site.

Status: Results of the 1991 field tests demonstrated that indigenous phenol-utilizers could effectively degrade TCE and cis-DCE at concentrations of 40 and 50 mg/L, respectively. Over 90% of the cis-DCE and 85% of the TCE were degraded in the 2 meter biostimulated zone through the continuous addition of 12 mg/L of phenol. Thus, phenol oxidizers were found to be

much more effective than methane oxidizers for TCE and c-DCE removal. During the 1992 field season better than 95% TCE removal was obtained with up to 1 mg/L TCE. Greater than 95% vinyl chloride removal was also obtained. These results are highly encouraging, and possibilities for full-scale application are now being sought. This project is now completed.

Clients/Users: State and EPA regulators, industries, and consulting engineers concerned with chlorinated solvents and related compounds present in groundwater.

**Transformation of Chlorinated Hydrocarbons by Reduced Metallocoenzymes--
Kinetic Model Development and Applications to Environmental Systems: Martin
Reinhard, Stanford University**

Goal: This project is aimed to (1) reveal the role of the reducing agent in coenzyme-catalyzed transformation of chlorinated hydrocarbons, (2) develop kinetic models describing the systems, and (3) elucidate the transformation pathways, and (4) evaluate transformation products.

Rationale: Transition-metal coenzymes have been known to catalyze reductive transformation of halogenated organic contaminants in biological systems as well as *in vitro*. The chemistry of this type of reactions is important in two respects: it may (1) shed light on the fates of these pollutants *in vivo* and/or the detoxification processes in microbial systems; (2) provide information for the development of novel remediation technologies. The mechanisms of organohalide transformation involving metallocofactors are not yet explicated. In addition, the type and strength of the reductant have been shown to impact the degradation rate and the product distribution, but the effects and causes are not well-characterized in the literature.

Approach: This project consists of a series of studies on the transformation of carbon tetrachloride (CTET) in the presence of a coenzyme, which is reduced either by a thio-reductant (cysteine or dithiothreitol) or titanium(III) citrate. Experiments are conducted in homogeneous aqueous solutions containing a reductant and a cofactor, either hematin or vitamin B₁₂, at room temperature under light-excluded, anaerobic, and abiotic conditions over a wide range of pH's. The disappearance of CTET is monitored over time to obtain rate constants. Reaction products, primarily chloroform and carbon monoxide, are quantified to obtain mass balances. Attempts will also be made to identify intermediates where possible to help establish transformation pathways. Plans are to study unsaturated chlorinated substrates (e.g., tetrachloroethene) in sequential stages.

Status: A paper entitled "Reductive Transformation of Carbon Tetrachloride in Aqueous Solution Containing Titanium(III) Citrate and a Metallocoenzyme—Reaction Kinetics and Mechanism" was submitted to Environmental Science and Technology. A kinetic model and reductive transformation pathways of CTET with both vitamin B₁₂ and hematin in Ti(III) citrate aqueous medium at neutral and alkaline pH were proposed. Spectroscopic and kinetic data and data from isotopic experiments were obtained to identify the reaction intermediates. At the present stage, kinetic data and transformation product yields of CTET with thio-reducing agents are being sought.

Client/Users: Environmental consultants, engineers, and industry who are looking for remediation alternatives, and researchers who are interested in the reductive dehalogenation of haloaliphatic compounds by metallocoenzymes.

Transformation of TCE by Methanotrophic Biofilms: Perry L. McCarty, Stanford University

Goals: The goals of this project are: (1) to develop and evaluate the overall performance of a biofilm model for cometabolic chlorinated aliphatic hydrocarbon (CAH) biodegradation, (2) to experimentally determine the minimum substrate concentration (S_{min}) required for biofilm

growth and the factors affecting it, and (3) to experimentally determine the rate at which methanotrophic organisms are inactivated within biofilms.

Rationale: Both in-situ and above ground biotransformation of CAHs by methanotrophs and phenol-oxidizing organisms have been studied for treatment of CAH-contaminated waters. Here, attached microorganisms or biofilms are operative. To date, observed CAH transformation rates by biofilms are orders of magnitude slower than maximum rates determined from dispersed growth studies. Many reasons for this difference have been suggested, including inhibition by methane or phenol, CAH transformation product toxicity, exhaustion of reducing power, diffusional constraints, and the presence in biofilms of only a small active biomass population. Because of the many interacting processes involved, the problem is complex and the major processes of importance are difficult to determine. In addition, for in-situ cometabolism using phenol or toluene, it is important to know factors affecting the extent of removal of the growth substrate, and the concentration that will remain.

Approach: A biofilm model that considers cometabolism of CAHs in the presence of the growth substrate, either methane or phenol, is being evaluated to examine the relative significance of the different biofilm processes and to predict their likely impact on CAH transformation rates. Trichloroethylene (TCE) is being used for model simulations and experimental studies. The model is general and can be applied to cometabolism of other CAHs and with different primary substrates for growth. The model is being used for hypothesis testing, and to indicate the processes of importance that are in need of further evaluation. Preliminary results have indicated the importance of the minimum substrate concentration required for bacterial growth (S_{\min}) and the rate of decay of active biomass. For many in-situ bioremediation schemes, the residual substrate concentration should be this same S_{\min} value. Factors affecting these process parameters will be experimentally evaluated.

Status: A methanotrophic biofilm model has been developed in which Monod kinetics with competitive inhibition is used to describe the oxidation of methane and TCE by the organisms in the biofilm. The model includes diffusion, active biomass growth, inactivation, decay, and CAH transformation product toxicity. Simulations suggest that a maximum TCE flux exists with respect to methane concentration. At low methane concentrations (approaching S_{\min}), there is insufficient methane for net growth of the biofilm. At high methane concentrations, competitive inhibition limits TCE transformation. A manuscript for the biofilm model has been accepted for publication. The model has also been extended to allow use of phenol or toluene as the primary substrate. An experimental procedure for determining S_{\min} has been developed, and consists of monitoring the methane concentration changes with time in cultures seeded with a small methanotrophic biomass inoculum. During the coming year, the experimental determination of factors affecting S_{\min} for methane should be completed and a similar study for phenol will be started. In addition, columns packed with glass beads will be fed phenol and TCE to examine the extent of substrate removal by attached organisms, and how CAH concentration affects the resulting S_{\min} value.

Client/Users: Researchers considering the important factors affecting biofilm processes for cometabolism of CAHs, consultants who are interested in factors that affect rates achieved in biofilm reactors to aid in design and optimization of reactor operation, and both researchers and consultants concerned with the extent of substrate removal for in-situ bioremediation.

Degradation of Chlorinated Aliphatic Compounds by Nitrifying Bacteria: Daniel J. Arp and Kenneth J. Williamson, Oregon State University (Partially Supported by the U. S. Department of Energy)

Goal: The objectives of this project are (1) to determine the rates of cometabolic degradation of chlorinated hydrocarbons by ammonia-oxidizing bacteria and to compare these rates with those obtained with other bacterial types such as methanotrophic bacteria; (2) to characterize the physiological response of nitrifying bacteria to the toxicity associated with cometabolic degradation of chlorinated compounds; and (3) to develop and optimize reactor designs suitable for using nitrifying bacteria in cleanup processes.

Rationale: Autotrophic nitrifying bacteria have several features which make them attractive candidates for use in bioremediation schemes. First, they possess a non-specific monooxygenase enzyme which is capable of oxidizing a large number of non-growth supporting substrates. Second, because ammonia is very water soluble it can be introduced into systems at high concentrations, thereby supporting high rates of cometabolic oxidation. Third, although these bacteria achieve high rates of substrate oxidation they exhibit low rates of biomass accumulation. The cometabolism of chlorinated aliphatic compounds by nitrifying bacteria involves aspects of all three of these features. Characterization of the bioremediation potential of these bacteria will involve a clear understanding of the individual significance and interrelation of these factors.

Approach: The rates of substrate (ammonia) and cosubstrate (chlorinated aliphatic) degradation will be determined using kinetic models which will allow (a) maximal specific rates and (b) most sustainable rates of cosubstrate oxidation to be determined. The commonly encountered metabolic toxicity which results from the cometabolic oxidation of chlorinated aliphatics will be investigated by quantifying the relationship which exists between the amount of cosubstrate oxidation and the extent of inactivation of individual enzyme activities. The ability of nitrifiers to recover from these toxic effects will also be determined. Using results from these physiological experiments various reactor designs will be studied and compared so as to determine an optimal configuration.

Status: Studies have been initiated for all three objectives. For the first objective both reactor-size (1l) and small scale (1ml) studies have been completed and used to determine the rate of TCE cometabolism by *Nitrosomonas europaea*. A "transformation potential" of 60 nmoles TCE/mg protein has been determined for this organism. These large and small-scale studies have also led to the development of a kinetic model which describes the effects of TCE on *N. europaea* in terms of three individual parameters: (1) the inhibition (2) the inactivation and (3) the recovery of AMO activity. For Objective #2 three other important questions relating to the physiological consequences of bacterial cometabolism are being considered. First, other chlorinated substrates are being examined to determine the general applicability of the model derived for TCE. Second, $^{14}\text{CO}_2$ uptake experiments are being used to monitor protein synthesis during cometabolism. These studies aim to determine what proportion of TCE cometabolism is due to preexisting and newly synthesized AMO. Third, an investigation of how cometabolism affects the regulation of expression of AMO is planned. These experiments will also utilize $^{14}\text{CO}_2$ labeling in addition to mRNA determinations using northern blotting techniques. A sequencing batch reactor design has been chosen to initiate the studies covered in the third

objective. The preliminary design and construction of this equipment has been initiated and it is expected that these studies will be conducted concurrently with single reactor studies of other chlorinated aliphatics (Objective #1).

Client/Users: Industrial/consulting engineers and state/federal regulators who are evaluating treatment options for chlorinated aliphatic compounds. Industrial and academic researchers in the field of cometabolism.

In Situ Treatment of Chlorinated Solvents: Perry L. McCarty, Stanford University (Supported by DuPont Chemicals)

Goal: The objectives of this study are to describe the bacterium or groups of bacteria that are responsible for conversion of tetrachloroethene (PCE) to ethene in aquifer samples taken from a contaminated site in Victory, Texas, and to examine the factors affecting the rate and extent of transformation.

Rationale: Several species of bacteria have been isolated and identified by others that have the ability to reductively dehalogenate chlorinated aliphatic hydrocarbons (CAHs). However, an individual or group of organisms responsible for the complete dehalogenation process from tetrachloroethylene (PCE) to ethene has not yet been identified. Whether or not the complete dehalogenation or the individual dehalogenation steps are the result of cometabolism or of energy metabolism is also not known. In addition, the various factors that affect the rates of dehalogenation have not been adequately evaluated. Such factors may include the electron donor used, the presence or absence of alternative electron acceptors, pH, and temperature. In order to understand the process better so that it can be more widely applied, its suitability for application at a given location can be better determined, and the economics of process implementation can be improved, definitive studies to better understand the nature of the organisms involved and factors affecting transformation rates are needed.

Approach: Anaerobic aquifer material from a contaminated site in Victoria, Texas, was obtained by DuPont Chemicals for this study. Microcosms were constructed of 125 mL bottles containing aquifer material and groundwater from the site. A small portion of the fluid is removed from the bottle periodically and replaced with groundwater amended with various primary substrates and PCE. Samples are analyzed for a range of CAHs and ethene, as well as for primary substrate, sulfate, and methane. The relationships between time and amount of primary substrate on CAH transformation is being evaluated. In separate studies, enrichment cultures are being developed using various electron donors, PCE, sulfate, and other nutrients, and serial dilutions of the cultures are being made as a first step in organism isolation. If satisfactory transformation of PCE is obtained by highly enriched cultures, then attempts will be made to isolate colonies from agar plates or roll tubes. Once isolated, the organisms will be characterized, and factors affecting PCE transformation will be studied in greater detail.

Status: Benzoate, acetate, and formate were all found to stimulate dehalogenation, although benzoate appears to be the better of the three. Enrichment cultures have been developed that retain their ability to reduce PCE to ethene. The enrichment cultures appear to perform PCE transformation satisfactorily so that attempts at isolation are being made. The project is progressing well and is on schedule.

Clients/Users: Regulators, consulting engineers, and industries seeking information on the potential for in-situ bioremediation of aquifers contaminated with chlorinated solvents and approaches for enhancing this remediation process.

Anaerobic Treatment of Chlorinated Solvent Contaminated Groundwater: Perry L. McCarty, Stanford University (Supported by EPA Biosystems Program)

Goal: The objectives of this study are to determine the factors affecting the rate and extent of anaerobic trichloroethylene (TCE) transformation to ethene in groundwater, and to identify the microbial communities responsible for the transformation.

Rationale: The complete anaerobic dechlorination of TCE to ethene has recently been reported both in laboratory cultures and at field sites. Little is known, however, about the microbial community responsible for this transformation. The electron donors capable of stimulating dechlorination and the factors that affect the rate and extent of this transformation have not yet been studied.

Approach: Aquifer material was obtained by personnel from the U. S. EPA Robert S. Kerr Environmental Research Laboratory from a site contaminated by TCE in St. Joseph, Michigan, which has shown natural anaerobic dechlorination. This material was provided to the WRHSRC and was anaerobically transferred into 25 mL test tubes which act as small laboratory columns. The fluid in the test tubes is periodically exchanged with filter-sterilized groundwater from the site and amended with TCE and a series of different primary substrates. The effluent fluid from the columns following incubation is analyzed for dechlorination, substrate consumption, and electron acceptor usage.

Status: Several different substrates have been tested for their ability to stimulate dechlorination in the columns. Dechlorination to ethene has been observed with all substrates tested, although at varying rates and to varying extents. This transformation has been observed under both sulfate-reducing and methanogenic conditions. Currently, the microbial community responsible for this transformation is being investigated. Potential competitive inhibition and other factors affecting the rate and extent of dechlorination have yet to be studied.

Client/Users: Environmental consultants, engineers, industry, and governmental agencies interested in in-situ bioremediation and in the reductive dechlorination of chlorinated aliphatic hydrocarbons by microorganisms.

Enhancement of Biodegradation through the Use of Substituted Porphyrins to Treat Groundwater Contaminated with Halogenated Aliphatics: Martin Reinhard, Stanford University; Kerry Sublette, Tulsa University; Michael McInerney, University of Oklahoma (Supported by the U. S. Department of Energy)

Goal: This project is a collaborative effort of three laboratories, Stanford University, Tulsa University and the University of Oklahoma. The objectives are three fold: (1) assess whether porphyrin augmentation improves the performance of dehalogenating cultures, especially for the treatment of chlorinated ethanes and ethenes (University of Oklahoma), (2) assess whether

immobilized porphyrins can be used for treating waste streams containing chlorinated ethanes and ethenes (Tulsa), and (3) define optimal conditions for dehalogenation reactions with porphyrins, especially with respect to porphyrin type/reductant combination and solution conditions, and to identify the reaction products.

Rationale: Chlorinated aliphatic hydrocarbons are common contaminants in groundwater at many government and non-government sites. Conventional treatment technologies such as activated carbon and air stripping do not destroy the contaminants, but simply transfer them from one medium to another. In contrast, metal-containing porphyrins can catalyze the reduction of several classes of hazardous chemicals, including many halogenated solvents. Better understanding of porphyrin-mediated dehalogenation reactions could potentially allow for (1) abiotic treatment in reactors containing immobilized porphyrin or (2) treatment in anaerobic microbial systems which have been augmented with porphyrins.

Optimization of Porphyrin Mediated Dehalogenation (Stanford):

Approach: The transformation of tetrachloroethylene (PCE) by different combinations of porphyrin and reductant will be studied under different reaction conditions. The porphyrins to be considered are Vitamin B₁₂, which has a cobalt center, and hematin, which has an iron center. The bulk reductants will be titanium (III) citrate, dithiothreitol, cysteine, and iron(0) powder. The reaction conditions include primarily temperature and pH. The most promising system(s) with respect to rate and degree of disappearance will be studied in more depth. That is, a mass balance will be obtained and some effort will be made to elucidate the mechanisms. Once the PCE system is understood, other chlorinated substrates will be tested.

Status: Several porphyrin-reductant combinations are being tested. During the initial phase, work has focused on understanding the role of iron powder as a bulk reducing agent because this reductant is capable of transforming PCE on its own, i.e. without the addition of porphyrin mediator. Currently, the rate of reaction and product distribution of PCE in iron(0) systems are being determined. This systems appears especially promising since potentially harmful intermediates such as trichloroethylene, isomers of dichloroethylene and vinyl chloride were not detected. Methods are being developed to quantify possible products of PCE transformation including ethene and ethane. The half live of PCE transformation by iron alone is on the order of 2-4 days at 50°C. Efforts are underway to obtain a mass balance.

Transformation Reactions of Immobilized Porphyrins (Tulsa University):

Status: A method has been developed for the reductive dechlorination of PCE. By using vitamin B₁₂, PCE was converted to trichloroethylene and a mixture of E,Z isomers of 1,2-dichloroethylene. Batch experiments were conducted in 15-ml serum bottles with no head space. Analysis was performed using GC and GC/MS. The following reductants were investigated (in order of effectiveness): cysteine < 2-mercaptoethanol < HS⁻ < dithiothreitol (DTT) < Ti(III) citrate. Only DTT and Ti(III) citrate were selected for further study. It was found that a reaction temperature of 45°C and a pH of 9 were optimum. A variety of substituted Co³⁺-hematoporphyrins were investigated, but none of them showed any catalytic activity. With Ti(III) citrate as the reducing agent, 96% PCE was converted in 19 h, with DTT, 92% PCE were

converted in 70 h. TCE was the predominant product (95/5 ratio). B12 will be immobilized in an investigation of PCE dechlorination in a packed-bed reactor.

Effect of Reduced Porphyrins on Anaerobic Culture Performance (University of Oklahoma):
Status: This subcontract will be awarded in early 1994.

Client/User: Environmental consultants, engineers, and industries who are looking for decontamination alternatives, and researchers interested in the reductive dehalogenation of haloaliphatic compounds by metalloporphyrins.

Moffett Field In-Situ Bioremediation Study in Support of Full Scale Application: Perry L. McCarty and Mark N. Goltz, Stanford University (Supported by the U. S. Air Force)

Goal: To obtain supporting information for the proposed full-scale evaluation of in-situ aerobic biodegradation of chlorinated aliphatic hydrocarbon (CAH) compounds at an Air Force facility with respect to the possible presence of a suitable biodegrading population, the effectiveness for 1,1-dichloroethylene (1,1-DCE) degradation, the appropriate chemicals for addition, and methods for optimizing field operations.

Rationale: In order to conduct a full-scale evaluation of in-situ bioremediation of chlorinated solvent contamination, as discussed in the companion project which applies bioremediation technology to a contaminated Air Force site, supporting information from the laboratory and a controlled field site is required. This project will complement the full-scale study, by providing these necessary data.

Approach: Recent studies conducted by Stanford University at the Moffett Field site have demonstrated that trichloroethylene (TCE) can be effectively biodegraded cometabolically through the introduction into the subsurface of a primary substrate (such as phenol) and oxygen to support the growth and energy requirements of a native population of microorganisms. However, several tasks remain before the process can be implemented at a "real-world" site. These tasks are: (1) to evaluate if a CAH degrading population similar to that found at Moffett is present at the site, (2) to evaluate how the presence of 1,1-DCE will impact the efficacy of TCE degradation, (3) to evaluate the effectiveness of alternative substrates, such as toluene, (4) to evaluate the effectiveness of hydrogen peroxide as an oxygen source, and (5) to determine the optimum approach for full-scale field evaluation of in-situ CAH biodegradation for application at the site. Studies in the laboratory and the Moffett Field site will be conducted to answer these questions, prior to and in conjunction with implementation of a full-scale field study.

Status: Experimental results have been obtained from Moffett which can be used to make predictions regarding the impact of 1,1-DCE on degradation effectiveness, the effectiveness of toluene as an alternative substrate, and the effectiveness of hydrogen peroxide as an alternative oxygen source. The presence of 1,1-DCE was found to seriously reduce the effectiveness of oxidative biodegradation of TCE, probably due to 1,1-DCE transformation product toxicity. Toluene was found to be as effective as phenol for cometabolism of CAHs. Hydrogen peroxide was found to be a suitable alternative to pure oxygen as a source of oxygen for in-situ biodegradation.

Clients/Users: Researchers studying in-situ bioremediation; and state and EPA regulators, industries, and consulting engineers with interests in biotreatment systems for organically contaminated groundwaters.

AROMATICS

In-situ Biological Treatment of Aromatics in Groundwater: Martin Reinhard, Stanford University (Supported by the U. S. Navy)

Goals: The objective of this study is to (1) develop and characterize microbial consortia capable of transforming aromatic hydrocarbon compounds under anaerobic conditions and to understand the effect of environmental factors on the transformation processes, and (2) evaluate potential in-situ application of anaerobic processes for bioremediation of a gasoline contaminated field site.

Rationale: Although most gasoline constituents are readily degraded in aerobic surface water systems, the groundwater environment associated with hydrocarbon spills is typically anaerobic, thus precluding aerobic degradation pathways. In the absence of oxygen, degradation of gasoline components can take place only with the utilization of alternate electron acceptors such as nitrate, sulfate, carbon dioxide, and possibly ferric iron. The potential for transformation of these compounds under field conditions using alternate electron acceptors and the rate of such transformations has yet been adequately assessed.

Approach: Anaerobic transformation of various monoaromatic hydrocarbons is being evaluated in the laboratory and an in situ bioremediation experiment. In the laboratory, microbial consortia from aquifer solids and other sources are being evaluated in microcosms for anaerobic biotransformation of benzene and selected alkyl-substituted monoaromatic compounds. Potential biotransformation intermediates, biotransformation kinetics, and the effect of nutrient addition and alternate electron acceptors (nitrate and sulfate) are being determined. Anaerobic degradation of gasoline hydrocarbons using nitrate as a primary electron acceptor was evaluated in bioreactors and is now being tested in a field scale injection experiment at a gasoline-contaminated aquifer at the Seal Beach site in Southern California. The field research is being developed and carried out in cooperation with staff of the Naval Facilities Engineering Service Center, Port Hueneme, CA.

Status: In laboratory microcosm studies, benzene, toluene, p-xylene, and o-xylene, have been biotransformed under sulfate reducing conditions, and toluene, ethylbenzene, and m-xylene have been biotransformed under anoxic, denitrifying conditions. Work is ongoing to determine if developing nitrate reducing and sulfate reducing conditions sequentially would be a viable remediation scheme to biotransform the full range of BTEX compounds. At the Seal Beach site, results from bioreactor experiments were consistent with the laboratory microcosm studies and indicated that toluene and ethylbenzene biodegradation was enhanced by nitrate addition. It is likely that several electron acceptors played a role in the overall activity observed in the bioreactors. To date, two injection experiments have been completed at the Seal Beach site and a third experiment is underway. The second experiment verified reproducibility of results of the first experiment, and continued the development of experimental protocol and evaluated adjacent wells for usefulness in later experiments. The first experiment confirmed experimental protocols using a conservative tracer. Nitrate was added to the groundwater in a third experiment and

significant reduction in all the BTEX aromatics was observed. A subsequent "controlled release" injection experiment is planned to verify the results of the nitrate enhancement experiment, and laboratory microcosms are planned to confirm that losses observed were indeed due to biological activity.

Client/Users: Researchers interested in anaerobic biotransformation of aromatic hydrocarbons and aquifer bioremediation; and state and EPA regulators and industry concerned with gasoline and aromatic hydrocarbon remediation.

Microbial Degradation of Toluene Under Sulfate-Reducing Conditions--The Role of Iron: Martin Reinhard and Dunja Grbić -Galić , Stanford University

Goal: The goal of this project is to explore two phenomena that are potentially important to remediation of gasoline-contaminated aquifers but are not well-studied: sulfidogenic toluene degradation and the stimulation of this process by iron. These phenomena have been observed in bacterial enrichment cultures originally inoculated with fuel-contaminated soil collected near the Patuxent River (Maryland). The emphasis is on elucidating degradation pathways and the nature of iron's effect (for example, whether iron reduces sulfide toxicity or is an essential nutritional requirement, and whether iron stimulates only the first step in toluene degradation or multiple steps).

Rationale: Toluene, a U. S. EPA priority pollutant, is a water-soluble constituent of refined petroleum products (e.g., aviation fuels and gasoline) and is a widespread contaminant of groundwater near leaking underground storage tanks, landfills, and other uncontrolled releases of fossil fuels. The ability of native bacteria at such contaminated sites to degrade toluene has important environmental implications; such organisms are probably the primary determinant of the rate of decontamination in the absence of remediation. If remedial action is taken, such organisms may be an important factor in the remediation scheme. The development of anaerobic conditions and the presence of sulfate in contaminated aquifers could foster sulfidogenic toluene degradation. Iron, the fourth most abundant element in the earth's crust, could have an important effect on the rate of sulfidogenic degradation of hydrocarbons.

Approach: Experiments have been performed to explore the importance of sulfide removal in the absence of iron; for example, zinc was substituted for iron in enrichment cultures to see whether toluene degradation would be stimulated. In addition, studies were made to determine whether iron stimulates the degradation of metabolic intermediates of toluene degradation. To accomplish this task, stable isotope-labeled toluene and gas chromatography/mass spectrometry were first used to identify metabolites of toluene degradation. Enrichments were then constructed using intermediates as sole, primary substrates. Attempts are also being made to isolate the one or more species in the enrichment culture that engage in toluene degradation.

Status: Experiments with enrichment cultures that compared the effects of adding ferrous sulfate vs. zinc sulfate have demonstrated that sulfide toxicity, not a nutritional iron limitation, is the factor being ameliorated by the presence of iron in the cultures. This result applies both to toluene and to a transient intermediate of toluene degradation, benzoate. Several methods designed to identify additional transient intermediates (including inhibition by fluoroacetate and isotope dilution using suspected intermediates) have thus far only confirmed that benzoate is an

intermediate; further attempts will be made to isolate other transient intermediates. Two dead-end metabolites, benzylsuccinic acid and benzylfumaric acid, have been identified as minor products of toluene degradation. It appears that the yield of these by-products has decreased over the past year, without a commensurate increase in toluene mineralization or decrease in nonvolatile carbon production (as determined using radiolabeled toluene). Attempts at isolating sulfate-reducing bacteria are continuing. In addition, culture samples have been sent to the laboratory of Dr. J. Tiedje (Michigan State University) to try to determine the number (and possibly the identity) of species in these mixed cultures by using 16S rRNA analysis.

Client/Users: State and EPA regulators, industry, and consultants concerned with cleanup or natural bioremediation of sites contaminated by gasoline or aviation fuel; researchers interested in geochemical factors affecting the anaerobic degradation of monoaromatic hydrocarbons.

Biotransformation of Ordnance Wastes Using Unique Consortia of Anaerobic Bacteria: A. Morrie Craig, Oregon State University (Supported by the U. S. Navy)

Goals: Trinitrotoluene (TNT) is a toxic munitions pollutant which contaminates more than 1400 U. S. military facilities. Commercial companies now estimate over \$70 billion in costs if TNT is detoxified by incineration. The goal of this project is to develop a rapid complete biological method to remediate TNT-contaminated soils employing anaerobic microbes to be used in slurry bioreactors or for *in situ* addition of exogenous microbes derived from animal gut flora.

Rationale: Previous HPLC experiments have identified transient metabolites as aminonitrotoluenes. Recent GC/MS experiments have identified aniline and other deaminated compounds. Evidence indicates that the biological systems under study rapidly degrade TNT and are able to remove nitrogen atoms off of the aromatic ring. The whole rumen fluid as well as isolate G.8 is able to reductively deaminate some aromatic compounds, and under some circumstances to de-methylate them. This suggests the presence of a reductive deaminase type enzyme.

Approach: Based on previous research results, the recent focus has been on two principal areas of investigation: 1) identification of the major metabolites of TNT produced in a whole rumen fluid incubation and 2) construction and operation of a laboratory-scale, flow-through bioreactor using ruminal and aerobic bacteria. Using the rumen from sheep and goats as a source of anaerobic microbes, a consortium of bacteria has been discovered, as well as a pure isolate (G.8), which are transforming TNT. Uniformly ring labelled ^{14}C -TNT has been used in incubations, metabolites of which were monitored using HPLC, TLC, and GC/MS. The main thrust has been to determine mass balance of TNT degradation and also to determine that no toxic intermediates are formed.

Status: The evidence gathered over the past year supports the basic premise that ruminal anaerobes have novel abilities to biodegrade TNT. A strong base has been developed which has increased the ability to address the long-term goal of practical application of ruminal anaerobes to decontaminating munitions-containing soil. Further work in completing mass balance is in progress. In addition, a second question is being addressed which indicates that microbes from the rumen can degrade compounds outside of the rumen environment, in soil matrices and at non-biological temperatures. Bioreactors have been conditioned to address this question. This

coming year efforts will begin for "reducing to practice" the treatment of munitions-contaminated waste with rumen derived bacteria.

Client/Users: The U. S. Navy and other DOD units, their consultants, and regulatory agencies who are interested in the biotransformation of munitions; and researchers who are exploring new microbial consortia for aromatic compound degradation.

The Effect of Environmental Conditions on Reductive Dechlorination Rates: Sandra L. Woods, Oregon State University

Goal: The goal of this project is to develop an understanding of the effect of environmental conditions on the rates of reductive dechlorination reactions.

Rationale: Reductive dechlorination is a common anaerobic biodegradation mechanism for chlorinated aromatic compounds. This research will test the hypothesis that the rate of reductive dechlorination reactions depend upon the apparent EH. The sulfate/sulfide system will be studied to better understand the oxidation/reduction conditions within the system.

Approach: The project has two phases. In the first phase, a reactor system was developed to allow measurement of biodegradation rates under constant conditions of biomass, pH, sulfate, sulfide, and acetate concentrations. In the second phase, batch experiments are being conducted to measure degradation rates under varying, but constant, environmental conditions. A model anaerobic system fed acetate, pentachlorophenol, and nutrients has been selected for study.

Status: Phase 1 - Development of a reactor system. The reactor system has been developed and has the ability to monitor and maintain a constant pH, apparent oxidation-reduction potential, and acetate, biomass, and sulfide concentrations. Hydrogen peroxide is used to raise the apparent EH from the "natural" EH observed for the system of -260 mV. Titanium citrate is used to lower the EH.

Phase 2 - Biodegradation experiments. Experiments have been conducted to determine the rate of pentachlorophenol reductive dechlorination by a PCP-acclimated consortium at constant pH, acetate and biomass concentrations at stable apparent EH values of -60, -160, -260, and -360 mV. The rate of pentachlorophenol reductive dechlorination appears to decrease when the EH is increased from the "natural" value of -260 mV to -160 mV. At -60 mV, reductive dechlorination was not observed. The rate did not increase significantly when the EH was lowered to -360 mV by use of titanium citrate. However, addition of methanol as an alternative electron donor increased the rate of PCP dechlorination by a factor of three.

Client/User: Consultants and regulators concerned with site characterization for bioremediation or above-ground biological treatment of chlorophenols, and researchers interested in biotransformations in a complex system.

HEAVY METALS

Heavy Metals in Ceramic Matrix: Heavy Metals/Clay Interactions in Ceramic Processing: James O. Leckie, Stanford University (Partially Supported by the U. S. Department of Energy)

Goal: The goal of this research is to evaluate a method for nonhazardous rendering of heavy metal bearing industrial waste sludges by incorporation into a ceramic matrix.

Rationale: Past and continuing practice and research suggest that precipitation of heavy metals from industrial wastewaters will continue to be used as the main process for removing heavy metals from industrial wastewater. In addition, the need for disposing of the residual sludge materials from the wastewater treatment process will also continue. However, as wastewater treatment and residual disposal requirements become more strict, the development and application of innovative treatment methods becomes necessary. At the present time, there is not a comprehensive data base for evaluating the leachability and properties of ceramics incorporating heavy metal sludges.

Approach: The project is comprised of seven main tasks. Task 1 involves a comprehensive literature search in the field of ceramic production methods and chemistry. Task 2 is concerned with choosing ranges in the major variables that are relevant to producing ceramic samples and production of ceramic pellets for preliminary evaluation. Task 3 involves ceramic production in the form of ceramic pellets. Task 4 requires evaluation criteria of the ceramic pellets from both a practical and scientific standpoint. Leaching criteria such as chemical condition, sample size, and grinding of the samples will be completed first. Next, chemical analysis using atomic absorption/spectrophotometry (AA) followed by spectroscopic studies using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and extended X-ray absorption fine structure (EXAFS) will be carried out. Task 5 will involve evaluation and refinement of the variables chosen in Task 2 so that optimal conditions for the ceramic product are chosen. Task 6 is concerned with bench-scale production of the ceramic product using the optimal conditions chosen in Task 5. Task 7 requires evaluation of various uses for the ceramic products such as an additive in cement, construction fill, etc.

Status: Task 1 is ongoing and task 2 has been completed. For task 2, the following variables have been chosen: sintering temperatures: 950⁰ C, 1050⁰ C and 1100⁰ C; times at sintering temperatures: 27-36 minutes and 43-58 minutes; clay/sludge ratios: 10/1 and 4/1; heavy metal carriers: lime and soda ash; heavy metals: nickel (II) and lead (II); sludge additions: dry sludge (non uniform size) and dry sludge (uniform size). In addition, task 3 involving the production of ceramic pellets is well under way. A 0.53% (on a dry basis) Ni(II) sludge has been formed, characterized using AA techniques, and mixed with clay and water in the production of pellets. Using this sludge, ceramic samples have been produced at the following variables: 950⁰ C sintering temperature, 27-36 minute time at sintering temperature, 10/1 clay/sludge ratio, and dry sludge addition (non uniform size). These samples are awaiting further analysis.

Client/User: The results of this study should be of interest to industries producing heavy metal sludges as well as hazardous waste conversion industries.

Lead Sorption, Transport, and Remediation in Natural Soils and Subsoils: Peter O. Nelson, Oregon State University

Goal: The overall purpose of this research is to investigate conditions that enhance the mobility of lead in contaminated soils for in-situ remediation by a pump-and-treat process, or alternatively, to chemically immobilize lead through sorption or precipitation processes. The study will increase the understanding of lead chemistry in soils and groundwaters through both physico-chemical techniques and computer modeling.

Rationale: Although lead is often considered "immobile" in soils, dissolved lead in groundwater exceeds the EPA drinking water MCL in numerous lead-contaminated soils. Better understanding is needed of processes that control lead mobility in soils, including sorption-desorption, precipitation-dissolution, and complexation; and the effects on these processes of environmental conditions such as pH, soil organic matter content, metal speciation, surface chemical properties of soil mineral phases, and reaction time (kinetics).

Approach: Several parameters will be varied in order to ascertain their effects: pH, nature and amount of ligands, the nature and amount of competing cations, soil mineral phase composition, and reaction time. Batch reactor experiments will be used to initially study sorption and desorption kinetics and to determine equilibrium constants for lead sorption. Continuous-flow packed-beds (soil columns) will be used to more closely simulate field conditions of porous media flow. Soil columns are particularly useful for investigation of diffusion-limited sorption and desorption kinetics. This latter is necessary for transport modeling and the preliminary evaluation of "in situ" chemical remediation processes. In addition, the liquid-to-solid ratios of natural soil systems cannot be duplicated in batch studies. Data from both batch and soil column studies will be used in computer modeling studies to simulate environmental conditions.

Status: Partial funding of this project was received in November, 1992. The scope of the project has been reduced accordingly. A computer equilibrium model was developed to simulate lead chemical behavior in soil. The sorbing surface in soil was represented by hydrous ferric oxide, and factors investigated included pH, surface site concentration, ionic strength, and organic chelators. Controlling pH below 6.0 and addition of chelating agents such as EDTA offer the most promise for reducing lead adsorption and enhancing its mobility. Solution pH values above 6.0 and high density of surface sites enhance lead adsorption and greatly reduce its mobility. Batch laboratory experiments are in progress using hydrous-ferric-oxide-coated sand as a representative soil sorbing surface.

Client/Users: Research results from this study will provide information to better enable water quality managers to predict the movement of lead in soil, including the potential dangers from the mobilization of metals from contaminated soils into groundwaters. Specifically, the results will be used to predict the conditions necessary to chemically enhance mobilization of lead from contaminated soils in "pump and treat" in-situ extraction schemes, or alternatively, to chemically immobilize lead through sorption or precipitation processes.

TRAINING AND TECHNOLOGY TRANSFER PROJECT DESCRIPTIONS

TRAINING AND TECHNOLOGY TRANSFER

Hazardous Waste Training: Kenneth J. Williamson and Peter O. Nelson, Oregon State University

Goal: To promote training activities related to hazardous substance management.

Rationale: The Center can effectively promote training activities desired by other Federal agencies within EPA Region 9 and 10.

Approach: The Center in consortium with the University of California Extension Program in Hazardous Materials Management sought support to serve as one of the regional EPA training centers for lead paint abatement.

Status: The Center has conducted six workshops within Oregon and Washington. Eight additional workshops are scheduled for Oregon, Washington, Idaho, and Alaska. The Center was successfully chosen for an extension of the EPA grant for 1993-94.

Advanced Topic Workshops: Kenneth J. Williamson and Lewis Semprini, Oregon State University

Goal: To provide workshops on advanced topics to regulators, consultants, industrial personnel, and researchers.

Rationale: A need exists for transfer of results from the basic and applied research conducted at the Center.

Approach: The Center has developed several workshops to be conducted upon demand.

Status: The workshops are offered when adequate demand is generated.

Continuing Education Program: Kenneth J. Williamson, Oregon State University and Donald C. Olcott, Continuing Education, Oregon State University

Goal: To maintain a program in hazardous substance education for professionals in the State of Oregon.

Rationale: An education program is not available in hazardous substance management and site remediation for persons in the Portland metropolitan area.

Approach: A series of six courses have been developed to be offered through OSU's continuing education program. The courses are transferable for graduate credit and a certificate of completion is offered for those students successfully completing the courses.

Status: The series of courses are on-going and are offered on a two-year cycle. Attendance has steadily increased and about 70 persons are presently in the program seeking the certificate of completion for the six courses.

Conference Sponsorship: Kenneth J. Williamson and Lewis Semprini, Oregon State University

Goal: To actively promote conferences to address technical aspects of hazardous substance research and education.

Rationale: Conferences are a highly efficient and cost-effective way to achieve the transfer of technology.

Status: This year the Center sponsored or co-sponsored the following conferences:

The 1993 Idaho Regional Conference on Hazardous Materials, Pocatello, Idaho, April, 1993.

The 1993 Responsible Hazardous Materials Management Conference, Portland, Oregon, September, 1993.

In-situ and Onsite Bioreclamation Conference, San Diego, California, April, 1993.

Field Application of Remediation Technologies: Perry L. McCarty, Stanford University, and Kenneth J. Williamson, Oregon State University

Goal: To seek funding to support field applications and demonstrations of innovative remediation technologies developed within the Center.

Rationale: Field application represent one necessary step in the ultimate transfer of technology.

Approach: Funding is being sought to support field applications in relation to several technological developments from the research within the Center.

Status: Several projects have been funded (see below).

Field Test of In-Situ Vapor Stripping for Removal of VOCS from Groundwater: Steven M. Gorelick, Stanford University (Supported by the U. S. Department of Energy)

Goal: This project is aimed at demonstrating an in-situ method for removing VOCs from groundwater. Through simple gas injection into a well, this method enables removal of VOCs from contaminated groundwater without bringing the water to the ground surface. Recirculation of groundwater is accomplished via air-lift pumping. Theoretical work was carried out previously in the group of Professor Gorelick in the School of Earth Sciences at Stanford. The current effort is a pilot scale field demonstration at the U. S. Department of Energy Hanford Site in Richland, Washington where groundwater is contaminated with carbon tetrachloride. This test will provide valuable information regarding the efficacy of the in-situ VOC removal system at the Hanford Site and potentially other sites that are contaminated with VOCs.

Rationale: Many contaminated sites contain groundwater with high concentrations of dissolved VOCs. The in-well VOC removal system is an in-situ alternative to pump and treat. It creates an in-well air stripper which volatilizes the VOCs contained in the groundwater, and removes these contaminants as a vapor. The stripped VOC vapor is contained within the well, extracted under a vacuum, and treated at the ground surface. By conversion of a groundwater

contamination problem into a simple vapor extraction system, the method has the advantage of not requiring removal, handling, treatment, storage, and disposal of contaminated groundwater. The expense of lifting the water all the way to the surface for treatment is avoided. There is no need for a surface air-stripping tower when using this method. If the water is co-contaminated with tritium (as at Hanford), the tritium can be left in the groundwater to decay while the VOCs are stripped and removed.

Approach: The proposed in-situ VOC removal system is proposed for demonstration at the Hanford Site where groundwater is contaminated with carbon tetrachloride. The demonstration unit will consist of a single VOC-removal well and two monitoring wells. Prior to the field demonstration, a laboratory mockup of the well system will be tested to evaluate the evolution of bubbles in the well and to calibrate the relation between air injection and water flow rate. The overall approach to the demonstration itself will be to conduct a 3 month initial test. Based on the results of that test, additional sensitivity studies will be performed to assess design parameters such as gas injection rate, gas type, gas temperature, gas-line submergence depth, and controls on gas bubble size.

Status: A Conceptual Test Plan was developed for the field demonstration. Models are being developed to provide three-dimensional predictions of groundwater flow and VOC removal as sequentially cleansed water moves through the saturated and unsaturated zones. The laboratory mockup will be tested in April 1994. An initial monitoring well is also to be installed in April. With data from the laboratory and the monitoring well, further predictive simulations will be done for the site. The remaining monitoring well and stripping well will be in place by late Summer of 1994. This Fall there have been four meetings. These meetings involved regulators, engineers, and citizen interest groups, and other PIs. In addition, the PI was involved in a private meeting with EPA and Washington Department of Ecology regulators who wanted to better understand the technology and be sure that their concerns are addressed. All of these "stakeholder" meetings have gone very well, and there is general enthusiasm for this demonstration.

Client/users : Regulators, industries and federal facilities with groundwater contamination by VOCs, and consulting engineers responsible for the design of treatment systems to remediate VOC contaminated groundwater.

System Design for Enhanced In-Situ Biotransformation of Carbon Tetrachloride: Application to DOE's Arid Site Integrated Demonstration: Peter K. Kitanidis and Paul V. Roberts, Stanford University, and Lewis Semprini, Oregon State University (Supported by U. S. Department of Energy)

Goal: To assist in the design of a nutrient delivery and mixing system for the pilot scale evaluation of in-situ bioremediation of carbon tetrachloride at the Hanford DOE site; to participate in the experimental design of the in-situ bioremediation tests; and to help in the interpretation of the results of the pilot-scale field experiments.

Rationale: The project is part of the larger Arid Site Integrated Demonstration that is being conducted at the Hanford DOE Facility. The specific application is bioremediation of carbon tetrachloride contamination at the 200-West area using mixing wells and chemical injection.

Approach: Specific tasks include: (a) Interpretation of field data and data from well and tracer tests, (b) development and application of hydrodynamic and transport models, (c) improvement of the understanding of the kinetic rates for the carbon tetrachloride transformation process, by conducting laboratory experiments and incorporating results into models, (d) utilization of results from models to assist in the design of the nutrient delivery system, (e) evaluation of the ability of indigenous microcosms from the Hanford subsurface to aerobically cometabolically degrade chloroform.

Status: Models for preliminary design of the delivery system have been applied. The well has been drilled. Field data are being interpreted. Batch soil microcosms and continuous flow soil microcosms packed with Hanford core material have been initiated. A stainless steel column reactor has been fabricated for conducting laboratory experiments that will mimic the recirculation process at the site.

Client/Users: DOE, industry interested in bioremediation of carbon tetrachloride or the design of delivery systems.

Full-Scale Evaluation of In-Situ Bioremediation of Chlorinated Solvent Groundwater Contamination: Perry L. McCarty and Mark N. Goltz, Stanford University (Supported by the U. S. Air Force)

Goal: To evaluate at full scale the efficiency and effectiveness of in-situ aerobic bioremediation of chlorinated aliphatic hydrocarbon compounds at an actual hazardous waste site.

Rationale: Full-scale implementation of an innovative technology, working with organizations in the user community, is an ideal way to communicate knowledge gained by research and put it into practice. A full-scale application of in-situ aerobic biodegradation of chlorinated solvents is justified based upon several years of research at Stanford University and elsewhere, and by field demonstrations that the process can operate efficiently with indigenous microorganisms. This project is a cooperative activity between the U. S. Air Force, the U. S. Environmental Protection Agency, and other parties with interest in this activity (to include citizen groups).

Approach: Recent studies conducted by Stanford University at the Moffett Field site have demonstrated that trichloroethylene (TCE) can be effectively biodegraded cometabolically through the introduction into the subsurface of a primary substrate (such as toluene or phenol) and oxygen to support the growth and energy requirements of a native population of microorganisms. In this study, the knowledge that has been gained at Moffett and elsewhere will be applied to a hazardous waste site. This will be among the first full-scale applications of in-situ aerobic chlorinated aliphatic hydrocarbon biodegradation.

It is anticipated that the remediation system will consist of a single well, screened at two depths. In operation, a submersible pump, installed between the two screens, would draw water into the well at one screened interval and discharge the water out of the second screened interval. The well would have feed lines to introduce a primary substrate and oxygen into the discharge water. Once the system is in operation and models developed to simulate the processes occurring in the field based on system performance, modifications could be introduced (such as investigating

alternative sources of oxygen, varying the length of time between the primary substrate and oxygen pulsing, etc.) in order to better understand and optimize the system.

Status: A contaminated Air Force site is being sought that has the desired characteristics so that preliminary design of the bioremediation system can commence.

Clients/Users: Researchers studying in-situ bioremediation; and state and EPA regulators, industries, and consulting engineers with interests in biotreatment systems for organically contaminated groundwaters.

Remediation of Contaminated Soil from the Baldock Station Maintenance Facility: Kenneth J. Williamson and Sandra Woods, Oregon State University (Supported by Oregon Department of Transportation)

Goal: The goal of this project is to demonstrate the successful bioremediation of a variety of chlorinated herbicides using sequential anaerobic/aerobic treatment.

Rationale: Sequential anaerobic/aerobic biological treatment has been successfully used to degrade a variety of chlorinated aromatic compounds under laboratory conditions. This project is an extension of laboratory results to a controlled field demonstration.

Approach: Currently, approximately 155 cubic yards of contaminated soil are stored at the Baldock Maintenance Facility, Portland, Oregon. The soils are contaminated with a variety of herbicides; known contaminants include 2,4-D, 2,4,5-T, Silvex, and Dichlorprop. The bioremediation procedure will involve an initial anaerobic phase followed by an aerobic phase. Under anaerobic conditions, the phenoxy herbicides are expected to be reductively dechlorinated. The resulting phenolic compounds are expected to degrade to carbon dioxide and water in the presence of oxygen.

In the field portion of the study, soil in one of the containers will be treated by recirculating nutrient-containing water under anaerobic conditions. The water will be sampled periodically to determine degradation rates and when dechlorination is complete, pure oxygen will be introduced into the recirculation stream. Following the aerobic incubation, the soil will be assayed for residual herbicide concentrations.

Status: Analytical methods are being developed to measure concentrations of herbicides and metabolic products in the soil. Dechlorination rates, approximate duration of anaerobic incubation required prior to aerobic incubation, and aerobic degradation rates are being determined for soil samples incubated under optimal conditions.

Client/Users: The results will be used by Oregon Department of Transportation personnel to treat their contaminated soil to meet Oregon Department of Environmental Quality standards for disposal into a municipal landfill.

1993 WRHSRC PUBLICATIONS

Documents either published or submitted for publication during this year of WRHSRC activity are as follows:

A. Refereed Journal Articles

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C. Chapters in Other Books or Bound Proceedings

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D. Project Reports

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F. Conferences and Workshops Sponsored or Cosponsored

The 1993 Idaho Regional Conference on Hazardous Materials, Pocatello, Idaho, April, 1993.

The 1993 Responsible Hazardous Materials Management Conference, Portland, Oregon
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G. Patents

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