



**WESTERN REGION
HAZARDOUS SUBSTANCE RESEARCH CENTER**

1997 ANNUAL REPORT

Stanford University
Oregon State University

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1997 ANNUAL REPORT**

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WESTERN REGION HAZARDOUS SUBSTANCE RESEARCH CENTER 1997 ANNUAL REPORT

ADMINISTRATION

Perry L. McCarty
Director, WRHSRC
Department of Civil Engineering
Stanford University
Stanford, CA 94305-4020
Telephone: (650) 723-4131
FAX: (650) 725-9474
E-mail: mccarty@ce.stanford.edu

Kenneth J. Williamson
Director, Training and Technology Transfer
Department of Civil Engineering
Oregon State University
Corvallis, OR 97331
Telephone: (541) 737-6836
FAX: (541) 737-3099
E-mail: williamk@ccmail.orst.edu

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 22 faculty and 4 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 (civil engineering, engineering, science, earth sciences, medicine, and veterinary medicine), and many different disciplines (chemical engineering,

chemistry, hydrogeology, hydrology, medicine, microbiology, and petroleum engineering). 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. Martin Reinhard, the Assistant Director, is in charge of the Center's analytical program. 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. Martin Blunt	Prof. Daniel J. Arp
Prof. Mark N. Goltz ^a	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. John S. Selker
Prof. James O. Leckie	Prof. Lewis Semprini
Prof. Keith Loague	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	
Prof. Alfred M. Spormann	

^aCurrently with the Air Force Institute of Technology, Dayton, Ohio, but still active with the WRHSRC

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 1997 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>
Linda M. Abriola	University of Michigan	Physical Processes, Hydrology
Douglas R. Christensen	Jacobs Engineering	Engineering
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 Hoeppe	Govt/U.S. Navy	Microbiology
Michael C. Kavanaugh*	Malcolm Pirnie	Physical/Chemical Processes
Richard G. Luthy	Carnegie Mellon University	Chemical/Biological Processes
Stephen Schmelling	Govt/EPA, Ada Lab	Groundwater Remediation

James M. Tiedje
John L. Wilson†
John Wise
*Chairman
†Vice Chairman

Michigan State University
New Mexico Technical University
Govt/EPA, Region 9

Microbiology
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
Jerry Jones	Govt/EPA, Kerr Lab.	Groundwater Remediation
David Kennedy*	Kennedy/Jenks Consultants	Treatment Technology
Jon Kindschy	Univ. California Ext. Service	Hazardous Substances Training
Gregory Peterson	Peterson Process Engineering	Treatment Technology
Winona Victory	Govt/EPA, Region 9	Training/Tech Transfer

*Chairman

Table 4. CENTER FUNDING

<u>Funding Sources</u>	<u>FY 1997*</u>	<u>Funds to Date</u>
EPA: Centers Program	\$75,000	\$8,928,015
EPA: Other	0	\$2,950,816
Other Govt: Federal†	0	\$7,310,195
Other Govt: State@	0	\$48,252
Consortium	13,750	\$3,116,604
Private Sector#	<u>\$5,000</u>	<u>\$2,142,452</u>
TOTAL	\$93,750	\$24,496,334

*Oct. 1, 1996 - Sept. 30, 1997

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

#Aluminum Company of America, Allied Signal Corporation; BMG Engineering AG; Brown and Caldwell; CH2M HILL; Chevron; DuPont Chemicals; Electric Power Research Institute; Gas Research Institute; Hewlett-Packard Company; Metcalf&Eddy; Monsanto Company; Montgomery Watson, Inc.; Kennedy/Jenks; Kleinfelder, Inc.; McLaren/Hart; Monsanto; Orange County Water District; Schlumberger Technologies; Shell Development Corporation, Woodward-Clyde Corporation

TABLE 5. STUDENT SUPPORT

<u>Student Support</u>	<u>Number*</u>	<u>Funds to Date†</u>
B.S.	13	\$95,877
M.S.	35	\$963,777
Ph.D.	100	\$4,800,802

Post Doctoral	<u>24</u>	<u>\$1,506,203</u>
TOTAL	172	\$7,366,659

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

†Includes tuition, travel, supplies, etc.

DIRECTOR'S REPORT

This past year marked the completion of the ninth year of WRHSRC activity, and this also marked the end of the second project period for the Center. During this year, minimal funds were received for this completion, but the research program was nevertheless very active through use of funds received at the end of the previous fiscal year. This year a new proposal was prepared to begin a third project period. Such continuation required a site visit by an external peer review committee. The peer review committee visited the Center over a two day period to review plans and progress to date. They provided a very strong endorsement for both the research and the training and technology transfer activities of the WRHSRC and recommended full funding for a third project period. Such funding was received at the end of the fiscal year, so that next year the funding level will be seen to rise back to a normal level.

During this past year, the Center faculty and research staff essentially completed the 23 separate research projects remaining from the second project period. Eleven of these projects were supported through the Research and Re-Education for Department of Defense (R2D2) program. An additional five research projects were ongoing at minority academic institutions (MAI) through sponsorship by the WRHSRC with financial support for this purpose from the U.S. EPA. As in the past, all WRHSRC 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.

The other significant phase of WRHSRC activities is the Training and Technology Transfer (TTT) program. The six field demonstration projects that got underway during the second project period have also been completed. Two of these at Edwards Air Force Base (in-situ cometabolic degradation of TCE and in-situ vapor stripping of TCE) were supported by the U.S. Air Force with additional support for the vapor stripping project from the U.S. DOE. Another project on in-situ biodegradation of petroleum hydrocarbon at Seal Beach Naval Weapons Laboratory received support from the U.S. Department of Navy. This project is continuing, but with funds received outside of the Center. Thus, it is no longer considered a Center project. This is true of several projects now being conducted by Center faculty. The integrated team approach to solution of complex environmental problems that was fostered by the Center is providing benefits to the Center faculty who are now able to receive funding for hazardous substance research outside of the Center itself.

Another major TTT project that has been ongoing for three years is the Technical Outreach Services for Communities (TOSC) program to aid communities impacted by hazardous waste problems. Many communities within the EPA Region 9 and 10 states have benefited from the

independent review and assistance that the WRHSRC has provided when requested to do so. In addition, the TTT function of the Center continues to include sponsorship of conferences and sessions concerned with hazardous waste remediation.

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 hydrogeology 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 biotically and also 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 (intrinsic bioremediation or natural attenuation) 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 and PCBs) is directed toward predictions of transformation potential and transformation rates, the determination of transformation products, the biochemistry and genetics of the processes involved, 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 and to successfully monitor the process. 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.

HIGHLIGHTS OF THE YEAR

One of the highlights for the year was the successful completion of the first two project periods for the WRHSRC, and the high praise provided by the external review panel appointed by EPA to review the past activities and future plans of the WRHSRC in conjunction with its renewal proposal. The panel commended the highly successful interactions between Center faculty in addressing the highly complex physical, chemical, and biological processes occurring in groundwater, as well as the number and high quality of major research and demonstration accomplishments. Their report has provided us with renewed enthusiasm for both the research and the training and technology transfer activities of the Center.

Another major highlight of this year was the completion of the first full-scale evaluation of in situ cometabolic biodegradation of trichloroethylene (TCE) in groundwater. This was accomplished through the injection into groundwater of toluene, hydrogen peroxide, and oxygen at a Superfund site at Edward's Air Force Base in southern California. Organisms that oxidize the toluene produce an enzyme (toluene ortho monooxygenase) that fortuitively degrades TCE. The novel system used does not require that any groundwater be brought to the surface, TCE is biodegraded in situ. This rather simple treatment system involves two wells with pumps that cause the groundwater to circulate between them so that the chemicals required can be added, mixed with the contaminants, and then introduced back into the aquifer for in situ biodegradation. This led to the degradation of 97 to 98% of the 1200 µg/l of TCE in the 60 to 80 m wide plume of regional flow that was caused to pass through this treatment system. This system has now been piloted at an industrial site and found to be successful there, and is under active consideration as the preferred treatment alternative for that site. Detailed results of the Edwards' demonstration are to be reported in the January 1998 issue of *Environmental Science and Technology*.

The Edwards' demonstration represents the culmination of basic laboratory and field experimental work conducted during the nine years of WRHSRC activity. Twenty-three faculty and staff members, not only from Stanford and Oregon State, but also from Michigan State University, the University of Western Florida, and the University of Minnesota, together with 30 graduate students participated in this research. To date there have been 50 WRHSRC sponsored journal publications, 14 conference reports, 7 book chapters, 13 doctoral dissertations, and 3 patents issued that are related to this technology. The full scale demonstration required support and administrative approvals from a variety of agencies, including the U.S. EPA Region IX, California EPA, the Lahonton Regional Water Quality Control Board, and the U.S. Air Force. The site demonstration itself was financially supported by the Armstrong Laboratory Environics Directorate, Tyndall Air Force Base, the Headquarters U.S. Air Force Environmental Quality Division, and Woodward-Clyde Consultants. Technical

support for construction and operation of the demonstration site was provided by EarthTech, and support for all phases was provided by the Edwards Air Force Base.

The many other activities of the Center are indicated in the summary of research listed in the following and the publications resulting from Center research reported at the end of this report.

FUTURE DIRECTIONS

The WRHSRC plans to continue 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 extensive, 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. The several field demonstration projects that have been conducted through Center activity represent the applications of findings from the several basic research projects that the WRHSRC has been conducting since its inception in 1989. The field demonstrations not only represent the best way to transfer the results of our basic research to show how they apply in practice, but also, the field demonstrations will undoubtedly uncover difficulties in implementation that will require basic research studies for best resolution. Thus, we anticipate that future basic research studies will result largely from our demonstration experiences. We also anticipate that with success in the field, we will be called upon with greater frequency by the engineering community to assist them in implementing our findings on a broader scale. This we must be prepared to do and will put some of our future efforts in this direction.

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			
Three-phase Flow in Fractured Media	Martin Blunt and Paul Roberts	1997	\$302,449
Physics of Dissolution of Nonaqueous Phase Liquids: Pore Networks and Field Simulations	Steven M. Gorelick	1997	\$159,610
Modeling VOC Emissions from Hazardous Waste Sites	Lynn M. Hildemann	1997	\$166,507

Upscaling Pore-Scale Hydrodynamics and the Transport of Reactive Solutes	Peter K. Kitanidis	1997	\$159,709
Effects of Redox Zones on the Fate and Transport of Contaminants in the Saturated Subsurface; Characterization and Simulation	Keith Loague	1997	\$121,422
The “Bubble Wall”: A Passive In Situ System for Treatment and/or Containment of Contaminated Groundwater	J.D. Istok, V.A. Fry, J.S. Selker, and S.M. Gorelick	1997	\$297,685
Redox Transformations of Organic and Inorganic Contaminants in the Subsurface Environment	John C. Westall and James D. Ingle	1997	\$117,804
Hydrocarbon and Biological Factors Affecting Aquifer Clogging During In-Situ Bioremediation	Perry L. McCarty	1997	\$190,883

Chlorinated Solvents

Reductive Transformation of Chlorinated Hydrocarbons by Reduced Ethenes Catalyzed by Vitamin B ₁₂ --Mechanistic and Kinetic Studies	Martin Reinhard	1997	\$178,567
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<u>Project Description</u>	<u>Principal Investigators</u>	<u>End Date</u>	<u>Total Budget</u>
Inhibition, Inactivation and Recovery: A Universal Model for Aerobic Comatabolic Degradation of Aliphatic Compounds	Daniel Arp, Michael Hyman, and Ken Williamson	1997	\$168,097
An Investigation of the Chlorinated Hydrocarbon Substrate Range of the Filamentous Fungus, <i>Graphium</i> sp.	Michael Hyman	1997	\$24,045

Aerobic Cometabolism of Chloroform, 1,1,1-trichloroethane, 1,1-dichloroethylene, and Other Chlorinated Aliphatic Hydrocarbons by Microbes Grown on Butane and Propane	Lewis Semprini and Daniel J. Arp	1997	\$234,502
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Mechanisms, Chemistry, and Kinetics of Anaerobic Biodegradation of cDCE and Vinyl Chloride	Perry L. McCarty and Alfred Spormann	1999	\$300,000
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Biochemical Mechanisms of PCE Dehalogenation by Strain MS-1, and its Potential for In-Situ Bioaugmentation	Pramod K. Sharma and Perry L. McCarty	1997	\$337,323
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Aromatic Compounds

Pathways of Anaerobic Toluene Metabolism by a Sulfate-Reducing Bacterium, Strain PRTOL1	Alfred M. Spormann	1997	\$189,616
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Anaerobic Ethylbenzene Oxidation in Denitrifying Strain EB1	Alfred M. Spormann	1997	\$151,585
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Development of a Vitamin B ₁₂ -Amended Bioremediation Process for the Reductive Dechlorination of Chlorobiphenyls at all Chlorine Positions	Sandra Woods	1997	\$144,357
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Heavy Metals

Development, Characterization, and Performance Evaluation of Ferrous-Ferric Oxide Adsorbents for Metal Removal from Contaminated Groundwater	Peter O. Nelson	1997	\$111,668
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Trace Element Adsorption in Porous Particle Packed Beds	James O. Leckie	1997	\$169,871
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<u>Project Description</u>	<u>Principal Investigators</u>	<u>End Date</u>	<u>Total Budget</u>
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Minority Academic Institution Projects

Probing the Redox Properties of Environmental Systems: Natural Phenolic Materials	Robin Helburn Northern Arizona University	1997	\$ 70,357
Detection of Microorganisms Capable of Anaerobic Degradation of Hazardous Substances in Natural Environments	Sara E. Silverstone California St. Univ., Bakersfield/State U. of New York	1997	\$111,405

TRAINING AND TECHNOLOGY TRANSFER PROGRAM SUMMARY

Demonstration Projects

Field Test of In-Situ Vapor Stripping for Removal of VOCS from Groundwater	Steven M. Gorelick	1997	\$641,709
Field Testing of Palladium-Catalyzed Hydrodehalogenation for Chlorinated Hydrocarbon Removal from Groundwater	Martin Reinhard and Paul V. Roberts	1997	\$321,149
Full-Scale Evaluation of <i>In Situ</i> Bioremediation of Chlorinated Solvent Groundwater Contamination	Perry L. McCarty, Mark N. Goltz, and Gary D. Hopkins	1997	\$611,061
Demonstration of an Interceptor Trench Technology for the Bioremediation of a Pentachlorophenol-Contaminated Ground Water	Sandra Woods	1997	\$284,800

Training and Technology Transfer Projects

Hazardous Waste Training	Kenneth J. Williamson Peter O. Nelson	1997	\$120,000
Continuing Education	Kenneth J. Williamson	1997	\$120,000
Conference Sponsorship	Kenneth J. Williamson	1997	\$120,000

Technical Outreach Services for
Communities

Kenneth J.
Williamson

1997

\$562,500

RESEARCH PROJECT DESCRIPTIONS

CHEMICAL MOVEMENT, FATE, AND TREATMENT

Three-phase Flow in Fractured Media: Martin Blunt and Paul Roberts, Stanford University (Supported by R2D2 Program)

Goal: To obtain a validated understanding of three-phase flow behavior of immiscible organic liquids (NAPLs) in fractured media, with particular application to steam injection. The project is oriented towards the study of steam injection as a remediation alternative both because of its relevance in treating fractured bedrock and low permeability lenses as well as the three-phase nature of steam injection displacements.

Rationale: Many DNAPL spill sites are underlain by fractured aquitards or bedrock. Treatment of such sites with a conventional pump and treat approach is likely to result in a long and costly remediation. Steam injection is an alternative clean-up option for such sites. However, our understanding of three-phase flow behavior is very incomplete. With this research, we plan to develop a set of relationships between phase saturation and relative permeability and capillary pressure of each phase in fractured media, as well as mass transfer relationships between fracture and matrix, based on our physical understanding of three-phase flow and on the results of visualization experiments both in micromodels and at the core scale using CT scanning.

Approach: Given our previous understanding of the physics of two and three phase flow, which has been captured in a three-dimensional, three phase network model, we have postulated the shape of the relative permeability and capillary pressure curves. The experimental research being carried out in this work seeks to validate the displacement mechanisms predicted for three phase flow, specifically double drainage, double imbibition and flow in thin layers, and the effect of the spreading coefficient on the importance of these mechanisms, by observing them in micromodels which have been etched with a realistic replica of a fractured sandstone matrix. In addition, at the core scale we are seeking to validate the shape of the relative permeability and capillary pressure curves, using CT scanning to determine the phase saturation before, during and after a sequence of displacements, including imbibition, drainage and steam injection.

Status: The shape of the relative permeability and capillary pressure relationships has been predicted by the network model. The micromodel experiments have shown that double drainage exists and is important even for non-spreading NAPLs (such as decane and higher hydrocarbons as well as many chlorinated solvents), and that flow in thin layers is an important mechanism for movement of small amounts of NAPLs in porous and fractured media, even at low NAPL saturations. The CT scanning experiments have been performed with three fractured cores. Analysis of the experiments is complete.

Physics of Dissolution of Nonaqueous Phase Liquids: Pore Networks and Field Simulations: Steven M. Gorelick, Stanford University (Supported by R2D2 Program)

Goal: The objectives of this study are: (1) to contribute to the understanding of interphase mass transfer by using pore network models to investigate NAPL dissolution; (2) to analyze how the rate of dissolution varies with multiphase properties ranging from pore-scale interfacial area to measurable entities such as fluid saturation and concentration; (3) to develop a physically-based relation between dissolution rate and measurable entities that reflects dynamic processes, such as varying interfacial area, fluid saturation, and the mass fraction of soluble species; (4) to enhance a 3-dimensional multiphase compositional simulator to account for nonequilibrium NAPL dissolution; (5) to explore the range of applicability of the local equilibrium assumption at the field scale and determine the impact of kinetically-mediated NAPL dissolution; and (6) to understand the role of intrinsic bioremediation at a NAPL-contaminated site and to investigate its effects in the context of nonequilibrium NAPL dissolution.

Rationale: During remediation of sites contaminated by NAPLs immobile NAPL blobs can serve as a long-term source of contamination as more soluble species partition into the aqueous phase. NAPL dissolution can be a rate-limited process dependent on dynamic pore- and field-scale phenomena. Few numerical models developed for hydrogeological applications exist that are multiphase, multicomponent and three-dimensional, and none of these account for rate-limited dissolution. Furthermore, in model applications involving nonequilibrium dissolution, dissolution rate coefficients are needed as input. The traditional approach has been to estimate these rates using correlation expressions developed from laboratory data. Traditional correlation expressions do not expressly account for dynamic processes, are not transferable to other data, and may not be applicable to field settings. Consequently, the validity of local equilibrium in NAPL dissolution in a realistic field setting is not well-understood.

Approach: This study involves 5 stages: (1) development of a pore network model representative of a real porous media; (2) development of a physically-based NAPL dissolution relation using the pore network model; (3) modification of a 3-dimensional compositional simulator to represent nonequilibrium NAPL dissolution; (4) hypothetical and field-data-based modeling studies investigating the limitations of the local equilibrium assumption on field-scale NAPL dissolution; and (5) an investigation of the feasibility of intrinsic bioremediation in the presence of field-scale factors limiting NAPL dissolution

Status: A pore network model, consisting of a simulated 3D array of pore tubes connected by chambers, was developed to represent the physics of nonequilibrium NAPL dissolution in porous media. Two-phase flow and transport of dissolved NAPL components were represented in the network, as well as local dissolution from the NAPL phase into the surrounding water film and corners. This local dissolution was based on a solution to one-dimensional diffusion equations and is a function of the water velocity in the corner of a NAPL-filled tube or chamber. The network model successfully matches data for laboratory drainage and imbibition, and predicts experimentally determined NAPL blob-size distribution. Furthermore, simulated results of effluent solute concentration are consistent with steady-state column data. A theoretical result of general interest is the determination of a relationship between the NAPL dissolution rate coefficient and Peclet number. Four distinct regimes of this relationship were identified, representing four different physical process controlling dissolution: pore diffusion, mixing and multiple contact, corner diffusion, and a transition zone. Corner diffusion controls NAPL dissolution in the high-Peclet regime, which is characteristic of nonequilibrium NAPL dissolution. Several relationships between NAPL dissolution rate coefficient and Peclet number

were generated for NAPL saturations during drainage and imbibition. These functions can be used to obtain a NAPL dissolution rate coefficients for input in a field-scale simulator for any specified Peclet number and NAPL saturation. The network model is currently being used to investigate the relationship between interfacial area, NAPL saturation, and dissolution rate coefficients .

Modeling VOC Emissions from Hazardous Waste Sites: Lynn M. Hildemann, Stanford University (Supported by R2D2 Program)

Goal: Many potentially toxic volatile organic compounds (VOCs) have been identified in the air downwind of waste disposal sites. An important potential impact of these hazardous emissions is the long-term inhalation exposures experienced by downwind residents. The goal of this project was to develop an integrated emission-dispersion model to evaluate the extent to which these emissions pose a hazard to human health.

Rationale: Because of the high cost of field experiments and the lack of standardized sampling methods, field measurements of airborne emissions from contaminated sites are difficult to obtain. Modeling approaches provide a less-costly alternative to evaluating the potential impacts of VOC emissions from contaminated sites. However, the emissions models currently existing can only be utilized for "screening-level" purposes due to the many fundamental oversimplifications made, which may seriously compromise the accuracy of the predictions. A more accurate approach is needed to reliably estimate the source emissions and to evaluate the risk posed to humans in the near vicinity of the source, as well as further downwind.

Approach: An integrated emission-dispersion model has been developed to predict concentrations of VOCs downwind of a contaminated site, as a function of site conditions and meteorological parameters. The performance of the dispersion model has been evaluated by comparing its predictions with available field measurements. The model can be utilized to predict concentrations downwind of a particular site, allowing the major factors that influence VOC emissions from the site and the subsequent dispersion in the atmosphere to be examined. The predicted concentrations can be compared with typical ambient levels of VOCs and concentration levels for which health effects are known, thereby providing a measure of the extent to which the added emissions contribute to the total airborne burden, and the extent to which these emissions pose a significant hazard to humans living downwind.

Status: A more complete analytical emission model has been developed that can predict VOC emissions from hazardous waste sites. The new model removes the major assumptions/simplifications inherent in the screening-level models, and incorporates most of the important mechanisms occurring in unsaturated subsurface landfill environments. An analytical dispersion model previously developed under WRHSRC sponsorship that accurately represents the dispersion phenomena within the atmospheric boundary layer has undergone further modifications to account for inversions aloft and partial absorption by the ground. An assessment of the performance of this model has recently been completed, in which model predictions in both the downwind and vertical directions were found to compare well with measurements from a published, comprehensive field study.

Upscaling Pore-Scale Hydrodynamics and the Transport of Reactive Solutes: Peter K. Kitanidis, Stanford University

Goal: (a) to improve understanding of hydrodynamics, mass transport, and biochemical reactions at the pore scale and (b) to derive physically valid mathematical representations of processes at the Darcy scale, where the pore details are not resolved. This research project focuses on mathematical analysis but is guided by experiments conducted by Professor McCarty and his co-workers in another project. Among the objectives of this project is to describe the mechanisms that control the growth of biofilms, such as shearing of biofilms at pore necks. A potential practical output of this research would be the derivation of relations between biomass and effective conductivity, dispersivity, and reaction rates in a porous medium with dynamically changing biofilms. Also accounting for sorption and desorption with characteristic times comparable to or slower than those of pore-scale diffusion and reaction.

Rationale: Fundamental understanding of the mechanisms and processes that affect in-situ bioremediation is best at the pore scale. The rates at which subsurface microorganisms transform pollutants is controlled to a great extent by the pore-scale physical mechanisms that supply nutrients and electron acceptors. However, in practice, one makes measurements and attempts to make predictions and assessments at a much larger scale. The most scientific approach is to derive relations among macroscopic variables by scaling up from the pore scale.

Approach: The approach adopted in this project is to study pore-scale hydrodynamics and rates of mass redistribution in detail at the pore scale. Idealized geometrical models of a porous media are used to obtain order of magnitude estimates of variables. Additionally, general methods of scaling up are applied to derive relations among macroscopic variables.

Status: The project started in March 1995 and has now been completed. A finite-element numerical model has been developed for the simulation of flow, transport, and biochemical reactions in pores. The model simulates: The growth of active biomass, the transport and transformation of a soluble electron donor (substrate) and the transport and transformation of a soluble electron acceptor. Using this model the following phenomena have been studied for some two-dimensional pore geometries: pore-scale hydrodynamics; dilution and mixing of solutes at the pore scale; mass transport limitations on reaction rates; and the growth, decay, and possible redistribution of biomass.

Effects of Redox Zones on the Fate and Transport of Contaminants in the Saturated Subsurface; Characterization and Simulation: Keith Loague, Stanford University (Supported by R2D2 Program)

Goal: Redox conditions influence the mobility and toxicity of metal contaminants and our ability to bioremediate organic contaminants. The goal of this project is to establish a physics and chemistry based simulation protocol that will enable us, and future workers, to quantitatively estimate the fate and transport of contaminants that are influenced or controlled by different redox conditions.

Rationale: Groundwater contamination sites are often characterized by a sequence of redox zones. Assessment of many subsurface contaminants depends upon quantitative

characterization of the development and fate of redox zones. The ability to simulate these zones will greatly enhance predictive modeling of the fate of many inorganic and organic contaminants at hazardous waste sites.

Approach: The primary research tool in the proposed effort is coupled numerical simulations of saturated subsurface fluid flow, solute transport, and chemical reactions. The approach for model development and testing in this study is (i) development of a coupled saturated subsurface fluid flow, solute transport, and geochemical models and boundary value problems based upon the massive data for the extensively studied field site located on Cape Cod, MA, (ii) sensitivity analysis for the chemical components/reactions and hydrologic variables essential to the development of a robust model of field-scale phenomena, and (iii) quantitative model performance evaluation based on both statistical and graphical criteria.

Status: The reaction network for redox zones was compartmentalized by focusing on the dominant reactions. The compartmentalized approach allows for a complex geochemical system, as a function of time and energy yield (i.e., Gibbs free energy), to be easily solved. Our method (i) solves the numerical system without evoking a redox parameter, (ii) improves the numerical stability of redox systems by choosing which compartment, and thus which reaction network, to use based upon the concentration ratios of key constituents, (iii) simulates the development of redox zones as a function of time without the use of inhibition factors or switching functions, and (iv) reduces the number of transport equations that need to be solved in space and time. We are currently completing the study by coupling the compartmentalized reaction network model to a two-dimensional solute transport code.

The “Bubble Wall”: A Passive In Situ System for Treatment and/or Containment of Contaminated Groundwater: Jonathan D. Istok, Virginia A. Fry, John S. Selker, Oregon State University, and Steven M. Gorelick, Stanford University

Goal: The objectives of this project are to investigate the use of a “bubble wall” (a zone of trapped gas emplaced within the saturated zone of a groundwater aquifer) (1) to serve as a source of dissolved gas for use in in situ bioremediation or (2) to serve as a flow barrier for use in hydraulic containment.

Rationale: The rate of many microbially mediated reactions of interest in bioremediation is frequently limited by low dissolved gas concentrations (e.g. low dissolved oxygen concentrations often limit the rate of aerobic transformation of petroleum hydrocarbons). For this reason, a wide variety of methods have been proposed for increasing dissolved gas concentrations in contaminant plumes. Unfortunately, most existing methods (e.g., air sparging or the injection of gas amended water) are inefficient because of (1) the small solubility of most gases in groundwater, and (2) the limited degree of mixing that occurs between injected gas or gas enriched water and the contaminated groundwater. The “bubble wall” technology attempts to overcome these difficulties by using a zone or “wall” of trapped gas bubbles as a passive source of dissolved gas to contaminated groundwater flowing through the wall. The presence of trapped gas in the pore space of a bubble wall also reduces the hydraulic conductivity of the aquifer within the wall. This means that it may be possible to use a “bubble wall” as a flow barrier for use in hydraulic containment (e.g., in place of a slurry wall or sheet pile structure).

Approach: The investigation of the “bubble wall” technology is being performed using a combination of theoretical analysis, numerical modeling, and laboratory experiments. Theoretical analysis is used to develop continuum models to describe the mass transfer of gas from the trapped gas to the mobile aqueous phases and pore-scale models to describe the effect of trapped gas on the hydraulic conductivity and dispersivity of the porous media. Numerical models are used to determine the sensitivity of mass transfer to model parameters (e.g. particle size distribution, trapped gas volume, solubility and vapor pressure of dissolved gas, and pore water velocity) and to determine the effect of hydraulic conductivity reduction within a bubble wall on the regional groundwater flow field. Laboratory experiments are performed in one-dimensional columns and two-dimensional, vertical and horizontal physical aquifer models using a variety of porous media. The purpose of the laboratory experiments is to investigate methods for emplacement of trapped gas into saturated porous media to create a bubble wall, to validate models for mass transfer of gas from the bubble wall to groundwater, to determine the effect of trapped gas on hydraulic conductivity, and to validate pore-scale models.

Status: Bubble entrapment was found to be a strong function of the method of entrapment, but can be well understood when viewed in the context of dimensionless variables. Up to 20% of the pore space can be filled with stable gas, reducing permeability by a factor of more than two. The geometry of gas entrapment in homogeneous media is parabolic with an error-function gas flow density in lateral sections. These properties can be explained by considering the gas travel to consist of independent streams of bubbles with upward trending Brownian motion. In addition, lateral flow at textural interfaces was modeled using a Bousinesq approach, demonstrating that the extent of lateral bubble movement is linearly related to the slope of the interface, and increases with the inverse square root of the rate of flow. This result supports the field observation of ever smaller lateral gas movement at increasing distance from injection in stratified environments. The study is now complete.

Redox Transformations of Organic and Inorganic Contaminants in the Subsurface Environment: John C. Westall and James D. Ingle, Oregon State University (Supported by R2D2 Program)

Goal: The long-range goals of this project are: (1) to determine the "best" way to measure the redox conditions of the subsurface environment and (2) to determine how the redox transformations of selected target contaminants and redox sensors couple to the biogeochemical matrix under specific redox conditions.

Rationale: A clear understanding of the redox state and speciation of chemicals is required in virtually all aspects of hazardous waste management: (1) evaluation of disposal options, (2) risk assessments of contaminated sites, and (3) evaluation of clean-up options for contaminated sites. Specifically, the redox state of a contaminant affects its speciation and thereby its transport, fate and biological effects.

Approach: In characterizing redox transformations of contaminants, three components are considered: the redox-active contaminant, the biogeochemical matrix, and the redox sensor. The coupling between all components is being investigated on a species-by-species basis. The focus of this study is on transformations of major biogeochemical redox couples such as Fe(II)/Fe(III) and priority pollutant couples such as Cr(III)/Cr(VI) and As(III)/As(V) in "real"

soil systems due to microbial and chemical processes. In parallel experiments, different methods of determining the redox status of the biogeochemical matrix are being evaluated, such as the redox state of immobilized redox indicators, platinum electrode potential, concentrations of soluble matrix components (e.g., Fe(II)), and H₂ concentration.

Status: Organic redox indicators have been covalently immobilized on affinity chromatography beads (50- μ m diameter) which are packed in a spectrophotometric flow cell to allow contact with filtered reactor solution (biologically-active soil slurries, sludges, and ground water) and monitoring of the absorbance (and hence speciation) of the indicators. Two redox indicators, thionine ($E'^7 = +53$ mV vs SHE) and cresyl violet ($E'^7 = -81$ mV vs SHE), have been found to be particularly useful for delineating between Fe(III)-reducing conditions and sulfate-reducing conditions in soil and waste water slurries. They are reduced by quite different levels of Fe(II) and sulfide (HS⁻). Different methods to immobilize redox indicators in silicon sol-gels and in polyacrylamide gels are being explored to allow development of thin redox films for better applicability and faster response times. The feasibility of using redox indicators for H₂ determination in the field is also being tested.

Hydrocarbon and Biological Factors Affecting Aquifer Clogging During In-Situ Bioremediation: Perry L. McCarty, Stanford University

Goals: The goals of this project are: (1) to develop a laboratory apparatus for visually observing and quantifying the physical, chemical, and biological factors affecting bacterial attachment, growth, and hydraulic conductivity change in porous media, and (2) to make preliminary observations of bacterial growth and attachment as a function of variables such as pore shape, Peclet number, growth substrate, and bacterial species.

Rationale: One of the major concerns in the application of in-situ bioremediation of groundwater contaminants is the reduction in hydraulic conductivity and eventual clogging of an aquifer by growth of microorganisms. There have been many empirical studies of such biofouling over the last few decades, but a good understanding of factors affecting bacterial growth and aquifer clogging is still not available. One reason is that good visualization methods for observing the processes involved were lacking until recently. The visualization approach being proposed here is expected to add significantly to our understanding of the processes of importance.

Approach: An apparatus for visualizing the growth of bacteria on surfaces that simulate a groundwater aquifer and for measurement of fluid velocities as well is being constructed. This apparatus will be seeded initially with a mixed bacterial culture consuming acetate as a primary substrate. From the understanding that is obtained, pure cultures with different adhesion properties will be evaluated under a variety of growth substrates at different concentrations and with different fluid velocities and aquifer system geometries. The effect of disinfectants on the biofilms that develop will also be evaluated.

Status: This project was begun on April 1, 1995. A test system was constructed and operated with a mixed bacterial culture fed 10 mg/l acetate at a superficial velocity of 1.6 m/d. Two types of growth were observed, one was a uniform biofilm around the simulated aquifer media and the other was filamentous aggregates that sometimes spanned the pore spaces between

media. The design has been improved considerably for better visualization and for more automation in data collection so more data on the process can be obtained for evaluation. This project is closely connected with the modeling studies of the project "Upscaling pore-scale hydrodynamics and the transport of reactive solutes."

CHLORINATED SOLVENTS

Reductive Transformation of Chlorinated Hydrocarbons by Reduced Ethenes Catalyzed by Vitamin B₁₂ — Mechanistic and Kinetic Studies: Martin Reinhard, Stanford University

Goal: This project aims to (1) determine products and pathways of chlorinated ethene transformation by vitamin B₁₂ under different reducing conditions, (2) develop kinetic models describing the transformation, and (3) elucidate the mechanism.

Rationale: Transition-metal coenzymes such as vitamin B₁₂ have been shown to mediate the cometabolic dehalogenation of chlorinated hydrocarbon compounds in microbial systems. A detailed mechanistic understanding of this reaction may help in optimizing biological detoxification processes and the design of novel remediation approaches.

Approach: In this project, we are focusing on TCE and its metabolites as the substrates. The reaction is studied in aqueous solution containing Ti(III) as a reductant, vitamin B₁₂, and trace concentrations of substrate. To follow the reaction head space samples are taken and the disappearance of substrate and the formation of intermediates and products are measured over time using GC/MS, GC/FID, and GC/ECD. The (transient) products formed include dichlorinated ethylene isomers, vinyl chloride, chloroacetylene, acetylene, ethene, and ethane. Solutions were prepared in the glove box, and then spiked with a micromolar amount of saturated aqueous solution of the chlorinated substrate under light-excluded, anaerobic, and abiotic conditions. Rate constants and product yields are measured over relatively long reaction times so that the formation and decay of stable intermediates can be observed.

Status: We developed kinetic data of TCE transformation and quantified the volatile products and intermediates acetylene, chloroacetylene, ethene, 1,1-, cis- and trans-DCE, vinyl chloride. In separate kinetic experiments under identical conditions we studied the kinetics of the TCE intermediates, notably acetylene, chloroacetylene, and 1,1-DCE. Chloroacetylene, which was commercially not available, was synthesized. From the data, kinetic sub-models were developed for acetylene, chloroacetylene and 1,1-DCE. A paper describing these kinetic models is currently in revision. These kinetic sub-models serve as a basis for modeling the transformation of TCE.

Inhibition, Inactivation and Recovery: A Universal Model for Aerobic Cometabolic Degradation of Aliphatic Compounds: Daniel Arp, Michael Hyman, and Kenneth J. Williamson, Oregon State University

Goals: The aims of this project are two-fold. First, the further development and corroboration will be done of a mathematical model previously developed which describes the kinetics of aerobic cometabolism of trichloroethylene (TCE). This model was originally developed for the

soil nitrifying bacterium, *Nitrosomonas europaea* and describes TCE cometabolism in terms of an inhibition, an inactivation and a recovery process. The present study aims to extend these earlier studies to other organisms including toluene- and methane-oxidizing species. The second aim is to further investigate the physiological responses of *N. europaea* to the toxicity associated with the cometabolism of trichloroethylene.

Rationale: In situ bioremediation schemes have a considerable need for mathematical models that can accurately describe the kinetics of pollutant degradation. In particular, accurate models can provide important information for process design and for the interpretation of degradation studies. At a more fundamental level, there is also a considerable need to understand the molecular basis for the toxicity of various pollutants towards degradative organisms. In addition, it is important to understand the responses of the affected organisms to these toxic effects because these responses in turn affect the kinetics and modeling of the degradation process. In combination these large and small scale approaches should provide a comprehensive description of the kinetics and molecular consequences of aerobic cometabolism of chlorinated solvents.

Approach: The current approach for extending the modeling efforts is based on the quasi-steady-state reactor system which was previously developed for studies with *N. europaea*. In summary, a 1.7 gas-tight reactor vessel containing 0.5 L of reaction mixture is rapidly stirred using a magnetic stir bar. Primary substrates (e.g. ammonium) are supplied at a constant rate. Once steady state rates of activity have been established, an alternative pollutant substrate is added to the reactor and the kinetics of both the primary and secondary substrate degradation are monitored over a period of several hours. In addition, assays of residual enzyme activities are determined for small (< 2ml) samples removed from the reactor at regular intervals. Experiments investigating the mechanism and response of *N. europaea* to the toxicity associated with TCE and chlorinated solvent degradation are conducted on a smaller scale and over shorter times. The effects of these exposures are correlated with the losses of various enzyme activities and the response of the cells is subsequently monitored using radiolabeled $^{14}\text{CO}_2$ to monitor de novo protein synthesis.

Status: In previous studies, a methodology for conducting reactor-based studies with *N. europaea* was developed, and the mathematical model describing TCE cometabolism by this organism was formulated. Experiments were conducted with *Burkholderia cepacia* G4 to examine whether the model accurately describes the cometabolism of TCE by other organisms. The model does not accurately describe cometabolism in *B. cepacia* G4. Factors such as growth and substrate inhibition need to be further examined.

Short term, small scale assays examining inhibition, inactivation, and recovery associated with TCE cometabolism by the toluene oxidizer *B. cepacia* G4 have been initiated. These results reveal additional complexity in whole cell kinetics of toluene and TCE oxidation by *B. cepacia* G4 and further support the idea that mathematical models employing competitive inhibition may not adequately describe the kinetics of cometabolism. The effects of alkynes on toluene-2-monooxygenase (TOM) activity are under investigation. Although acetylene is a weak inactivator, longer chain alkynes are potent and specific inactivators of TOM.

The mechanism of TCE toxicity for *N. europaea* has been further investigated using short-term incubations. TCE cometabolism has significant effects on both AMO and HAO activities. Inhibitor treatments which specifically inactivate either AMO or HAO were used to compare effects seen in TCE cometabolism and several other chlorinated hydrocarbons. The results of TCE and chloroform cometabolism show that HAO is the probable target at low concentrations. In contrast, AMO is inactivated in cis-1,2-dichloroethylene experiments. These results lead us to conclude the site of action is not directly related to these enzymes. We are currently investigating our current hypothesis that TCE cometabolism exerts a significant effect on the electron transport in *N. europaea* cells.

An Investigation of the Chlorinated Hydrocarbon Substrate Range of the Filamentous Fungus, *Graphium* sp.: Michael Hyman and Lynda Ciuffetti, Oregon State University (Supported by R2D2 Program)

Goals: There are two main goals of this project. The first is to examine the ability of the filamentous fungus *Graphium* to cometabolically degrade a range of chlorinated C1 and C2 hydrocarbons. The second is to investigate the ability of this organism to degrade a series of alkyl ether compounds, either through cometabolism or through conventional metabolism where the compound is used as a carbon and energy source to support growth.

Rationale: *Graphium* sp. is one of the few fungi known to utilize gaseous n-alkanes as carbon and energy sources to support growth. Aerobic, gaseous hydrocarbon-utilizing microorganisms typically utilize monooxygenase type enzymes to initiate the oxidation of their growth supporting substrates. In many instances these monooxygenase enzymes exhibit relaxed substrate specificity's. The ability of monooxygenase-bearing bacteria to degrade non-growth supporting substrates through the process of cometabolism represents one of the most promising avenues for the bioremediation of simple chlorinated hydrocarbons. While most previous studies have concentrated on bacterial systems, the purpose of this present investigation is to determine whether a similar activity can be observed in hydrocarbon-grown fungal systems. As a prelude to these degradation studies, we are also interested in defining the basic physiology and biochemistry of hydrocarbon oxidation by *Graphium*. A fundamental understanding of these areas is of considerable importance to successfully control the activities of this organism for sustainable degradation purposes.

Approach: The experimental approach has been divided into two areas. First, the overall pathway of gaseous hydrocarbon oxidation by *Graphium* is to be defined. The general approach has involved determining the range of hydrocarbons and potential oxidation intermediates which support the growth of this organism. These quantitative studies have emphasized the yields of mycelia obtained from each substrate and the effects of inhibitors of alkane oxidation on these yields. The second approach involves examining the ability of *Graphium* to degrade chlorinated solvents through the process of cometabolism. The experimental approach involves growing *Graphium* on gaseous n-alkanes and then conducting short term (< 1h) incubations in the presence of suitable concentrations of each chlorinated hydrocarbon. Chlorocarbon degradation is then detected by gas chromatography.

Status: We have demonstrated n-alkane-grown *Graphium* can degrade numerous CAHs including all 4 trihalomethanes, HC 21, HC 22, chloromethane, dichloromethane, chloroethane, 1,2-dichloroethane and 1,1,2,2-tetrachloroethane. This fungus can also reductively dechlorinated CT to CF in the absence of oxygen and then consume CF when oxygen is introduced into the reaction. We have also demonstrated that *Graphium* can grow on the unusual substrate diethyl ether (DEE) and can degrade the gasoline oxygenate methyl tert butyl ether after growth on gaseous n-alkanes. Our recent research has focused on defining the growth substrates that will support this activity and we have demonstrated that *Graphium* will degrade all of the major gasoline oxygenates (MTBE, TAME and ETBE) after growth on propane, butane and isobutane.

Aerobic Cometabolism of Chloroform, 1,1,1-trichloroethane, 1,1-dichloroethylene, and Other Chlorinated Aliphatic Hydrocarbons by Microbes Grown on Butane and Propane: Lewis Semprini and Daniel J. Arp, Oregon State University (Supported by R2D2 Program)

Goal: The objectives of this study are: (1) to evaluate the ability of microorganisms grown on butane or propane to degrade a broad range of chlorinated aliphatic hydrocarbons (CAHs), (2) to obtain a better understanding of factors effecting the rates and extents of transformations of these compounds by these microorganisms, (3) to learn more about of biochemistry of the microorganisms and the associated cometabolic processes.

Rationale: In previously funded Center research, butane and propane were discovered as good cometabolic growth substrates for aerobic treatment of chloroform. Chloroform had previously been shown to be a fairly difficult substrate to degrade via aerobic cometabolism. Other contaminants such as 1,1,1-trichloroethane (TCA) and 1,1-dichloroethylene (1,1-DCE) have also been fairly resistant to aerobic cometabolism. Trichloroethylene (TCE) can be effectively degraded by microbes grown on phenol or toluene, however, these growth substrates are regulated chemicals that may be difficult to add for subsurface remediation. This research therefore focuses on evaluating the potential of butane and propane as substrates for CAH cometabolism.

Status: Transformation and kinetic studies evaluated the cometabolism of chlorinated methanes, chlorinated ethanes, and chlorinated ethenes by our butane grown enrichment obtained from the Hanford DOE site. Resting cell studies showed very high transformation capacities ($\mu\text{mole CAH/mg TSS cells}$) in the absence of an endogenous energy source. The chlorinated methanes transformation capacities were: chloromethane (CM), 23; dichloromethane (DCM), 5.8; and chloroform (CF), 0.6; showing transformation was more for effective for the less chlorinated methanes. The transformation of CF, however, promoted the most inactivation of butane-utilizing activity. The chlorinated ethanes transformation capacities ranged from 7.0 for chloroethane (CA) to 0.29 for 1,1,2-trichloroethane (1,1,2-TCA). The transformation and the resulting inactivation were strongly affected by the position of the chlorine substitution. 1,1-dichloroethane and 1,1,1-trichloroethane were more effectively transformed and caused less inactivation than their corresponding isomers with chlorine on both carbons, 1,2-dichloroethane and 1,1,2-trichloroethane. We suspect that the mechanism of cometabolism and the transformation products are causing these differences. The chlorinated ethenes had transformation capacities ranging from 2.7 for vinyl chloride to 0.1 for TCE. The dichloroethylene (DCE) isomers transformation capacities were: trans-DCE, 0.0; cis-DCE, 1.4; 1,1-DCE, 0.9, again showing large variations based on the position of the chlorine substitution. Butane-utilizers effectively transformed 1,1-DCE, however the transformation caused the greatest inactivation of all the compounds tested. Chloride release studies showed the chlorinated methanes and ethenes were the most completely dechlorinated (70 to 100%), while the chlorinated ethanes were the least dechlorinated (40 to 60 %).

Characterization of butane and chlorinated aliphatic degradation by three bacterial isolates was continued. *Mycobacterium vaccae*, *Pseudomonas butanovora*, and CF8 (an isolate from Hanford core material) all degrade chloroform when grown on butane. Studies with inactivators and inhibitors of CF degradation led to the hypothesis that each of these three bacteria produces a distinct butane monooxygenase. When cultures of each bacterium are exposed to ^{14}C acetylene, activity is lost. When proteins from these bacteria were examined by SDS-PAGE and autoradiography, different proteins were found to be labeled. Butane oxidation

is inhibited or inactivated by the same compounds which affect CF oxidation which provides further evidence that butane monooxygenase catalyzes the transformation of CF. A mixed culture (derived from Hanford core material) was grown in the presence and absence of CF. Cultures grew more slowly in the presence of chloroform. Chloroform degradation potential of resting cells taken from these cultures revealed a greater chloroform specific activity in the cultures not exposed to CF than those which were exposed to chloroform. PCR products (using a variety of primers) were similar whether the culture was grown in the presence or absence of CF, although distinct differences were also noted. These results reveal that the presence of CF during growth on butane does influence the microbial population.

Mechanisms, Chemistry, and Kinetics of Anaerobic Degradation of cDCE and Vinyl Chloride: Perry L. McCarty and Alfred M. Spormann, Stanford University (Supported by DuPont Chemicals and U.S. Department of Energy)

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, only one organism responsible for the complete dehalogenation from tetrachloroethylene (PCE) to ethene has so far been identified. Available evidence that the individual dehalogenation steps are the result of cometabolism or of energy metabolism was not known when this study began. 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 and PCE, cis-1,2-dichloroethene (cDCE), or vinyl chloride (VC) as electron acceptors.

Status: The original project was completed last year, but additional funding was provided last year to extend the project, but with similar objectives. Funding also was received this year from the U.S. Department of Energy to extend this work. 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. This

overall study clearly demonstrated that in the cultures developed there are two separate groups involved in the overall dehalogenation of PCE to ethene, the first is the group that converts PCE to c-DCE, and the second is the group that converts c-DCE to vinyl chloride and ethene. Rates of transformation were evaluated by a mixed culture growing on yeast extract. The rates of transformation of PCE and TCE to cDCE were about four times faster than for the conversion of cDCE to vinyl chloride and vinyl chloride to ethene. Organisms appear to obtain energy from the dehalogenation reaction while using the chlorinated organics as electron acceptors. Monod kinetics of the reactions when the CAHs are rate limiting have been completed. Preliminary enzymatic studies have been conducted on VC transformation, indicating that it is particulate and not highly oxygen sensitive. Efficient dehalogenation using benzoate as an electron acceptor can be attained by control of molecular hydrogen concentration.

Biochemical Mechanisms of PCE Dehalogenation by Strain MS-1, and its Potential for In-situ Bioaugmentation: Pramod K. Sharma and Perry L. McCarty, Stanford University

Goals: The goals of this project are to (1) determine the biochemical mechanisms involved in reductive dehalogenation of tetrachloroethene (PCE) to cis-1,2-dichloroethene (cDCE) by bacterial strain MS-1, which was isolated from Victoria, Texas, aquifer material, and is the first identified facultative bacteria with this reductive ability, (2) to determine the phylogeny and to develop molecular probes for strain MS-1, and (3) to evaluate at laboratory scale the potential for bioaugmentation with strain MS-1.

Rationale: Chlorinated solvents, the most frequently found organic groundwater contaminants at hazardous waste sites, are difficult and expensive to remove by physical or chemical means. Biological methods such as in situ bioremediation or bioaugmentation are an attractive alternative, but microorganisms that can rapidly transform highly chlorinated solvents such as PCE have proven to be difficult to isolate and grow. The few identified organisms that convert PCE to cDCE are all strict anaerobes. Strain MS-1, however, is a facultative bacteria that can grow rapidly under either aerobic conditions or fermentatively on a variety of substrates. Thus, it is a particularly useful organism for studying the biochemistry of this important process, about which little is currently known, and for potential use in bioremediation, especially for the first phase of a two-stage anaerobic/aerobic process where PCE is first converted to cDCE anaerobically, and then cDCE is oxidized aerobically by cometabolism with bacteria that grow on substrates such as phenol or toluene. If used for bioaugmentation, then it will be useful to have molecular probes available to monitor the activity and survival of strain MS-1 in an in-situ or above ground treatment system.

Approach: There are various mechanisms now proposed by which PCE is reductively converted to cDCE, such as CO dehydrogenase and Vitamin B₁₂. Through evaluation of cell-free extracts and then the purified enzyme system, the factors affecting PCE dehalogenation by strain MS-1 will be studied. Also to be determined is whether or not MS-1 can obtain energy for growth from PCE dehalogenation. Biochemical testing, cellular fatty acid finger printing, and 16s rRNA analyses will be used to determine how MS-1 is related to other microorganisms.

Status: This project was begun in March 1995. Strain MS-1 was found to be an enteric bacteria closely related to other enteric microorganisms. REP-PCR analysis indicated that none of the known closely related strains was identical to MS-1, but one of them, *Microbacterium agglomerans*, Group 5, from the American Type Culture Collection, was also found capable of dehalogenating PCE to cDCE. Two additional facultative strains with this ability, both pseudomonads, were also found this past year. MS-1 was introduced successfully into a 39 liter anaerobic fixed-film bioreactor following three months of methanogenic treatment of a mixture of yeast extract (500 mg/l), benzoate (500 mg/l), but without PCE (1 mg/l) conversion. PCE dehalogenation to cDCE began immediately after MS-1 introduction, indicating this organism can successfully carry out the observed dehalogenation in mixed cultures. MS-1 and the other isolated strains were found to gain energy and carbon for growth through oxidation of acetate and reduction of PCE to cDCE.

AROMATIC COMPOUNDS

Pathways of Anaerobic Toluene Metabolism by a Sulfate-Reducing Bacterium, Strain PRTOL1: Alfred M. Spormann, Stanford University

Goal: The objectives of this project are to determine the metabolic pathways involved in anaerobic toluene degradation in sulfate-reducing strain PRTOL1, and to study metabolites that can be used as indicators of anaerobic in situ bioremediation of BTEX compounds.

Rationale: Although some information is available about anaerobic mineralization of toluene in one denitrifying strain, it is not clear if all anaerobes that degrade toluene utilize the same biochemical pathway. Concomitant to toluene mineralization in all toluene-degrading denitrifying cultures that have been investigated as well as in PRTOL1 is the formation of two metabolites, benzylsuccinate and *E*-phenylitaconate (or benzylfumarate). These metabolites are not further metabolized by whole cells of the pure toluene-degrading cultures studied to date and have been assumed to be dead-end by-products. The relationship between these metabolites and toluene mineralization is not resolved. Recently, we detected these compounds at field sites where BTEX compounds were consumed under anaerobic conditions (Beller et al. 1995). We focus on experiments investigating the connection between benzylsuccinate formation and alkylbenzene metabolism.

Approach: Permeabilized cell assay and cell extract experiments are being used to investigate the initial biochemical steps involved in toluene degradation and benzylsuccinate formation. Denitrifying strain T (Dolfing et al. 1990), which grows anaerobically on toluene and *m*-xylene and forms benzylsuccinate and *E*-phenylitaconate during toluene metabolism, is being used in addition to strain PRTOL1 because it is more amenable to laboratory cultivation. In cell extract studies, we specifically investigate the biochemical reactions involved in the formation of benzylsuccinate and *E*-phenylitaconate. Recently, we demonstrated that benzylsuccinate formation is the first step in anaerobic toluene mineralization in denitrifying strain T (Beller and Spormann 1997, *J. Bacteriol.*, 179 (3) p.670-676).

Status: Benzylsuccinate synthase is a novel, unique enzyme that catalyzes the formation of a new carbon-carbon bond and of a new chiral carbon. We are investigating whether the (+)- or the (-)- enantiomer of benzylsuccinate, or both, are intermediates in anaerobic toluene mineralization. Benzylsuccinate formed by permeabilized cells of strain T are being analyzed by chiral HPLC and retention time are compared with authentic standards of each enantiomer. In further experiments, we test whether each enantiomer can be converted to *E*-phenylitaconate and benzoate by permeabilized cells. Both sets of experiments will demonstrate conclusively which benzylsuccinate isomer is formed and transformed by cells of strain T, respectively.

We also investigated whether toluene-mineralizing sulfate-reducing strain PRTOL1, a member of the delta subclass of proteobacteria, can activate toluene by addition to fumarate. Using permeabilized suspensions of toluene-grown PRTOL1 cells, we showed that *in vitro* benzylsuccinate formation from toluene plus fumarate was catalyzed at a rate that accounted for about 7% of the *in vivo* toluene transformation rate. This result, together with mass spectral data suggests that also in this organism anaerobic toluene is activated by benzylsuccinate synthase. Thus, toluene addition to fumarate may be a general mode of anaerobic toluene activation in

phylogenetically disparate groups of toluene-mineralizing bacteria. These results were recently published (Beller and Spormann, 1997, *Appl. Environ Microbiol.*, 63 (9), p. 3729-3731).

Furthermore, experiments are in progress to purify benzylsuccinate synthase. This project will be funded by the NSF.

Anaerobic Ethylbenzene Oxidation in Denitrifying Strain EB1: Alfred M. Spormann, Stanford University

Goal: The objectives of this study are to provide knowledge on the metabolic reactions and intermediates involved in anaerobic ethylbenzene oxidation, and to get a better understanding of the factors that control expression of the degradative enzyme activities.

Rationale: BTEX (benzene, toluene, ethylbenzene, and xylenes) are the most water soluble components of fuel. Leaking underground storage tanks and surface spills often contaminate soils and aquifers. Anaerobic, microbial degradation of BTEX has been observed to occur under natural conditions. Therefore, the degradative activity of microorganisms can potentially be used to remediate contaminated sites. Only recently, pure cultures of toluene or xylene degrading bacteria have been described. At the time this project was initiated, EB1 which was isolated at Stanford's Environmental Engineering and Science program, was the only anaerobic organism capable of complete ethylbenzene oxidation to CO₂ under anoxic conditions. To predict when and to what extent intrinsic bioremediation of fuel components, such as ethylbenzene, occurs and how these processes can be enhanced, a better understanding of the biochemical pathways and reactions involved is necessary.

Approach: Studies were conducted with strain EB1 which can metabolize ethylbenzene under denitrifying conditions. Cells grown anaerobically with ethylbenzene and nitrate as substrates are harvested anaerobically, concentrated, and subjected to cell suspension experiments. Suspensions are amended with ethylbenzene and nitrate, and the concentrations of ethylbenzene and nitrate are followed by GC and IC respectively. Potential intermediates during anaerobic degradation of ethylbenzene are detected using HPLC and the chemical nature of the compounds is identified by GC-MS. Based on the finding of intermediates isotope exchange studies will be employed to substantiate the proposed pathway. Results from the cell suspension studies will then be used to design enzyme assays with cell-free extracts.

Status: In experiments previously published (Ball et al., 1996) we identified the initial reactions in anaerobic ethylbenzene mineralization. Ethylbenzene oxidation is initiated by an anaerobic dehydrogenation reaction that results in 1-phenyl ethanol formation. Subsequent reactions convert 1-phenyl ethanol to benzoate via acetophenone as a transient intermediate. We focused on experiments to characterize the key enzymatic reactions of this pathway in cell free extracts of strain EB1. *In vitro* assays for ethylbenzene dehydrogenase and 1-phenyl ethanol dehydrogenase were developed in which the oxidation of the substrate is coupled to the reduction of *p*-benzoquinone. The specific activity of ethylbenzene dehydrogenase was approximately 10 nmol x min⁻¹ x mg protein⁻¹. Both enzymes activities were localized to the membrane fraction. The stereoselectivity of 1-phenyl ethanol dehydrogenase was investigated. In cell-free extracts, the specific activity of (*S*)-(-)- 1-phenyl ethanol oxidation was 9-fold higher than the rate for acetophenone formation from (*R*)-(+)- 1-phenyl ethanol. In competition experiments, we found that the presence of (*R*) - 1-phenyl ethanol did not effect the rate of *in vitro* (*S*)- 1-phenyl ethanol oxidation. Michaelis-Menten kinetic studies on 1-phenyl ethanol dehydrogenase yielded a K_m and V_{max} for (*S*)- 1-phenyl ethanol of 25 μM and 5 nmol x min⁻¹ x mg protein⁻¹. In an effort to develop an understanding of the ethylbenzene dehydrogenase reaction mechanism, transformation of halogenated ethylbenzenes, ethyltoluenes, styrene, and stable isotope labeled ethylbenzene was investigated.

Development of a Vitamin B₁₂-Amended Bioremediation Process for the Reductive Dechlorination of Chlorobiphenyls at all Chlorine Positions: Sandra Woods, Oregon State University (Supported by R2D2 Program)

Goal: The goal of this project is to develop a vitamin B₁₂-amended anaerobic process that will result in the complete reductive dechlorination of highly chlorinated biphenyls, especially those heavily substituted at the *ortho* position. Our objectives are (1) to determine the effect of parent compound structure on biotransformation pathways and kinetics, and (2) to demonstrate and optimize PCB reductive dechlorination in a laboratory-scale anaerobic process.

Rationale: Vitamin B_{12s} is a nucleophile with the ability to mediate reductive dechlorination of chlorobiphenyls at all positions. By coupling vitamin B₁₂ with a biological reductant, reductive dechlorination can be enhanced. A microorganism was selected for study due to its ability to reduce cobalt, and potentially, the cobalt center of vitamin B₁₂.

Approach: Reducing systems include a microbial consortium, chemically-reduced vitamin B₁₂, biologically-reduced vitamin B₁₂, and a consortium amended with vitamin B₁₂. We are separately evaluating the reduction of the catalyst and the transformations of chlorinated organic compounds. 2,3,4,5,6-Pentachlorobiphenyl (2,3,4,5,6-PCB) was selected as the model chlorobiphenyl for study because one ring is fully chlorinated. Other model compounds (for comparison) include the chlorinated phenols and chlorinated methanes.

Status: The project is being conducted in two concurrent parts: (1) evaluation of the microbial reduction of vitamin B₁₂ and (2) evaluation of the transformations mediated by vitamin B₁₂.

Biological reduction of vitamin B₁₂. This work was completed and reported in the most recent progress report and in Workman et al. (1997).

Vitamin B₁₂-catalyzed transformation of chlorinated methanes. The fully reduced vitamin B_{12s} rapidly dechlorinates chlorobiphenyls at all positions (Woods et al., 199x). However unlike vitamin B_{12s}, vitamin B_{12r} (produced in the *Shewanella alga* system) does not result in rapid dechlorination of 2,3,4,5,6-PCB. For comparison, the transformation of readily dechlorinated methanes [carbon tetrachloride (CT), chloroform (CF), and dichloromethane (DCM)] was examined in batch systems containing vitamin B₁₂, the metal-reducing non-dechlorinating bacterium *Shewanella alga* strain BrY, and an electron donor. Further investigation examined factors that affect the rate of CT transformation. Both cell concentration and vitamin B₁₂ concentration influenced the rate at which CT was transformed in this system. Rate dependence was seen only when vitamin B₁₂ concentrations were below 35 mM for high cell concentrations.

The transformation of a variety of halogenated methanes was examined. Bromoform, dibromomethane, dibromochloromethane, and chlorodibromomethane were transformed in the presence of BrY, lactate and vitamin B₁₂. The initial first-order rates determined for these transformations had the following pattern: bromoform>>carbon tetrachloride^adibromomethane> dibromochloromethane>bromodichloromethane>>chloroform.

Vitamin B₁₂-catalyzed transformation of chlorinated biphenyls. Previous work demonstrated rapid dechlorination of 2,3,4,5,6-PCB in a titanium citrate-reduced vitamin B₁₂s system. The reductive dechlorination pathway for 2,3,4,5,6-PCB indicated that chlorines are removed from all positions. Current work is focused on the factors affecting reductive dechlorination of PCBs by vitamin B₁₂s in a sediment/water system. 2,3,4,5,6-PCB was equilibrated with Willamette River sediment for approximately 6 months. Rapid removal of 2,3,4,5,6-pentachlorobiphenyl was observed in systems containing 333 mM vitamin B₁₂ and excess titanium citrate. The tetra-, tri-, di- and mono-chlorobiphenyls that have been observed are consistent with the intermediates observed for the aqueous system and with thermodynamic predictions based upon distribution coefficients estimated from free energies of formation.

HEAVY METALS

Development, Characterization, and Performance Evaluation of Ferrous-Ferric Oxide Adsorbents for Metal Removal from Contaminated Groundwater: Peter O. Nelson, Oregon State University (Supported by R2D2 Program)

Goal: The goal of this research is the development and characterization of a mixed oxidation state (ferrous-ferric) iron oxide composite adsorbent for simultaneous removal of adsorbable and electroactive metals from contaminated groundwater. The intended application of the sorbent material in an interceptor trench. As such, desirable properties of the sorbent material are high permeability, rapid reactivity with target metals, high capacity for metals removal, and regenerability.

Rationale: Remediation of metals-contaminated groundwater focused on ex-situ or in-situ treatment processes. Both methods are often limited by their expense and extended extraction time. An alternative to these approaches is in-situ treatment by interception of the contaminant plume by passive trench that removes or transforms contaminants in place. This study will increase our understanding of mixed oxidation state (ferrous-ferric) iron oxide for removal of adsorbable and electroactive metals in in-situ treatment in an interceptor trench.

Approach: Several approaches will be followed in preparation of the ferrous-ferric iron oxide adsorbent. Ferrous-ferric iron oxide adsorbent will be prepared by coating magnetite on silica sand or by coating commercially available magnetite with Fe(OH)₃(s) precipitate (ferrihydrite). The coated sand will be characterized to determine kinetics and equilibrium removal capacity of the sorbable and electroactive metals. Cr(VI) and Pb(II) are selected as the model metals to test the performance of the mixed oxidation state (ferrous-ferric) sorbent material. Batch reactor experiments will be used to determine sorption kinetics and equilibrium constants. Packed-bed column experiments will be used to more closely simulate field conditions of porous media flow.

Status: Results from Fe(II) dissolution experiments indicated that the amount of Fe(II) present in the bulk solution could not have reduced as much Cr(VI) as was experimentally observed, and the Fe(II) dissolution rate was slower than the Cr(VI) reduction rate. The reaction became independent of initial [Cr(VI)] when [Cr(VI)]/{MCS} ratio was greater than 0.38 mmole Cr(VI)/g MCS, indicating a saturation of surface sites. Cr(VI) reduction was hypothesized to

occur in three steps, transport from the bulk solution to the MCS surface, adsorption to the surface either as an outer-sphere complex or as an inner-sphere ternary complex with adsorbed Fe(II), and reduction by Fe(II). Fe(II) oxidation similarly was hypothesized to follow a multistep pathway that includes dissolution from magnetite, inner-sphere adsorption to the ferric oxide component of magnetite (either binary or as ternary complex with Cr(VI)), and oxidation by adsorbed Cr(VI). Initial Cr(VI) concentration, solution pH, and MCS concentration are directly related to the reduction reaction, and a Cr(VI) reduction rate equation was developed based upon these three parameters, as follows:

$$d[\text{Cr(VI)}]/dt = -k[\text{Cr(VI)}][\text{H}]^{0.2}\{\text{MCS}\}^{1.8}$$

The rate equation successfully predicted kinetics of Cr(VI) reduction by MCS.

Trace Element Adsorption in Porous Particle Packed Beds: James O. Leckie, Stanford University (Supported by R2D2 Program)

Goal: The objective of this project is to develop the empirical data base and mathematical model requisite to trace element treatment technology based on trace element adsorption onto packed beds of high adsorption capacity, porous alumina particles to bring waste streams into compliance with increasingly stringent NPDES standards. Research activities are to be directed toward establishing optimal design and operational characteristics for the proposed technology.

Rationale: Chemical precipitation has been the most widely used technique of trace element removal from wastewater for several decades. Though chemical precipitation has proved to be effective over a narrow range of operating conditions, it is beset with a number of problems including the inability of achieving increasingly stringent NPDES in-stream permit standards. Adsorption promises to be a more efficient method of trace element removal, especially over a wider pH range and to concentrations lower than those achievable by precipitation. Additional advantages include the ability to remove cations and anions simultaneously and the ability to regenerate the adsorbent by adjusting contacting solution conditions (e.g., pH, presence of ligands, etc.). Despite inherent advantages over precipitation, the potential of developing packed bed adsorption into a feasible treatment technology has not yet been thoroughly investigated.

Approach: The proposed technology will use packed beds of adsorbent particles for treating waste solutions as such a technology can be modularized and requires a small footprint and low maintenance. The project will use commercially available alumina particles that exhibit strong adsorption characteristics along with fast uptake rates for the target contaminants. Our studies have shown that for fast adsorption, the adsorbent should have significant pore volume in the macro- and mesoporous regions. Cadmium and selenite are being used as model contaminants for the study. The study will generate a high quality empirical database from extensive batch and column studies of adsorption. A mathematical model will be developed for simulating adsorption processes in continuous-flow column reactors. The model, once developed and verified, can be used to predict column adsorber performance and is intended to serve as a tool in designing and operating the proposed treatment scheme.

Status: On the basis of equilibrium and rate of sorption characteristics of 5 transition alumina solids (from ALCOA) for cadmium sorption, DD660 and DD431 have been selected for further study. The two adsorbents have been characterized using XRD, SEM, BET surface area measurements and potentiometric titrations. With both solids, equilibrium experiments have been conducted where the variables have been: total concentration of cadmium (10^{-3} M to 10^{-6} M), ionic strength (0.01 M to 0.1 M NaNO_3) and presence of ligands (chloride, thiosulfate and EDTA) at various concentrations. The data is currently being modeled using the surface complexation approach. Since, the effect of EDTA on cadmium sorption is more complex than that of the other ligands, EDTA-alone experiments and cadmium-EDTA ‘mixed-system’ experiments have been conducted at different EDTA concentrations and different Cd:EDTA ratios, respectively, to have a suitable dataset for an unambiguous interpretation of the sorption behavior. Additionally, rate of uptake experiments have been conducted with the selected solids at fixed pH. The variables that have been investigated are: cadmium concentration (10^{-3} M to

10^{-6} M), adsorbent particle size (0.1 mm, 0.5 mm and 1.0 mm), pH (7.5, 8 and 8.5) and presence of ligands (chloride, thiosulfate and EDTA) at two different ligand concentrations. The rate of uptake data will be modeled after the equilibrium sorption data has been adequately modeled using the surface complexation approach.

MINORITY ACADEMIC INSTITUTION PROJECT DESCRIPTIONS

Probing the Redox Properties of Environmental Systems: Natural Phenolic Materials: Robin Helburn, Department of Chemistry, Northern Arizona University

Goal: The long term goals of this project have been to: (1) use cyclic voltammetry to study the redox properties of some natural polyphenolic materials, and (2) investigate the redox properties and environmental applications of a colored water soluble organic free radical. We have proposed that the latter dye(s) (verdazyls) may be used to probe the free radical scavenging behavior or natural polyphenols in environmental and biological systems; we have found such hypothesis to be untenable, but are still characterizing the electrochemical properties of these interesting indicators.

In addition to the above projects, we have pursued a new goal that overlaps directly with the interests of our HSRC collaborator (i.e. sensor development). In the new project, a student has developed a simple method for interfacing probe-type sensors to portable calculators (i.e. for use in the field).

Rationale: The success of environmental remediation depends on our ability to obtain a scientific understanding of chemical processes occurring at a given site. An understanding of redox processes as well as methods for developing portable analytical tools constitutes useful and related research.

Approach: Standard cyclic voltammetry and step potential methods have been used to characterize the polyphenols and verdazyls. The sensor-calculator interfacing was performed using a Texas Instruments TI-85 calculator. The interface design was based on I²C technology.

Status: Accomplishments (publications, presentations and theses) to date: (1) A.B. Hickman, W. Delinger, R. Helburn. "Calculator Based Instrumentation: The Design of a Digital Interface Based on I²C Technology". *J. Chem. Ed.* 1998 (accepted). (2) N. Yardy, R.W. Zoellner, R. Helburn. A Combined Electrochemical and Computational Study of Quercetin and Redox Homologs. *Proceedings of the National Council on Undergraduate Research.* 1996. Vol. 3, 1668-1671 (formal publication planned). (3) A.B. Hickman. "Electrochemical Characterization of 1,3,5-Triphenylverdazyls; Design of a Digital Interface Between Calculators and Sensors Based on I²C Technology." (masters thesis). (4) R. Helburn, M.P. Eastman, A. Mayer. "Electrochemical Studies of a Series of Triphenylverdazyls". *Pacific Conference on Chemistry and Spectroscopy.* Irvine, CA October 21-25 1997 (invited talk).

Detection of Microorganisms Capable of Anaerobic Degradation of Hazardous Substances in Natural Environments: Sara E. Silverstone, State University of New York, College at Brockport

Goal: The goals of this project are to develop a quantitative method for in situ monitoring of anaerobic toluene, PCE, and ethylbenzene- degrading microbes using fluorescence-labelled oligonucleotide probes and to apply this method to field and laboratory studies of contaminated soils.

Rationale: The Stanford laboratories participating in the WRHSRC have isolated a number of novel microorganisms capable of degrading a variety of hazardous organic substances. The use of specific microorganisms in bioremediation requires knowledge about the competitive behavior of the strains and ways to stimulate their growth. In order to identify and study these organisms in soil microcosms and assess the feasibility of using them in bioaugmentation experiments, it is necessary to have a rapid and efficient method of detecting and enumerating the bacteria. To the extent that such organisms can be utilized in bioremediation, this research will be an important contribution to the design of hazardous waste cleanup strategies.

Approach: The approach is to construct fluorescent and digoxigenin-labelled, strain-specific 16S rRNA-directed oligonucleotide probes. Probe target sites are selected based on database searches for unique sequences. Hybridization conditions for each probe are optimized and strain-specificity of the probes is assessed. Protocols are being developed for the use of these probes in whole-cell hybridization in soils. Probes will be used to monitor the effects of environmental and nutritional parameters upon the relative population densities, metabolic state and spatial distribution of target organisms in soil microcosms and at contaminated field sites.

Status: Two 16S rRNA probes specific to the anaerobic toluene-degrader PRTOL1 were developed and used for monitoring the growth of PRTOL1 in a soil slurry amended with various carbon sources, and also capable of enumerating PRTOL1 added to Seal Beach soil to a minimum concentration of 10×10^5 cells/gram. Three highly specific probes were identified for the anaerobic ethylbenzene-degrader EB1 and hybridization conditions optimized for use in Seal Beach and Moffett Field soils. The 16S rRNA sequence was determined for the anaerobic PCE-degrader MS-1 and two highly specific probes were identified. These probes are currently being used in microcosm experiments using Moffett Field aquifer material. Results indicate that the Moffett Field aquifer contains no indigenous MS-1 that MS-1 can survive in Moffett Field aquifer microcosms for up to 21 days, after which time populations decline below 10×10^5 cells/ml.

TRAINING & TECHNOLOGY TRANSFER PROJECT DESCRIPTIONS

DEMONSTRATION PROJECTS

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

Goal: This project is aimed at demonstrating an in-situ method for removing VOCs from groundwater. Through simple gas injection into a well, this method enables removal of VOCs from contaminated groundwater without bringing the water to the ground surface. Recirculation of groundwater is accomplished via air-lift pumping. Theoretical and simulation studies have been carried out previously. Current effort is focused upon pilot scale field demonstrations at two locations: Edwards Air Force Base (AFB) near Lancaster, California, and the Savannah River Site, a Department of Energy facility near Aiken, South Carolina. At both places the principal groundwater contaminant is trichloroethylene. The demonstrations will provide information regarding the efficiency of the in-situ VOC removal system at these and potentially other sites that are contaminated with VOCs.

Rationale: Many contaminated sites contain groundwater with high concentrations of dissolved VOCs. The in-well VOC removal system is an in-situ alternative to pump and treat. It creates an in-well air stripper which volatilizes the VOCs contained in the groundwater, and removes these contaminants as a vapor. The stripped VOC vapor is contained within the well, extracted under a vacuum, and treated at the ground surface. By conversion of a groundwater contamination problem into a simple vapor extraction system, the method has the advantage of not requiring removal, handling, treatment, storage, and disposal of contaminated groundwater. The expense of lifting the water to the surface for treatment is avoided. There is no need for a surface air-stripping tower when using this method. If the water is co-contaminated with tritium, 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 being demonstrated at Edwards Air Force Base and the Savannah River Site. The demonstration unit at each site consists of a single VOC-removal well and several monitoring wells. The overall approach to the demonstrations is to conduct 3 month initial tests of the system. Based on the results of those tests, 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: Analysis of data from the in-well vapor stripping demonstration at Edwards AFB is nearly complete. The in-well vapor stripping demonstration commenced at Edwards AFB in mid-January 1996 and ran continuously for over 7 months. Stripping ratios of approximately 90 percent were maintained throughout the demonstration. Monitoring wells were sampled at approximately 1 week intervals during the demonstration, and then sampled periodically in the 2 months following the demonstration. A comprehensive hydrogeologic model has now been developed to explain hydraulic head observations and the concentration histories at all of the observation wells. Maximum likelihood parameter estimation and cokriging were used to estimate spatially variable hydraulic conductivity and effective porosity based on hydraulic heads and estimated advective travel times. We employed a streamline method to calculate

breakthrough curves. The data are best explained by advective-dispersive transport involving rate limited mass transfer between a mobile and an immobile domain. Longitudinal dispersivity and the first-order rate coefficients for mass transfer between mobile and immobile domains were determined by matching observed and simulated breakthrough/ recovery curves. The recirculation ratio for water near the well is approximately 70%. Current efforts involve conduct sensitivity analyses to explore the robustness of our model. In-well vapor stripping is currently being used at the "hot-spot" area at Edwards AFB.

Field Testing of Palladium-Catalyzed Hydrodehalogenation for Chlorinated Hydrocarbon Removal from Groundwater: Martin Reinhard and Paul V. Roberts, Stanford University (Supported by R2D2 Program)

Goal: This project aims to (1) establish the viability of hydrogen/palladium treatment for halogenated hydrocarbon removal by determining the catalyst lifetime and reaction kinetics in a continuous-flow packed bed reactor; (2) identify competitors/inhibitors in the process and minimize their effects; (3) quantify hydrogen consumption and determine effective supply methods; (4) scale up, optimize and implement the process at the field-scale.

Rationale: Palladium has been demonstrated to catalyze the reduction of halogenated hydrocarbons to alkanes by hydrogen. Batch studies with palladium indicate a rate of reaction several orders of magnitude higher than in the zero-valent iron system (another method currently under study). Chlorinated ethenes, including PCE and vinyl chloride, were completely removed from tap water within ten minutes at room temperature by 0.5% palladium on alumina at 0.1 atm of hydrogen pressure. (Schreier and Reinhard, *Chemosphere*, 31(6) pp 3475-3487, 1995.) This quick reaction time demonstrates palladium's great potential for application in pump-and-treat groundwater remediation. Although palladium has been used as a reduction catalyst for years in organic chemistry applications, the system has not yet been well characterized for groundwater treatment.

Approach: This project entails construction and testing of bench-scale continuous-flow reactors. For testing, we have been using artificially contaminated deionized (DI) water, groundwater from Livermore, California, and groundwater from the California Central Valley. Two bench-scale systems have been constructed, one which is operated in the flow-through mode and one which is operated in a rotating basket-mode. Base-line tests with deionized (DI) water have indicated 99% TCE removal at inlet concentrations ranging from 1.5 to 25 mg/L with no noticeable decrease in catalyst activity over 5 months. When actual ground waters is used, the catalyst is deactivated at rates that depend on water quality. The approach to identify deactivating water quality parameters has been to correlate the water quality with catalyst deactivation time and then to study the effect of the hypothesized parameters in separate experiments.

Status: Current efforts are directed towards establishing the reactivities of different VOCs and getting a better understanding of the catalyst performance under groundwater treatment conditions, specifically (1) quantifying the competing effects of oxygen and TCE reduction, (2) improving the methodology to characterize catalyst deactivation using spectroscopic methods, and (3) characterizing the effects of the water matrix on the process. We developed the methodology to evaluate samples of catalyst in column and rotating basket reactors and

different water matrices. A model was evaluated for examining the column performance in the presence of different catalyst poisoning substances and competing electron accepting substances. The rates of reductive dehalogenation of the most prevalent VOCs were measured in pure (Milli-Q) water. Tetrachloroethylene, trichloroethylene, the DCE isomers, carbon tetrachloride and 1,2-dibromo-3-chloropropane appear to react at diffusion limited rates with no evidence for catalyst deactivation. Freon 113 and chloroform react markedly slower, by approximately 80 and 90%, respectively, and the rates of 1,1- and 1,2-dichloroethane were too small to measure. In groundwater, rates were generally slower. Possible deactivating agents are carbonic acid, bicarbonate and carbonate ions. The field-scale test conducted by the Lawrence Livermore National Laboratory to treat TCE and tritium contaminated groundwater in a treatment well using a submersed Pd reactor is ongoing.

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 was justified based upon research at Stanford University and elsewhere that has shown 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, Woodward-Clyde Corporation, and other parties with interest in this activity.

Approach: 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. To demonstrate the technology at full-scale, a remediation system was installed at a TCE contaminated site at Edwards AFB. The remediation system consists of two wells, each screened at two depths. Each well connects two aquifers separated by an aquitard, the upper unconfined aquifer is 8 m deep and the lower confined aquifer is 6 m deep. In operation, a submersible pump, installed between the two screens, draws water at rates of 25 to 37 liters/min into the well at one screened interval in one aquifer and discharges the water out of the second screened interval in the second aquifer. The well has feed lines which introduce toluene, oxygen gas, and hydrogen peroxide (as a source of oxygen) into the discharge water. A biotransformation zone develops near the discharge side of each well, and the water circulates between the wells to clean the aquifer. An extensive automated sampling and analysis system monitors system operation.

Status: This one year successful evaluation was completed in March 1997. With pumping at 25 liters per minute at each well, and the introduction of 9 mg/l toluene, 30 mg/l dissolved oxygen, and 41 mg/l hydrogen peroxide for fouling control and additional oxygen, 83 to 85 percent TCE biodegradation was achieved with each pass through a treatment well. An estimated 60-m width of the TCE contaminated plume was treated with this system, reducing its upgradient TCE by about 98 percent from 1200 µg/l to 25 µg/l. Toluene concentration was reduced to 1.4 ± 0.6 µg/l at the 22m x 22m boundary of the steady zone. Potential clogging was successfully controlled.

Demonstration of an Interceptor Trench Technology for the Bioremediation of a Pentachlorophenol-Contaminated Ground Water: Sandra Woods, Oregon State University (Supported by R2D2 Program)

Goal: The goal of this project is to demonstrate the applicability of a permeable barrier technology for the bioremediation of groundwaters contaminated with pentachlorophenol (PCP).

Rationale: Pentachlorophenol (PCP) is a fully chlorinated aromatic compound that is biotransformed by reductive dechlorination, a common anaerobic biodegradation mechanism. The rate of PCP reductive dechlorination is rapid and results in the production of lesser chlorinated phenols. As the degree of chlorination decreases, reductive dechlorination rates also decrease. Under aerobic conditions, however, transformation of the lower chlorinated phenolic compounds is rapid and may result in complete mineralization. This project will demonstrate a passive, in-situ sequential anaerobic/aerobic biological treatment technique for PCP-contaminated ground water.

Approach: To allow for the physical, hydrogeological, biological, and regulatory conditions present, a diverse project team was assembled. Teams focused on the following: (1) design considerations for the physical development of the permeable barrier technology, (2) interactions of subsurface flow and mixing, (3) biological process design including evaluation of electron donors and carbon sources, (4) reactor construction, (5) sampling design, and (6) regulatory and legal constraints.

Status: The construction of a 23" cylindrical down-borehole reactor (basket) was completed. The reactor was installed in the 24" diameter borehole during mid-June, 1997. Work focused on testing and validation of the reactor's sampling and nutrient supply systems. In the absence of an inoculated biomass, several conservative tracer studies were conducted to characterize hydraulic conditions within the well and reactor. The observed retention time was approximately 24 hours.

Chlorophenol ground water concentrations were analyzed on a weekly basis beginning mid February, 1997. Maximum pentachlorophenol concentrations in the groundwater were measured in February at a level of approximately 1 mg/l. The spring and summer months marked a slow decline in aqueous concentrations. Minimum PCP concentration values of 0.2 mg/l were observed in July. Late summer and fall marked the increase in aqueous PCP concentrations and current levels are approximately 2.5 mg/L. Due to the variability in PCP concentrations, measurement of local ground water elevations and rainfall history was instituted to help predict seasonal chlorophenol variations. Observation of ground water elevations in the aquifer system show strong influence by the facility's pumping wells and regional rainfall.

The reactor system was removed and inoculated with cells during the first week of December, 1997. The reactor was modified to include two recirculating flow cells for the characterization of the environmental conditions within the anaerobic and aerobic zones. Redox and pH measurements are coupled to a real time data acquisition system. Chlorophenols and sulfate present in the system are monitored by GC/ECD or IC analyses with space and time.

Current work focuses on the collection of baseline data for the inoculated system with no injection of electron donors or acceptors. Nutrient injection will begin in January, 1998. PCP removal will be evaluated under varying reactor operating conditions (addition of imitation vanilla flavoring, oxygen, sulfate, reactor orientation within the borehole, etc.).

Mineralization of pentachlorophenol was verified in laboratory scale batch bioassays. Experiments were conducted in 250 mL serum bottles under sequential anaerobic/aerobic conditions using imitation vanilla flavoring as the electron donor/primary substrate. Progress curves were developed for replicate reactors using ¹⁴C-labelled PCP or unlabelled PCP. In reactors containing unlabelled PCP, transient production of 2,3,4,5-tetrachlorophenol and accumulation of 3,4,5-trichlorophenol was observed during the initial anaerobic phase. There was no significant removal of ¹⁴C from the aqueous phase in the replicates containing ¹⁴C-PCP under anaerobic conditions. Upon injection of O₂, there was immediate removal of 3,4,5-trichlorophenol in the unlabelled replicates concomitant with a decrease in ¹⁴C in the aqueous phase and a stoichiometric increase of ¹⁴CO₂.

TRAINING AND TECHNOLOGY TRANSFER

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

Goal: To promote training activities related to lead paint contamination and disposal.

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

Approach: The Lead Training Center is a consortium with the University of California Extension Program in Hazardous Materials Management and is funded by the EPA.

Status: The Center conducted 16 workshops within Oregon, Washington, and Idaho during 1997.

Workshop Type	Location	Date
Lead Inspector	Boise, ID	Jan. 27-29
Lead Risk Assessor	Boise, ID	Jan. 30-31
Lead Inspector	Corvallis, OR	March 3-5
Lead Risk Assessor	Corvallis, OR	March 6-7
Supervisors and Contractors	Portland, OR	May 6-9
Lead Inspector	Portland, OR	May 12-16
Lead Worker	Portland, OR	May 19-20
Lead Worker	Eugene, OR	June 9-10
Lead Worker	Portland, OR	June 30-July 1
Lead Inspector	Portland, OR	July 14-16
Lead Inspector	Seattle, WA	August 4-8
Lead Inspector	Eugene, OR	September 15-19
Lead Inspector	Portland, OR	October 13-15
Supervisors and Contractors	Portland, OR	October 20-23
Lead Inspector	Seattle, WA	November 10-14
Supervisor and Contractors	Seattle, WA	November 17-20

Continuing Education: Kenneth J. Williamson, Oregon State University

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

Rationale: Continuing education is needed to support professionals seeking training and education in the State of Oregon.

Approach: A certificate of completion program is offered in the Portland area which involves a curriculum of six courses taught on a two-year cycle.

Status: Two courses were offered during 1997. The program is presently being modified to include more community college participation.

Conference Sponsorship: Kenneth J. Williamson, Oregon State University

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

Rationale: Conferences are a highly effective way to achieve technology transfer.

Status: The Center sponsored or organized sessions for the following conferences:

The 1997 Idaho Regional Conference on Hazardous Materials, April, 1997.

Five Centers Technology Transfer Conference, October 1997.

Fourth International In Situ and On-Site Bioremediation Symposium, Battelle, April 1997.

TECHNICAL OUTREACH SERVICES FOR COMMUNITIES (TOSC) PROGRAM

Goal: The Technical Outreach Services for Communities (TOSC) Program is a community advocacy project designed to aid communities confronted with environmental contamination by hazardous waste sites.

The TOSC program is conducted with a staff of faculty, consultants, and research assistants including:

- Kenneth J. Williamson, Director
- Anna Harding, Associate Professor, Department of Public Health, Oregon State University
- Christopher Blakeman, Graduate Student, Department of Public Health, Oregon State University
- Alexandra Degher, Graduate Student, Department of Civil, Construction, and Environmental Engineering, Oregon State University
- Mary Masters, Technical Outreach Specialist
- Janet Gillaspie, Consultant

Rationale: TOSC provides interested community groups with technical information and assistance that can enable early and meaningful public participation in decisions which affect their health and welfare. The TOSC program also provides a viable alternative strategy for

Superfund-affected communities who do not qualify for a Technical Assistant Grant (TAG) from the US Environmental Protection Agency.

The TOSC program provides assistance to communities with an emphasis upon the following areas:

- remediation technologies
- health effects of exposure to hazardous substances
- risk assessment
- hazardous waste regulations and legislation

Approach: The Western Region's TOSC program is one of five nationally instituted community outreach pilot programs. Centered at Oregon State University, the TOSC team is comprised of university faculty and staff, as well as contracted environmental professionals, who specialize in civil and environmental engineering, risk communication, public health, information transfer, and community relations. Since its inception in 1994, the TOSC team has provided communities in northern and southern California and central Washington with technical assistance in efforts to help community residents gain a greater understanding of the effects of hazardous waste sites in their communities. Such information is provided through workshops, community meetings, and various other educational resources. TOSC also aided these communities in breaking the barriers of communication with local, state, and federal agencies.

Status: Activities during 1997 were as follows:

South Phoenix, Arizona: Assistance is being provided to Don't Waste Arizona (Steve Brittle), Phoenix, Arizona concerning impacts upon the community from a fire at the Quality Printed Circuits Co. (QPC) site in 1992. Environmental sampling was initiated in 1996 by EPA Region IX based upon health concerns by the community. Work includes:

- Review of EPA sampling plan and sampling results
- Development of cluster analysis of community mortalities
- Review of mortality report by Arizona Dept. of Health Services
- Tabulation and analysis of questionnaires from existing health study
- Analysis of data about chemical inventories before fire at QPC facility

Progress to Date: The statistical analysis of existing health study is underway by comparing census tract mortality data prior to and following event. TOSC has received DRAFT Final Report of present sampling from Region IX, EPA, and will provide review and comment.

Ketchikan, Alaska: *On Hold As of 12/1/97* Assistance is being provided to a citizen group (Eric Hummel) concerning hazardous material releases to the bay from the Ketchikan Pulp mill. A remediation plan is presently being developed by Ketchikan Pulp Company under EPA and Alaska Department of Environmental Conservation.

Progress to Date: TOSC met with community to develop work plan; however, efforts to consolidate community concerns and representation have not been successful. TOSC is awaiting further progress and notification from community representatives.

Sitka, Alaska: Continue work with Citizen's Advisory Committee, Sitka, Alaska (Bill Janes, DEC), related to hazardous material releases from Alaskan Pulp mill. Work involves:

- Review sampling plan and risk analysis from Foster Wheeler, consultants for Alaska Pulp Company
- Education of the community about health problems associated with low level dioxin exposure and recommended residual concentrations
- Review health analyses by Alaskan Department of Health
- Review of remediation plan to be developed

Progress to Date: Reviewed sampling plan for land and water sampling sites. Conducted educational program related to hazards associated with low level dioxin exposure. Presently reviewing sampling results and risk assessments.

Oakland, California: Continue work with Citizen's Advisory Committee, Environmental Services, City of Oakland, Oakland, California. Work involves:

- Development of soil cleanup matrix based upon major chemical(s) of concern for use with Oakland Brownfield sites
- Conduct a series of meetings involving City personnel, the Citizen's Advisory Committee, and other involved citizens related to adoption of soil cleanup matrix and limited risk cleanup strategies.

Progress to Date: Conducted an educational workshop on soil cleanup levels and risk assessment. Worked with CAC and Environmental Services personnel in five meetings to seek agreement concerning adopting a cleanup matrix driven remediation program for Brownfield sites. TOSC provided an analysis of the city's Urban Land Redevelopment programs. TOSC will provide assistance to the city in public education and outreach regarding the Urban Land Redevelopment programs.

Casmalia, California: Continue work with local citizen group associated with the Casmalia Resources Hazardous Waste facility. Work involves:

- Assistance with development of active involvement with PRPs
- Review of consent decree issued by Region 9, EPA, for the Casmalia facility

Progress to Date: Reviewed background material. TOSC assisted the community in review of consent decree and provided information to the community on the necessary steps to become incorporated as a non-profit organization. Presently attempted to integrate community group with PRPs in charge of site maintenance.

North Island Naval Station, San Diego, California: Continue work with the North Island Naval Station Restoration Advisory Board (RAB). Work involves:

- Review of contractor reports and documents for RAB
- Attend RAB meeting to comment on proposed remediation plans

Progress to Date: Provided input at several RAB meetings including review of background information. TOSC provided technical assistance related to incineration option, risk of worker exposure to TCE, and management of contaminant migration to the Bay. TOSC will provide review and assessment of proposed remediation plans for other areas of site.

Los Angeles, California: Began work with Los Angeles Restoration Advisory Board (RAB). Work to be determined.

Progress to Date: Contacted RAB and starting to develop proposed working agreement.

Tustin, California: Providing assistance to established RAB dealing with remediation activities at a Marine Corps Air Station. RI/FS completed. TOSC assistance involves:

- Review and comment on RI/FS documents
- Ongoing educational programs for RAB members related to remediation plans and activities

Progress to Date: Document review underway. TOSC conducted presentation at RAB related to review of options.

Bayview-Hunters Point, California: In process of initiating assistance to the Southeast Alliance for Environmental Justice (SAEJ) community advocacy group. Issues of concern is related to planned Brownfields redevelopment of Hunters Point Naval Base near San Francisco. TOSC may provide:

- Review of Phase I site assessment data being used to direct redevelopment plans
- Other potential assistance being negotiated at this time

Union Hills Subdivision, Phoenix, Arizona: Assisting neighborhood citizens group to investigate “sick building syndrome” type illness associated with some subdivision residences. Chemical exposures are likely causative factor of some resident morbidity; however, a source, or sources, are unknown following Arizona Dept. of Environmental Quality and U.S. EPA investigations. Work to include:

- Provide information regarding chemical sensitivities, and names of experts in this field to community leaders
- Review EPA’s investigation documents

Progress to Date: Information from chemical sensitivity literature search and review, names of nationally recognized researchers and physicians have been sent to community. Document review completed, preparing draft assessment report.

Eastern Michaud Flats NPL Site, Pocatello, Idaho: Assistance is being provided to a local non-profit community group, the Portneuf Environmental Council (PEC), concerning an ongoing U.S. EPA *Superfund* project. Remediation involves contaminant assessment and mitigation at two operating commercial phosphorus production facilities. Work to include:

- Review of air risk assessment for the site

Progress to Date: Document review initiated. Assessment of EPA airborne contaminant sampling and analysis to be drafted.

1997 WRHSRC PUBLICATIONS

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

A. Refereed Journal Articles

Anderson, J. E. and P.L. McCarty, "Effect of Chlorinated Ethenes on S_{min} for a Methanotrophic Mixed Culture," *Environmental Science and Technology*, **31**(8), 2204-2210 (1997).

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- Kitanidis, P.K., "A Variance-Ratio Test for Supporting a Variable Mean in Kriging," *Mathematical Ecology*, **29**(3), 335-348 (1997).
- Kitanidis, P.K. and B.B. Dykaar, "Stokes flow in a slowly varying two-dimensional periodic pore," *Transport in Porous Media*, **26**(1), 89-98 (1997).
- Lang, M.M., P.V. Roberts, and L. Semprini, "Model Simulations in Support of Field Scale Design and Operation of Bioremediation Based on Cometabolic Degradation," *Ground Water*, **35**(4), 565-573 (1997).
- Lin, J.S. and L. Hildemann, "A Generalized Mathematical Scheme to Analytically Solve the Atmospheric Diffusion Equation with Dry Deposition," *Atmospheric Environment*, **31**(1), 59-71 (1997).
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B. Articles Submitted or in Press

Abrams, R.H., K. Loague, and D.B. Kent, "Development and testing of a compartmentalized reaction network model for redox zones in contaminated aquifers," submitted 1997.

Cao, J., and P.K. Kitanidis, "Adaptive finite-element simulation of Stokes flow in porous media," *Advances in Water Resources*, in press.

Donaldson, J.H., J.D. Istok, and K.T. O'Reilly, "Dissolved Gas Transport in the Presence of a Trapped Gas Phase: Experimental Evaluation of a Two-Dimensional Kinetic Model," *Ground Water*, in press.

Haggerty, R. and S.M. Gorelick, "Modeling mass transfer processes in soil columns with pore-scale heterogeneity," *Soil Sci. Soc. Am. J.*, in press.

Keller, A.A. and P.V. Roberts, "High Resolution, Non-destructive Measurement and Characterization of Fracture Aperture," submitted 1997.

Khaodhiar S., M.F. Azizian, and P.O. Nelson, "Removal of Hexavalent Chromium, and the Effects of Competing Cations and Anions in a Magnetite-Coated Sand, Synthetic Groundwater System," submitted 1997.

McCarty, P. L., M.N. Goltz, G.D. Hopkins, M.E. Dolan, J.P. Allan, B.T. Kawakami, and T.J. Carrothers, "Full-Scale Evaluation of *In Situ* Cometabolic Degradation of Trichloroethylene in Groundwater through Toluene Injection," *Environmental Science and Technology*, in press.

Semadeni, M., P.-C. Chiu, and M. Reinhard. "Reductive Transformation of Trichloroethene Catalyzed by Cobalamin: Reactivities of the Intermediates Chloroacetylene, Acetylene, and the Dichloroethylene Isomers," submitted 1997.

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D. Project Reports

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- Hopkins, G. D., M.N. Goltz, J.P. Allan, M.E. Dolan, and P.L. McCarty, "Full-Scale In-Situ Cometabolic Biodegradation of Trichloroethene-Contaminated Groundwater through Toluene Injection," Extended Abstract, American Chemical Society, Div. Environmental Chemistry, San Francisco, 233-235 (1997).
- Lowry, G.V., P.V. Roberts, W. McNab, and M. Reinhard, "Catalytic Reduction of Halogenated Ethenes, Ethanes and Methanes Using Hydrogen and a Palladium Catalyst," American Chemical Society National Meeting, San Francisco, Spring 1997.

Munakata, N., W. McNab, W. Haag, P.V. Roberts, and M. Reinhard, "Effects of Water Matrix on Pd-Catalyzed Hydrodehalogenation," American Chemical Society National Meeting, San Francisco, Spring 1997.

F. Theses/Dissertations

Hamamura, N., *Chloroform Cometabolism by Butane-grown Bacteria: Diversity in Butane Monooxygenases*, M.S. Thesis, Oregon State University, Corvallis, OR (1997).

Lin, J.S., *Derivation and Evaluation of Analytical Pollutant Dispersion-Deposition Models*, Ph.D. Dissertation, Department of Civil Engineering, Stanford University, Stanford, CA (1997).

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