



**WESTERN REGION
HAZARDOUS SUBSTANCE RESEARCH CENTER**

1994 ANNUAL REPORT

Stanford University
Oregon State University

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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.

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. The Center has two Assistant Directors, Martin Reinhard, who is in charge of the Center's analytical program, and Mark N. Goltz, who assists in both the research and the training and technology transfer activities of the Center. Marilyn C. King is the Center's Administrative Assistant.

Table 1. KEY PERSONNEL AT THE WRHSRC

<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. Lynn M. Hildemann	Prof. James D. Ingle
Mr. Gary D. Hopkins	Prof. Jonathan D. Istok
Mrs. Marilyn C. King	Prof. Peter O. Nelson
Prof. Peter K. Kitanidis	Prof. Lewis Semprini
Prof. James O. Leckie	Prof. John C. Westall
Prof. Abdul Matin	Prof. Kenneth J. Williamson
Prof. Perry L. McCarty	Prof. Sandra L. Woods
Prof. Martin Reinhard	
Prof. Paul V. Roberts	

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 the SAC and TTTAC during this past year are listed in Tables 2 and 3, respectively. They represent federal and state governments, industry, consulting firms, and universities. The Center budgets for the 1994 fiscal year and since the Center's inception are listed by category of support 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 listed in Table 4.

Table 2. SCIENCE ADVISORY COMMITTEE

<u>Member</u>	<u>Affiliation</u>	<u>Expertise</u>
Douglas R. Christensen	Jacobs Engineering	Engineering
John Conomos	Govt/USGS	Hydrology
David E. Ellis	Du Pont Chemicals	Chemical/Biological Processes
David Frank	Govt/EPA, Region 10	Hydrogeology
John Glaser	Govt/EPA, Cincinnati Lab	Physical/Chemical Processes
Ronald Hoepfel	Govt/U.S. Navy	Microbiology
Michael C. Kavanaugh*	ENVIRON	Physical/Chemical Processes
Richard G. Luthy	Carnegie Mellon University	Chemical/Biological Processes
James M. Tiedje	Michigan State University	Microbiology

John L. Wilson†
John Wise
*Chairman
†Vice Chairman

New Mexico Technical University
Govt/EPA, Region 9

Hydrology
Planning

Table 3. TRAINING AND TECHNOLOGY TRANSFER ADVISORY COMMITTEE

<u>Member</u>	<u>Affiliation</u>	<u>Expertise</u>
James T. Allen	Govt/ California	Treatment Technology
Michael Anderson	Govt/Oregon	Hydrology
John J. Barich	Govt/EPA, Region 10	Regulations
Kenneth Bigos	Govt/EPA, Region 9	Air Pollution
Lynn Coleman	Govt/Washington	Regulations
David Kennedy*	Kennedy/Jenks	Treatment Technology
Jon Kindschy	Univ. California Ext. Service	Hazardous Substances Training
Gregory Peterson	CH2M-HILL	Treatment Technology
Mary Peterson	Battelle Pacific Northwest Lab.	Treatment Technology
M. R. Scalf	Govt/EPA, Kerr Lab.	Groundwater Remediation
Kenneth Sutherland	Hewlett-Packard	Treatment Technology
Winona Victory	Govt/EPA, Region 9	Training/Tech Transfer

*Chairman

Table 4. CENTER FUNDING

<u>Funding Sources</u>	<u>FY 1994*</u>	<u>Funds to Date</u>
EPA: Centers Program	\$987,000	\$6,943,015
EPA: Other	\$1,000,000	\$1,635,816
Other Govt: Federal†	\$542,979	\$3,735,195
Other Govt: State@	\$48,252	\$48,252
Consortium	\$371,743	\$1,733,065
Private Sector#	\$212,500	\$1,882,241
TOTAL	\$3,162,474	\$15,977,584

*Oct. 1, 1993 - Sept. 30, 1994

†Department of Energy; Department of Navy, U.S. Air Force
@Oregon Department of Transportation

#Allied Signal Corporation; Brown and Caldwell; CH2M HILL; Chevron, DuPont Chemicals; 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

TABLE 5. STUDENT SUPPORT

<u>Student Support</u>	<u>Number*</u>	<u>Funds to Date†</u>
M.S.	19	\$496,028

Ph.D.	73	\$3,832,930
Post Doctoral	<u>18</u>	<u>\$1,098,471</u>
TOTAL	110	\$5,427,429

*Total numbers in researcher-years participating on Center Projects since 1989

†Includes tuition, travel, supplies, etc.

DIRECTOR'S REPORT

The WRHSRC has 19 faculty members representing two universities and five disciplines (chemistry, engineering, hydrogeology, medicine, and microbiology). 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 supported 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.

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 field demonstrations and further implementation of new and innovative technology developed through the Center. 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. Five field projects were underway this past year to demonstrate new technologies developed within the WRHSRC at pilot and full scale.

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 the problem of chlorinated solvent contamination is multidisciplinary with active research at both Stanford and Oregon State and combined expertise in microbiology, chemistry, hydrogeology, hydrology, and engineering. The group is directing its combined efforts towards obtaining better fundamental understanding of the chemistry, microbiology, and geohydrology involved, and in finding engineering methods for in situ treatment, including the subsurface mixing of chemicals that can help enhance natural processes for destroying the contaminants of concern or for physically removing them from the subsurface. Projects emphasize both aerobic and anaerobic biological transformations of carbon tetrachloride, tetrachloroethylene, trichloroethylene, dichloroethylenes, and vinyl chloride, as well as reductive dehalogenations of the same compounds abiotically by heavy metals and substituted porphyrins. A continuum of projects from basic laboratory studies through analytical simulation model development, to field demonstrations provide an integrated whole from conceptualization to implementation. Feedback between the different activities helps insure that the major technical problems in technology development and implementation are appropriately addressed.

The thrust group studying aromatic compounds and a portion of that studying chlorinated solvents have focused on anaerobic processes. A great deal of evidence has been obtained that aromatic compounds, such as the BTEX group from gasoline, and chlorinated aromatic compounds, such as pentachlorophenol, 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 at Stanford (with focus on BTEX compounds) and Oregon State (with focus on pentachlorophenol) is directed toward predictions of transformation potential and transformation rates, the determination of transformation products, and the development of engineering methods to enhance the intrinsic rates of anaerobic transformations. It may be that in some cases, the most environmentally sound and least expensive alternative is the no-treatment alternative, an approach that relies on intrinsic bioremediation. 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. As with the chlorinated solvent studies, both laboratory and field investigations and their integration are underway.

A third associated thrust area is the modeling of transport and fate processes and groundwater-management strategies. These studies are conducted partly independent of the other thrust groups, but increasingly are becoming integrated into them as the need arises. 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 activities here are being integrated quite closely into the chlorinated solvent field activities.

A fourth perhaps small, but nevertheless important thrust area of the WRHSRC is concerned with heavy metals. Chromium and lead are among the most frequently found hazardous substances found 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 HIGHLIGHTS

The major focus of research activities for the WRHSRC, and indeed its major mission, has been the conduct of basic research that will help resolve problems with hazardous waste cleanup. Proof of the success of our efforts relies to some extent on the degree to which the results of this basic research find their way into cleanup practice. There is a big step between discovery of a principle and its use in solving a practical problem. For this reason, the WRHSRC has taken on the mission, within its training and technology transfer responsibilities, to demonstrate technologies that have grown out of the basic research program. We believe that our involvement in such demonstrations will help hasten application. It also involves our research team in the practical side of the problems they study. Technical barriers that are uncovered by attempts at practical application then tend to feed back rapidly into the basic research program.

We are pleased that during this past year, and with the above benefits in mind, several efforts towards technology demonstration have begun.

One major field and demonstration effort is that by Prof. Martin Reinhard and his group on anaerobic biological degradation of benzene, toluene, ethylbenzene, and xylenes (BTEX), the group of gasoline contaminants at the Seal Beach Naval Weapons Station. This effort resulted from a basic finding that he and his colleagues were instrumental in uncovering over the past several years, that is that aromatic hydrocarbons can be biodegraded in the absence of oxygen. While once seriously questioned, this phenomenon is now widely accepted. It offers the possibility that the BTEXs in groundwater can be destroyed in place without human intervention, a process termed intrinsic bioremediation. Indeed, this past year EPA sponsored along with the U.S. Air Force a major conference on this subject, with most papers directed towards intrinsic anaerobic BTEX biodegradation. A major question is how one can insure that such biodegradation is occurring at a given site. Laboratory studies at Stanford and elsewhere have now demonstrated the presence of intermediate compounds in anaerobic BTEX degradation, such as benzylsuccinic acid and benzylfumaric acid, that can serve as key indicators of the occurrence of anaerobic transformation. Their presence has been confirmed in the Seal Beach studies where BTEX compounds are being injected into a gasoline contaminated aquifer to provide evidence for biological activity under a variety of anaerobic conditions. Field confirmation of this important laboratory finding has now been provided and is proposed as a method to verify in-situ anaerobic transformation at other sites.

Another highlight is the cooperative involvement of the WRHSRC in demonstrations at the Edwards Air Force Base in the Mojave Desert in Southern California. Two efforts at full-scale evaluation of treatment processes stemming from our research are underway. One, led by Prof. Steven Gorelick, is the demonstration of a new in-situ air stripping process for removal of volatile organic compounds from groundwater. This involves air injection into a well in such a manner that the volatile compounds are transferred to an air stream without the need to bring the water to the ground surface, and at the same time, the groundwater is caused to circulate throughout the aquifer in order to bring untreated groundwater to the air-stripping system. The second demonstration is the full-scale implementation of in-situ cometabolic biodegradation process for trichloroethylene removal under the direction of Prof. Mark Goltz. This process has been developed through extensive laboratory and modeling studies at Stanford and field pilot evaluation at the Moffett Federal Airfield. The in-situ process proposed will cause groundwater to circulate between two treatment wells that are screened in upper and lower sections. Toluene will be added as the primary substrate for growth of key organisms along with hydrogen peroxide to serve as an oxygen source. This will represent a 10 to 30 fold increase in scale of the process successfully evaluated at Moffett, and will be used to treat a contaminated plume rather than chlorinated solvents purposely added to the aquifer. There is widespread interest in both of these processes and the WRHSRC is working with groups at other federal facilities where interest in demonstration has also been indicated.

A fourth field effort is that with the Oregon Department of Transportation for biodegradation of chlorinated pesticides (i.e., Silvex, Dichloroprop, 2,4,5-T and 2,4-D) in contaminated soil. Here, Profs. Kenneth Williamson and Sandra Woods of Oregon State University are bringing expertise gained through several years of research on anaerobic and aerobic transformation of chlorinated aromatic compounds towards solution of a practical problem in Oregon. Anaerobic biological treatment as a first stage of treatment to remove chlorine atoms from the pesticide molecule is

being undertaken, with a second stage planned of aerobic treatment for further degradation of the pesticides. Anaerobic treatment as a first stage for dehalogenation of industrial chemicals that are otherwise highly resistant to aerobic treatment has been a major theme of research within the WRHSRC. Such field demonstrations will help speed the practical application of this innovative process and may save the Oregon Department of Transportation significant disposal costs.

FUTURE DIRECTIONS

The WRHSRC is continuing its basic research thrusts toward cleanup of important contaminants, including petroleum hydrocarbons, halogenated aromatic compounds, chlorinated solvents, and heavy metals. They collectively pose the most difficult and expensive problems faced in restoration of contaminated sites in the United States. Some new initiatives that are just getting underway address the major problem here of nonaqueous phase liquids (NAPLs). How to contain and remediate NAPLs is perhaps the most challenging problem faced in the hazardous substance arena. No clear solutions to this difficult problem are yet evident, but because of its immensity, basic research to help better define the nature of this problem is essential to its eventual solution.

Other new research activities are a direct result of problems uncovered in our attempts to implement through field demonstrations processes that have evolved from basic laboratory studies. One of the most costly components of aerobic in situ biodegradation of groundwater contaminants, such as being undertaken at Edwards Air Force Base for TCE biodegradation, is that for getting oxygen into groundwater. This high cost results largely from the poor solubility of oxygen. A new project just being initiated will seek more cost-effective methods for such oxygen transfer. Another technical issue with biological processes in groundwater is the potential for aquifer clogging through microbiological growth. A new basic study to determine more about the processes involved in biological clogging so that we can better address this practical problem is now getting underway. In addition to the above, new initiatives include exploration of other primary substrates that may offer efficiency and cost-effectiveness advantages for aerobic in-situ bioremediation of contaminants, and approaches that reduce the toxicity of intermediate products from contaminant transformation. The biological processes resulting in anaerobic transformation of BTEX compounds and chlorinated solvents are still poorly understood, and new basic studies with pure cultures of transforming organisms isolated in our studies are being pursued, as well as studies on the formation and decomposition of intermediates with the purpose of developing monitoring tools for evaluating the effectiveness of both intrinsic and engineered in-situ biodegradation. We believe that continuation of the initial basic research thrusts of the WRHSRC on environmentally significant, widespread, and difficult contamination problems faced by the nation is the best approach for us in the coming years.

Three additional ventures that are just starting within the five EPA-sponsored HSRCs, and thus will become a highly active part of the WRHSRC are the Minority Academic Institution (MAI) program, the Technical Outreach Services for Communities (TOSC) program, and the program to assist displaced Department of Defense personnel in transition to careers in environmental engineering and science. The MAI program is designed as a cooperative activity between the WRHSRC and institutions with a large minority population and with an interest in developing research and educational programs in hazardous substance control. Through a competitive solicitation, five cooperative research ventures, one training and technology transfer study, one faculty enhancement activity, and two student training programs have been chosen by the

advisory committees of the Center for funding. These should all be underway by summer 1995. The TOSC program is being conducted under the direction of Prof. Kenneth Williamson, and has as its function helping communities within federal regions 9 and 10 to understand the nature of hazardous waste problems they may face and how they may seek financial and technical assistance and advice. This activity will be conducted in cooperation with the EPA regional offices. The third activity is directed towards military personnel and DOD civilians who have been displaced from employment with DOD. Not only is financial assistance being provided to help in undergraduate and graduate education, but these students will be provided the opportunity to participate in hazardous substance research activities through the WRHSRC.

Table 6. WESTERN REGION HAZARDOUS SUBSTANCE RESEARCH CENTER PROGRAM SUMMARY

RESEARCH PROGRAM SUMMARY

<u>Project Description</u>	<u>Principal Investigators</u>	<u>End Date</u>	<u>Total Budget</u>
Chemical Movement, Fate, and Treatment			
Aquifer Remediation Design in the Presence of Kinetic Limitations	Steven Gorelick	1995	\$ 235,769
Determination of Macroscopic Transport Parameters for Biologically Reacting Solutes in Aquifers	Peter Kitanidis	1995	\$ 218,774
Radon-222 Method for Locating and Quantifying Contamination by Residual Non-Aqueous Phase Liquids in the Subsurface	Lewis Semprini	1994	\$ 143,079
Redox Transformations of Inorganic Pollutants: Coupling to the Biogeochemical Matrix	John Westall James Ingle	1994	\$ 158,151
Process Submodel Formulation and Parameter Estimation for Simulation of Bioremediation	Paul Roberts Lewis Semprini	1994	\$ 199,625
Modeling Strategies for Optimizing In-Situ Bioremediation	Peter Kitanidis Paul Roberts Lewis Semprini	1994	\$ 243,001
Chlorinated Solvents			
Transformation of TCE by Methanotrophic Biofilms	Perry McCarty	1995	\$ 123,272
Degradation of Chlorinated Aliphatic Compounds by Nitrifying Bacteria	Daniel Arp Kenneth Williamson Michael Hyman	1995	\$ 216,515
In-Situ Treatment of Chlorinated Solvents	Perry McCarty	1995	\$ 215,000

Anaerobic Treatment of Chlorinated Solvent Contaminated Groundwater	Perry McCarty	1994	\$ 125,000
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<u>Project Description</u>	<u>Principal Investigators</u>	<u>End Date</u>	<u>Total Budget</u>
Transformation of Chlorinated Organics by Reduced Metallocoenzymes - Kinetic Model Development and Applications to Environmental Systems	Martin Reinhard	1995	\$ 222,414
Enhancement of Biodegradation Through the Use of Substituted Porphyrins to Treat Groundwater Contaminated with Halogenated Aliphatics	Martin Reinhard Kerry Sublette Michael McInerney Joseph Suflita Ralph Tanner	1994	\$ 299,999
Moffett Field In-Situ Bioremediation Study in Support of Full-Scale Evaluation Application	Perry McCarty Gary Hopkins Mark Goltz	1995	\$ 394,834

Aromatic Compounds

In Situ Biological Treatment of Aromatics in Groundwater	Martin Reinhard	1994	\$ 268,750
Microbial Degradation of Toluene under Sulfate-Reducing Conditions - The Role of Iron	Martin Reinhard	1995	\$ 233,075
Biotransformation of Ordnance Wastes Using Unique Consortia of Anaerobic Bacteria	A. Morrie Craig	1994	\$ 150,000
The Effect of Environmental Conditions on Reductive Dechlorination Rates	Sandra Woods	1994	\$ 154,818

Heavy Metals

Incorporation of Nickel in a Ceramic Matrix: A Method for Treatment and Disposal of Heavy Metal Containing Wastes	James Leckie George Redden	1995	\$ 211,950
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Lead Sorption, Transport, and
Remediation in Natural Soils and
Subsoils

Peter Nelson

1994

\$ 101,260

TRAINING AND TECHNOLOGY TRANSFER PROGRAM SUMMARY

<u>Project Description</u>	<u>Principal Investigators</u>	<u>End Date</u>	<u>Total Budget</u>
Hazardous Waste Training	Kenneth Williamson Peter Nelson	1995	\$ 90,000
Advanced Topic Workshops	Kenneth Williamson Lewis Semprini	1995	\$ 90,000
Continuing Education Program	Kenneth Williamson Donald Olcott	1995	\$ 90,000
Conference Sponsorship	Kenneth Williamson Lewis Semprini	1995	\$ 90,000
Remediation of Contaminated Soil from the Baldock Station Maintenance Facility	Kenneth Williamson Sandra Woods	1994	\$ 40,200
Field Test of In-Situ Vapor Stripping for Removal of VOCS from Groundwater	Steven Gorelick	1995	\$ 235,459
Full-Scale Evaluation of In-Situ Bioremediation of Chlorinated Solvent Groundwater Contamination	Perry McCarty Mark Goltz Gary Hopkins	1995	\$ 611,061
Evaluation of Strategies for Full Scale Bioremediation of the Seal Beach Site Using Anaerobic Microbial Processes	Martin Reinhard Gary Hopkins Peter Kitanidis	1995	\$ 106,250

RESEARCH PROJECT DESCRIPTIONS

CHEMICAL MOVEMENT, FATE, AND TREATMENT

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 rate-limited contaminants.

Rationale: In recent years, it has become clear that the cleanup of polluted 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, it soon removes much lower concentrations, which are generally far above water quality standards, and can remain so for decades. Contaminants dissolved in mobile water move quickly toward the well, but slow desorption and diffusion of immobile contaminant limits the rate at which groundwater can be remediated. These rate-limiting diffusion and desorption processes have been extensively documented and are frequently cited as a fundamental reason for the failure of conventional remediation strategies. However, these processes have not been incorporated into the design of aquifer remediation, and 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: We have derived a new model of mass transfer that is shown to be a general form of the family of diffusion models and first-order mass transfer models. This "multi-rate" model is currently able to represent diffusional mass transfer into or out of spheres, cylinders, and layers, as well as first-order surface reactions. Most importantly, it is able to model any mixture of these components, thus providing new insights into field-scale mass transfer in a heterogeneous medium. To date we have used the model (1) to successfully predict solute uptake into a mixture of grain sizes from the Borden aquifer, and (2) to investigate the effects on aquifer remediation of a heterogeneous mixture of clay layers, clay pods, grain aggregates, and surface reactions. In the latter application, we show that understanding the variations in rates of mass transfer is likely the key to making accurate predictions of remediation times. Within the past year, two of our manuscripts have been published and a third is now complete and awaiting review. We continue to develop several new ideas on aquifer remediation in the presence of rate-limited mass transfer.

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

Goal: This research aims to improve our understanding of scale effects on the transport and fate of biologically reacting chemicals in heterogeneous formations. Our 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 (c) 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.

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 a major obstacle to implementing thorough 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 predictions indicate that radon would become depleted in the aqueous phase when NAPLs are present. Thus, spatial and temporal changes in the radon concentration in subsurface fluids might be used to locate and quantify NAPL contamination.

Status: Laboratory studies have been performed that verified the NAPL-Radon equilibrium partitioning model proposed. Radon transport through columns was retarded due to the partitioning, and the degree of retardation increased as the residual saturation increased, as predicted by transport theory. Current studies are evaluating how the aqueous radon concentrations change during the remediation of the NAPL in the laboratory columns. A numerical model is also being developed to simulate the results of the laboratory and field studies. The method has been tested in two controlled field studies at the CFB Borden test site in Ontario, Canada. In the first study groundwater radon concentrations decreased by a factor of 2 to 3 in the fairly uniform DNAPL source zone emplaced in the shallow sand aquifer. A NAPL residual saturation of 3% was estimated using the field observations and the NAPL-Radon equilibrium partitioning model. This agreed well with the 3.8% residual saturation based on mass balances. In the second study 5 liters of DNAPL 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 of both the field and laboratory studies indicate that the radon deficit method has potential for both locating and quantifying subsurface NAPL contamination, and potentially monitoring the progress of remediation.

**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 contaminant affects its speciation and thereby its transport, fate, and biological effects.

Approach: In characterizing redox transformations of inorganic contaminants, we consider three components: the redox-active inorganic contaminant, the geochemical matrix, and the redox sensor. Coupling of redox processes must be understood at three linkages -- contaminant and

matrix, sensor and matrix, and contaminant and sensor. Each linkage must be investigated on a species-by-species basis, without the a priori assumption of equilibrium. The focus of this study is on transformations of Cr(III)/Cr(VI) in biogeochemical matrices of Fe(II), Fe(II)-minerals, Mn(IV)-minerals, and soils. In parallel experiments, transformations of redox indicators are investigated spectrochemically and electrochemically, toward the goal of developing alternative redox sensors that can be deployed in-situ.

Status: This project began in March, 1992. We have developed a reactor system ("redox-stat"), with which we can monitor redox conditions and control the redox status of a biologically active reactor at any selected level, making it possible to carry out a wide range of experiments under controlled conditions. A unique external loop allows for continuous filtering prior to on-line spectrophotometric measurement or measurement of dissolved species with other sensors. Numerous redox indicators have been electrochemically and spectrochemically characterized in simple solution experiments. Ten redox indicators which react reversibly with several reductants and oxidants were further studied. The selected indicators couple with a platinum electrode to "poise" the redox potential of the system over the EH 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. In more complex systems with minerals or soil, adsorption of the indicators on the surface of the solids precludes spectrophotometric measurements. To alleviate this problem, two indicators have been immobilized on an affinity chromatography gel and packed in a flow cell for spectrophotometric monitoring in the external loop. The immobilized indicator thionine has redox characteristics similar to the "free" dissolved indicator and is reduced by components of a soil solution in the reactor with the potential measured at a Pt electrode falls below about 0 V and the concentration of Fe(II) is relatively high. Currently, the immobilized indicator is being studied in soil matrices in the laboratory in preparation for field applications.

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. Work in the past year assessed the applicability of adaptive control engineering to in situ bioremediation systems.

Status: This two year project, which was initiated in September 1992, concluded in September 1994. Advances in 1993-94 resulted in improved understanding 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 were explored. The investigation encompassed both the two-well and single vertical well circulation systems. The optimal substrate delivery policy entails introducing the substrates at the rate at which they are required for net microbial growth. A control method for monitoring and adjusting the substrate delivery rates is proposed.

Modeling Strategies for Optimizing In-Situ Bioremediation: Peter K. Kitanidis and Paul V. Roberts, Stanford University, and Lewis Semprini, Oregon State University (Supported by the 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 enhanced 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. This project is now completed.

CHLORINATED SOLVENTS

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.

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 being used for hypothesis testing, and to indicate the processes of importance that are in need of further evaluation. Simulations have indicated the importance of the minimum substrate concentration required for bacterial growth (S_{\min}) and the rate of decay of active biomass. 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. 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. Experimental determination of factors affecting S_{\min} for methane are underway and a similar study for phenol has been started.

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

Goal: The objectives 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 that will allow (a) maximal specific rates and (b) most sustainable rates of cosubstrate oxidation. 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*. These studies have 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. Other chlorinated substrates including chloroform, 1,1-dichloroethylene and 1,2-dichloroethane have been examined to determine the general applicability of the model derived for TCE. $^{14}\text{CO}_2$ uptake experiments have been used to monitor protein synthesis during cometabolism. These studies aim to determine what proportion of cometabolism is due to preexisting and newly synthesized AMO. An investigation of how cometabolism affects the expression of AMO has recently been initiated. TCE-dependent inactivation of AMO activity does not directly correlate with an equivalent loss of catalytically active AMO. This loss of AMO activity profoundly alters the number and type of polypeptides synthesized by the cells in the presence of ammonia. These preliminary studies suggest that the cellular response to TCE toxicity is more complex than the simple replacement of lost enzyme activity.

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 Victoria, 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. A pure culture has been isolated that transfers PCE to cis-1,2-dichloroethylene (c-DCE), and is being characterized. The project is progressing well.

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. This study is now complete.

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

Goal: This project is aimed at (1) revealing the role of the reducing agent in coenzyme-catalyzed transformation of chlorinated hydrocarbons, (2) developing kinetic models describing the systems, (3) elucidating the reaction pathways, and (4) evaluating transformation intermediates and 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 both respects: it may (1) shed light on the fate of these pollutants *in vivo* and/or the cometabolic processes in microbial systems; (2) provide information for the development of novel remediation technologies. The mechanisms of organohalide transformation involving metallocofactors in media containing an excess reducing agent are not yet resolved. In addition, the type and strength of the reductant have been shown to significantly impact cofactor reactivity, pollutant degradation rate, and product distribution, but the effects and causes are not well-characterized.

Approach: This project entails kinetic studies of the transformation of carbon tetrachloride (CTET) by metallocoenzymes which are reduced either by a thio-reductant (cysteine or dithiothreitol) or titanium(III) citrate. Experiments are conducted in homogeneous aqueous solutions containing reductant (in excess) and a cofactor, either hematin or vitamin B₁₂. Kinetic experiments are conducted at room temperature under light-excluded, anaerobic, and abiotic conditions. The disappearance of CTET and the appearance of products, primarily chloroform and carbon monoxide, are measured as a function of pH. Radiolabeled ¹⁴CCl₄ was used to evaluate mass balances.

Status: The transformation of CTET by reduced vitamin B₁₂ or hematin in cysteine solution has been studied over a wide range of pH. Rapid transformation was observed at pH ≥ 8 with the highest transformation rates occurring at pH 11.5 and 9.5 with B₁₂ and hematin, respectively. Most of the transformation products were water-soluble and only two volatile products, CHCl₃ and CO, were identified. In all cases, the total volatile products accounted for less than 30% of the mass balance. In cysteine solution, a kinetic transition due to deactivation of the cofactor was observed in both coenzyme systems. As in the case of titanium(III) citrate, hematin exhibited a more significant deactivation than vitamin B₁₂. The reduction of B₁₂ to B_{12r} was found to be the rate-limiting step and the pentacoordinated cob(II)alamin-cysteine thiolate complex is hypothesized to be the species reacting with CTET. This project is expected to be completed in March, 1995.

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, Joseph M. Suflita and Ralph S. Tanner, 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) evaluate different reductant/metallocoenzyme systems with respect to their ability to dehalogenate halogenated aliphatics.

Rationale: Both microbial and abiotic dehalogenation methods can be used to degrade chloroaliphatics. This project examined whether the two methods could be combined to obtain an overall superior process.

Dehalogenation by Metallocoenzymes and Zero-Valent Iron Powder (Stanford University):

Approach: Transformation by iron(0) powder was one of the abiotic dehalogenation methods that was evaluated. Iron(0) was chosen because it is reactive towards PCE as well as a range of substrates without the involvement of porphyrin. The reaction variables that were studied included temperature and pH. Once the PCE system is understood, other chlorinated substrates will be tested. Metallocoenzymes studied include Vitamin B₁₂, which has a cobalt center, and hematin, which has an iron center. Soluble bulk reductants used were titanium (III) citrate, dithiothreitol, and cysteine. The most promising reaction systems will be further evaluated in combination with immobilized porphyrins (U. of Tulsa) and in biological cultures (U. of Oklahoma).

Status: Efforts are ongoing to understand the role of iron, a potential bulk reducing agent for porphyrin systems, in the transformation of PCE. PCE is converted by iron to ethene and ethane which typically account for about 15-30% of the mass balance. Trichloroethylene is observed as a reactive intermediate whose maximum concentration is less than about 2% of the initial PCE concentration. The possibility that the reactivity of iron towards PCE is due to the nature of the buffer and the type of water used needs further investigation. The project was suspended in October 1994 due to a lack of funds.

Transformation Reactions of Immobilized Porphyrins (Tulsa University):

Approach: After conducting batch experiments to evaluate reaction conditions with different reductants, fixed-bed reactors with immobilized cyanocobalamin were tested for their efficacy to remove PCE from water.

Status: By using vitamin B₁₂, PCE was converted to trichloroethylene and a mixture of cis- and trans-isomers of 1,2-dichloroethylene. 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. 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 has been immobilized in an investigation of PCE dechlorination in a packed-bed reactor using Duolite S-761 as the solid support. With citrate as the reductant, PCE (0.18 mM) conversion was 55% at residence times of 1.75 and 3.5 h. The product distribution was 94% TCE and 6% DCE at the lower residence time. DCE formation increased to 45% at the higher residence time. The subcontract was completed October 1994.

Effect of Reduced Porphyrins on Anaerobic Culture Performance (University of Oklahoma):

Approach: Whole cell suspensions of *Desulfomonile tidjie*, a PCE-dehalogenating bacterium, were incubated with and without vitamin B₁₂ amendments under a range of conditions. Different sulfur reductants including cysteine, hydrogen sulfide and DTT were used.

Status: The rates of dehalogenation in the cell suspensions were the same as those without B₁₂. This was true with many different experimental conditions, including different experimental conditions, the presence of different reductants, and different concentrations of cysteine-sulfide. Abiotic dehalogenation of PCE in the presence of B₁₂ was not observed. The preliminary data indicate that *D. tidjie* was dehalogenating chlorinated alkenes at a faster rates than organisms that contain high levels of corrin factors. Possible failure to stimulate dehalogenation may be related to membrane permeability problems associated with the use of whole cells, the kind of reductant used, and the concentrations of B₁₂ reductants used. This subcontract was completed October 1994.

Moffett Field In-Situ Bioremediation Study in Support of Full Scale Application: Perry L. McCarty, Gary D. Hopkins, 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 a 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 complements the full-scale study by providing these necessary data.

Approach: Recent studies conducted 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 full scale. These tasks are: (1) to evaluate if a CAH degrading population similar to that found at Moffett Field 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: Laboratory microcosm studies of cores taken from the demonstration site at Edwards AFB (see the companion project titled Full-Scale Evaluation of In-Situ Bioremediation of Chlorinated Solvent Groundwater Contamination) have shown that the microorganisms at the site are capable of aerobically cometabolizing TCE in the presence of either phenol or toluene. From studies at Moffett Field, it was seen that the presence of 1,1-DCE seriously reduced the effectiveness of oxidative biodegradation of TCE, probably due to 1,1-DCE transformation product toxicity. Therefore, one of the selection criteria that was used in choosing Edwards as the demonstration site was that 1,1-DCE not be present as a co-contaminant. Toluene was shown to be as effective as phenol for cometabolism of CAHs, and due to regulatory considerations, will be used for the full-scale demonstration. Hydrogen peroxide, which was found to be a suitable alternative to pure oxygen as a source of oxygen for in-situ biodegradation, will also be used in the full-scale demonstration. Based on the Moffett Field results, the plan at Edwards to demonstrate in-situ aerobic cometabolism of TCE is to pulse in a primary substrate, toluene, while continuously adding hydrogen peroxide as an oxygen source.

AROMATICS

In Situ Biological Treatment of Aromatics in Groundwater: Martin Reinhard, Stanford University (Supported by the U. S. Navy and Chevron Research and Technology Company)

Goal: 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 intrinsic or enhanced bioremediation of gasoline contaminated field sites.

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 ferric iron. The potential for transformation of these compounds under field conditions using these alternate electron acceptors and the rate of such transformations has not 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 in a field scale injection experiment at a gasoline-contaminated aquifer at the

Seal Beach site in Southern California. Controlled release experiments were conducted whereby approximately 1000 L of treated water that was amended with tracer and nitrate or sulfate as the electron acceptor and controlled amounts of benzene, toluene, ethylbenzenes and m- and o-xylene isomers. 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 with Seal Beach sediment as the inoculum, benzene, toluene, p-, m- and o-xylene, have been biotransformed under sulfate reducing conditions. Benzene is mineralized the slowest and only if the other BTEX compounds are removed first. Toluene, ethylbenzene, and m-xylene but not benzene were transformed under anoxic, denitrifying conditions. 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. Three controlled BTEX release injection experiments were conducted to test BTEX transformation in situ. Removal was slow in the absence of nitrate but, when nitrate was added, significant reduction in all the BTEX aromatics was observed. Under denitrification conditions, transformation was complete within 8 days for toluene, ethylbenzene, and m-xylene and within 75 days for o-xylene whereas benzene removal was not observed. Under sulfate-reducing conditions, toluene, m- and o-xylene were transformed and completely removed over a period of 40 to 50 days, whereas benzene and ethylbenzene removal was not observed over a period of 80 days. Taking laboratory and field evidence together, the data indicate that the potential exists for all BTEX compounds to degrade in-situ if appropriate conditions are maintained.

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

Goal: The goal 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. The isolation of a pure sulfidogenic, toluene-degrading culture is an objective that would facilitate the study of these processes.

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. This required initial investigations with gas chromatography-mass spectrometry to identify metabolites of toluene degradation. Serial dilutions with toluene in liquid medium were used to isolate a toluene-degrading bacterium from enrichment cultures.

Status: Experiments with mixed enrichment cultures that compared the effects of adding ferrous sulfate vs. zinc sulfate 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 benzoate, a transient intermediate of toluene degradation. Over the past year, a novel sulfate-reducing, toluene-degrading organism, strain PRTOL1, was isolated from the enrichment cultures. Characterization of this organism is being conducted. Mineralization of toluene to CO₂ by strain PRTOL1 has been demonstrated with radiolabeled toluene, and the stoichiometry of sulfate consumed relative to toluene consumed has been shown to be consistent with theoretical predictions. Benzylsuccinic acid and benzylfumaric acid, two dead-end metabolites that were identified as minor products of toluene degradation in the enrichment cultures, are also produced by strain PRTOL1. The ability of strain PRTOL1 to utilize a range of electron donors and acceptors has been tested using cell suspensions. The 16S rRNA gene sequence of strain PRTOL1, which was analyzed at Michigan State University, has shown that PRTOL1 is indeed a novel bacterium. This project will be completed in February 1995.

Biotransformation of Ordnance Wastes Using Unique Consortia of Anaerobic Bacteria: A. Morrie Craig, Oregon State University

Goal: Trinitrotoluene (TNT) is a toxic munitions pollutant which contaminates more than 1400 U.S. military facilities. We would like 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: Recent GC/MS experiments have identified aniline and other deaminated compounds. This evidence indicates that our biological systems 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, our 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, we have discovered a consortium of bacteria, 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 G.8 isolate was capable of reducing the TNT nitro group to an amino group and was also involved in deamination as a co-metabolite, resulting in nitrogen free compounds such as toluene or o-cresol. Our results support co-metabolic transformation. The reduction (deamination) and oxidation (hydroxylation) reactions took place simultaneously when the amino group was present. The patterns of TNT metabolite transformation were dependent upon the type of electron acceptors. The presence of nitrates in the medium stimulated the reduction of para-positioned nitro groups, and nitrites stimulated the deamination and hydroxylation processes. The absence of such primary energy sources as nitrates or nitrites stimulated the reduction of the ortho-positioned nitro groups. An appropriately designed sequencing reactor system, or other alternatives to control such energy sources as nitrates, or nitrites in the TNT degradation system, might result in full transformation of TNT to o-cresol or toluene. Though the full transformation of TNT was not achieved from the experimental processes described, it is promising that clear pathways and limiting factors were identified for the degradation of TNT.

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 redox potential, or EH, of the reaction medium.

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 various, controlled environmental conditions. A model anaerobic system fed acetate, pentachlorophenol (PCP), and nutrients has been selected for study.

Status: A reactor system was developed to control and/or monitor pH, apparent oxidation-reduction potential, and acetate, biomass, sulfate, and sulfide concentrations. An additional platinum electrode has been added to monitor apparent redox measurements and to help identify possible poisoning of the controlling platinum electrode. Both hydrogen peroxide and potassium ferricyanide have been used to raise and control the apparent redox potential above the “natural” system potential of -250 to -260 mV, and both titanium citrate and hydrogen have been used to lower the apparent redox potential. Pentachlorophenol dechlorination has been modeled as first order with respect to PCP concentration. When multiple PCP additions are made, without manipulating redox potential, the rate of dechlorination has been observed to increase with the number of PCP additions. This suggests either induction of enzyme(s) or growth of a sub-population responsible for dechlorination. Overall biomass concentration changes relatively little during a typical experiment. The trend of increasing dechlorination rate with multiple PCP additions has been shown to persist during “mild” redox potential increases of 50 to 150 mV. However, dramatically decreased dechlorination rates have been measured during 250 mV perturbations. PCP dechlorination continues at elevated redox potentials that essentially halt acetate consumption and methane production, lending support to the hypothesis of a separate dechlorinating sub-population.

HEAVY METALS

Incorporation of Nickel in a Ceramic Matrix - A Method for Treatment and Disposal of Heavy Metal Containing Wastes: James Leckie and George Redden, Stanford University

Goal: Ceramic material is proposed as a method for incorporating toxic heavy metals in a solid form that has structural integrity and is resistant to chemical degradation and leaching. This project is exploring the conditions under which nickel can be bound in a ceramic matrix using pure and industrial grade kaolinite. The intent is to determine optimal conditions for producing a ceramic material from nickel contaminated clay that effectively resists leaching of the metal under acidic conditions, and to determine the mechanism by which the nickel is bound in the solid matrix.

Rationale: Although the cost of materials and energy is high when compared to other treatment methods, there are several distinct compensating advantages to this approach: 1) It is possible to treat metal containing wastes on site and produce a material that is not classified as a hazardous waste, thus reducing regulatory problems and off-site transportation/disposal costs, 2) The ceramic product is significantly lighter than the liquid containing wastes (further reducing transportation costs), 3) The ceramic product is marketable for a number of applications such as light weight filler for concrete, and 4) The incorporated heavy metals may be more resistant to leaching than in other matrices thus making release to the environment following disposal less likely. The mechanism by which the ceramic matrix isolates heavy metals is not known. Two

possibilities are chemical bonding in the alumino-silicate matrix, and encapsulation of metal oxides, carbonates, etc. Finding optimum conditions for producing heavy metal containing ceramics is dependent on this information.

Approach: Using a bench top furnace, kaolinite clay mixed with nickel containing solutions are being sintered under a range of relevant conditions to produce ceramic pellets. The pellets are characterized for mineral and chemical content, ground, and exposed to acidic leaching conditions (consistent with EPA standard tests) to determine the rate and extent of nickel extraction as functions of surface parameters. Solution and solid data is collected to determine the extent of solid dissolution, changes in surface chemical composition, and to distinguish between solute adsorption and leaching from solid phase(s). Scanning Electron Microscopy and X-ray Photoelectron Spectroscopy will be used to verify or analyze changes in surface structure and composition.

Status: The first series of extraction experiments have been completed. The effect of sintering on reducing nickel extractability under acidic conditions has been clearly demonstrated. The full range of solution parameters and nickel mass balance is currently being determined. XRD analysis has shown the effect is the conversion of kaolinite to nickel containing mullite and possibly other mineral phases. The study will focus first on fully characterizing the first series of materials and extraction products, including spectroscopic analysis, to determine the state of nickel in the Al-Si oxide matrix before proceeding to expanding and optimizing the conditions of ceramic production.

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 our 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. Data from both batch and soil column studies will be used in computer modeling studies to simulate the effects of changing environmental conditions on lead mobility.

Status: A chemical equilibrium computer program (HYDRAQL) was calibrated for Pb chemistry in soil including the effects of adsorption (surface complexation model) using hydrous ferric oxides (HFO) as a surrogate for the active soil sorbing phase and model organic compounds to simulate natural organic ligands. The primary factors affecting the mobility of lead were predicted to be pH and surface site (HFO) concentration. Batch laboratory experiments using hydrous-ferric-oxide-coated sand to represent the soil sorbing surface are generally in good agreement with the computer model simulations of the factors affecting lead mobility. Soil column experiments have been initiated with the sorbing phase used in batch experiments (HFO). Further experiments are planned to further investigate the effect of EDTA and soil organic matter on lead mobility.

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 fourteen 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 1994-95.

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. Six persons have received certificates 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 1994 Idaho Regional Conference on Hazardous Materials, Pocatello, Idaho, April, 1994.

The 1994 Responsible Hazardous Materials Management Conference, Portland, Oregon, September, 1994.

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 Dichloroprop. 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: Laboratory studies using contaminated soils have been completed. The studies demonstrated that elevated temperatures of above 30° C would be required to obtain remediation of the stored soils. Carbon additions of about 200 mg C/L would be required to maintain anaerobic conditions. Under fully anaerobic conditions, the laboratory results suggest that all four of the herbicides will degrade. Field studies have been initiated using sucrose (250 mg/L) as the carbon source. One field container has been fully flooded and the degradation of the herbicides is being monitored versus time. If the carbon is depleted, a feed solution will be recirculated.

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 without bringing the water to the ground surface. Theoretical work was carried out previously at Stanford. Current effort is focused upon pilot scale field demonstration at a new site: Edwards Air Force Base (AFB) near Lancaster, California, where groundwater is contaminated with trichloroethylene. Attention is also focused upon the U. S. Department of Energy Hanford site in Richland, Washington, where groundwater is contaminated with carbon tetrachloride. The demonstrations will provide valuable information regarding the efficacy of the in-situ VOC removal system at 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. Recirculation of groundwater is accomplished via air-lift pumping. 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 to the surface for treatment is avoided. There is no need for a surface air-stripping tower. 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 in-situ VOC removal system is proposed for demonstration at Edwards Air Force Base and the Hanford Site. The demonstration unit at each site will consist of a single VOC-removal well and several monitoring wells. The overall approach to the demonstrations will be to conduct 3 month initial tests. 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 laboratory mockup of the in-well stripping process was tested from May to September 1994. Model predictions about the type of flow observed and stripping efficiency at selected air injection and water pumping rates were confirmed. Rapid progress has been made at Edwards AFB. Two monitoring wells were installed in September. Aquifer testing was conducted in October and November. Installation of the pilot demonstration well and several additional monitoring wells will follow. The pilot demonstration well was to be completed in late summer of 1994, but the well casing was damaged during installation. A new pilot well is being installed. Numerical simulation of groundwater flow and VOC removal has been performed for each site. Subsequent models will incorporate subsurface information obtained from additional borings and tracer test analyses.

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

Goal: To evaluate at full scale the efficiency and effectiveness of in-situ aerobic cometabolic 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 researchers at the Moffett Field pilot 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. The proposed remediation system will consist of two wells, each screened at two depths. In operation, a submersible pump, installed between the two screens, will draw water into the well at one screened interval and discharge the water out of the second screened interval. The well will have feed lines to introduce toluene and hydrogen peroxide (as a source of oxygen) into the discharge water. A biotransformation zone will be developed near the discharge side of each well, and the water will circulate between the wells to clean the aquifer.

Status: A TCE-contaminated site at Edwards AFB has been selected for this demonstration. Characterization (chemical, microbiological, and hydrogeological) and modeling of the site has commenced. Laboratory microcosm studies of cores taken from the demonstration site have shown that the microorganisms present are capable of aerobically cometabolizing TCE in the presence of either phenol or toluene (see the companion project titled Moffett Field In-Situ Bioremediation Study in Support of Full Scale Application). A work plan is in preparation and discussions with base and regulatory personnel, as well as community groups, are ongoing, in order to obtain approval to proceed with the full-scale demonstration.

Evaluation of Strategies for Full Scale Bioremediation of the Seal Beach Site Using Anaerobic Microbial Processes: Martin Reinhard, Gary Hopkins, and Peter Kitanidis, Stanford University

Goal: The goal of this project is to develop a plan for the remediation of the Seal Beach gasoline site using anaerobic microbial processes. Specifically, we are developing a hydraulic and process model for large-scale implementation of the processes we have been investigating in the laboratory, in pilot reactors and on a small field scale. By the end of this project year (September 1995) we will recommend a strategy for cleaning up large sections of the site based on the results of the field and laboratory studies and hydraulic modeling.

Rationale: Field and laboratory work has indicated that BTEX contamination can be removed biologically under anaerobic conditions using different electron acceptors or acceptor combinations. We have studied in detail nitrate- and sulfate-reducing and methanogenic conditions. All these conditions appear to have specific advantages and disadvantages and it

appears that a combination of conditions could yield the best result. It is not clear, however, which of the possible electron acceptor combination should be chosen.

Approach: The approach has been to simulate different treatment options by releasing controlled amounts of BTEX compounds into a small test zone of the aquifer. The BTEX compounds were added to approximately 1000 L of water to which was added nitrate, sulfate, or carbonate salts as the electron acceptor. The water was then removed from the test zone in small batches and analyzed for BTEX compounds and nitrate and sulfate. Laboratory experiments were also conducted to explore the factors that affect BTEX degradation rate under anaerobic conditions.

Status: Two sets of replicate release demonstrations under nitrate- (EO4 and EO5) and sulfate-reducing conditions (EO6 and EO7) have been completed and the first under methanogenic conditions (EO8) is ongoing. Under denitrifying-conditions toluene, m-xylene, and ethylbenzene were found to be rapidly degraded (within days) while o-xylene was degraded at a slower rate. The rate of benzene degradation was much slower but appeared to be significant. To evaluate the results of the controlled release demonstrations, a two-dimensional model for solute transport was developed and tested. The model is now being used to evaluate the aromatic degradation rate observed in the controlled release experiments and will serve as a basis for large scale implementation of the technology. Current efforts focus on the development of kinetic models to characterize contaminant transformation under various anaerobic conditions and to incorporate these kinetic models into the large-scale model. The next step will be to use the large-scale models for the design and interpretation of intermediate-scale controlled release experiments planned for the 1995/6 project year. For the longer term, we will proceed to develop a model more advanced than existing models and well-adjusted to represent the in-situ biodegradation of fuels in groundwater.

1994 WRHSRC PUBLICATIONS

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

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B. Articles Submitted or in Press

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- Beller, H.R. and M. Reinhard, "The Role of Iron in Enhancing Anaerobic Toluene Degradation in Sulfate-Reducing Enrichment Cultures," *Microbial Ecology*, in press, 1995.
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- Reinhard, M., Shang, S.B., Kitanidis, P.K., Orwin, E., and Hopkins, G.D., (Stanford University), C. LeBron (NFESC), "Intrinsic and Nitrate Enhanced BTEX Biotransformation," submitted 1994.

C. Chapters in Other Books or Bound Proceedings

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