



WESTERN REGION
HAZARDOUS SUBSTANCE RESEARCH CENTER

1989 ANNUAL REPORT

Stanford University
Oregon State University

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I. WESTERN REGION HAZARDOUS SUBSTANCE RESEARCH CENTER

II. CENTER DIRECTOR

Perry L. McCarty
Department of Civil Engineering
Stanford University
Stanford, CA 94305-4020
(415) 723-4131

III. 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. This includes 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, 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 rapidly 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 all aspects of hazardous substance usage and disposal.

The research and training activities focus on the major hazardous substance problems in EPA Regions 9 and 10, including chlorinated and non-chlorinated solvents, petroleum products, pesticides, and toxic inorganic ions 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.

Faculty members currently participating in the Center's research, training, and technology transfer activities are listed in Table 1. The budget for the first year of Center activity is contained in Table 2.

Table 1. Faculty Members Participating in the WRHSRC

Name	Title	Research and Teaching Interests
Stanford University		
David L. Freyberg	Associate Professor	Hydrology
Dunja Grbic'-Galic	Associate Professor	Microbiology
Steven M. Gorelick	Associate Professor	Hydrogeology
Peter K. Kitanidis	Associate Professor	Water Resources, Hydrology
James O. Leckie	Professor	Heavy Metals, Nuclear Waste
Perry L. McCarty	Professor	Environmental Engineering
Martin Reinhard	Professor, Research	Organic Chemistry
Paul V. Roberts	Professor	Physical/Chemical Processes
D. Werner North	Consulting Professor	Risk Assessment
Oregon State Univ.		
Jonathan D. Istok	Assistant Professor	Water Resources, Hydrology
Peter O. Nelson	Associate Professor	Chemical/Biological Processes
Kenneth J. Williamson	Professor	Physical/Biological Processes
Sandra L. Woods	Assistant Professor	Biological Transformations

Table 2. Center Budget for the year beginning February 27, 1989.

	FY 1989 FUNDS	FUNDS TO DATE
EPA: Centers Program	\$1,000,000	\$515,007
EPA: Other	0	0
Other Federal	130,000	0
Consortium	207,513	101,598
Non-Federal	186,467	72,211
TOTAL	\$1,523,980	\$688,816

IV. CENTER DIRECTOR'S REPORT

The Western Region Hazardous Substance Research Center is focusing its activities on the development of alternative and advanced processes for treatment of hazardous substances in the surface and subsurface environment. Development of a greater understanding of processes governing the movement and fate of contaminants in ground water, and the development and evaluation of schemes for ground water clean up represents a major focus of the Center's current activities. There are several reasons for this focus. One is that ground water contamination is among the major current environmental problems with hazardous substances in the western region and the nation

as a whole. The team of researchers assembled in the Center have a long history of research on ground water problems, so this is a well suited topic for the Center to address. In addition, this focus complements very well the focus of other research centers that address hazardous substance problems, both within Regions 9 and 10 and in other parts of the country. By carefully focusing on a small set of the several environmental problems of significance, a better possibility for solving important, but complex problems, results. This focus has allowed us to develop a team of researchers from several different disciplines whose combined expertise is vital to successfully resolve the complex physical, chemical, biological, and geological facets of the problem.

In addition to subsurface contamination, the Center is addressing the development of new treatment systems that are capable of removing, concentrating, and if possible, destroying hazardous substances. Such processes are urgently needed in order to treat hazardous-substance- containing waste streams from industries and municipalities. The Center's studies on ground water are helping to define new processes that have good potential for application in surface treatment systems as well. For example, studies on ground water processes have lead to the finding that there are naturally occurring microorganisms with the capability to destroy man-made organic chemicals that were previously believed to persist in the natural environment. Often these microorganisms grow slowly, or degrade the compounds fortuitously by co-metabolism while consuming other organic materials for food. Efforts are being made to capture this natural ability in engineered systems so that the reaction rates can be greatly increased and the overall process can be better controlled. The development of such advanced treatment systems requires new engineering concepts and increased knowledge about the physical, chemical, and biological processes involved. Again, a team approach is essential to address the various difficult issues inherent in complex technology development.

The Center was initiated in the Spring of this year with 14 separate projects, six to address subsurface contamination, four to focus on above ground treatment systems, and four to research basic mechanisms of hazardous substance removal and transformation that are applicable both in above ground and subsurface treatment systems. Three of these are supported by industry. Since its inception, five additional projects have been added to the Center's activities, one is funded by the U.S. Department of Navy, and the others are funded by industry. Industries have found the interdisciplinary activity fostered by the Center to be beneficial to the solution of their environmental problems. This is anticipated to be a strongly positive aspect of the Center's program.

In addition to research, the Center has fostered training and technology transfer initiatives. Through Kenneth Williamson, Head of this program, training and technology transfer needs throughout the region-pair were determined through many discussions with state and federal regulatory agencies and from input by the Center's Training and Technology Advisory Committee. One need is for the development of a university-based continuing- education hazardous substance training program, and another is the establishment of an annual hazardous substance conference in the Northwest region, similar to programs presently in operation in California. Another is a series of seminars to present results of research that has direct application in the field. Initiatives in this direction this year have been two short courses on hazardous substance chemistry and management in Oregon, and an advanced workshop on chemical transformations in

ground water and biological approaches to in-situ remediation. In addition, an International Conference on Processes Governing the Movement and Fate of Contaminants in the Subsurface Environment was cosponsored by the Center and the International Association on Water Pollution Research and Control. These various training and technology activities are vital to the rapid implementation of research findings, which is of great importance today because of the newness and complexity of the hazardous substance problems.

V. HIGHLIGHTS FOR 1989

Ground water contamination continues to be one of the country's most pressing environmental problems. Contamination has resulted from a variety of past activities including seepage from waste storage lagoons and dumps, accidental spills, and leaking underground storage tanks. While preventive measures are now being taken to reduce the incidence of such contamination, the country is faced with the consequences of poor waste practices in the past. Indeed, the majority of designated and potential super fund sites have ground water contamination as the major health concern. The WRHSRC has several research activities with the goal of better understanding the movement and fate of chemicals in subsurface systems, and the development of engineered processes for cleaning contaminated ground waters. Two of the research areas being pursued are highlighted here. Also as a highlight, the Center co-sponsored at Stanford an international conference which brought the leading scientists and engineers together to address important ground water contamination issues. This is also discussed in the following.

Research Highlights

Among the most prevalent ground water contaminants are chlorinated organic solvents, such as trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA), gasoline and other petroleum hydrocarbons including benzene, toluene, and xylene (BTX), and a broad group of homocyclic and heterocyclic aromatic compounds that are associated with preserving wood. The latter include polynuclear aromatic hydrocarbons (PAH) and pentachlorophenol (PCP). In the past, most of these compounds were thought not to be degraded by natural biological processes under the environmental conditions existent in soils and groundwaters. In recent years, however, research by the WRHSRC faculty and others has clearly demonstrated that this is not the case. Native bacteria often can adapt to these potentially harmful and persistent chemicals, and either mineralize them to harmless inorganic end products, or transform them into other chemicals, which may or may not be less harmful than the parent chemical.

A major emphasis in the Center's activities is to obtain greater knowledge of natural biological processes, both to obtain a better understanding of how hazardous chemicals move in the natural environment and to take advantage of the natural processes in engineered systems for contaminant control. Biological degradation is particularly

attractive as it has the potential for ridding the environment of harmful chemicals, rather than simply moving them from one location to another. In order to apply biological treatment at contaminated sites, knowledge of interrelated chemical, physical, and geological phenomena is required and research by an interdisciplinary team is essential. There are two particularly exciting research areas that have stemmed from past studies at the Center and elsewhere, and are highlighted here. One is the use of methanotrophic bacteria for in-situ biodegradation of chlorinated solvents. The other is research on the natural degradation of aromatic hydrocarbons in the absence of oxygen.

In-Situ Biodegradation of Chlorinated Solvents

About 10 years ago, the chlorinated solvents including TCE and TCA were not considered to be biodegradable. Since then, through research at the Center and elsewhere, it was observed that TCE and TCA sometimes disappear slowly in ground water. This was found to be the result of both biological and chemical processes that occur in the absence of oxygen (anaerobic processes). The transformations result generally in formation of other less-chlorinated products. For example, TCE is biologically reduced to dichloroethylene (DCE) and vinyl chloride (VC), while TCA is biologically reduced to 1,1-dichloroethane (1,1-DCA) or chemically converted to 1,1-dichloroethylene (1,1-DCE) and acetic acid. In some instances, complete mineralization to harmless end products can occur, but often the final step occurs so slowly that it is difficult to make use of it in an engineered system.

EPA researchers John T. Wilson and Barbara Wilson reported in 1985 from experiments with soils that TCE degradation occurred when oxygen and natural gas were added to soil. This important finding was shown to result from growth of methanotrophic bacteria that consume methane and oxygen in order to derive energy for growth. Fortuitously, the enzyme (MMO) used by these organisms to oxidize methane, also initiates the oxidation of TCE by the process of co-metabolism. Subsequently, the TCE intermediate formed is chemically hydrolyzed and the products are converted by other bacteria to harmless end products. A four-year laboratory and field study to evaluate the potential for this complex process at the Moffett Naval Air Station in Mountain View, California, and supported by EPA has just been completed by Center faculty. The objective was to obtain a basic understanding of the biological, chemical, and physical processes involved, to demonstrate the potential for the process at field scale, and to develop methodologies for application of the process to contaminated sites. Methanotrophic bacteria were found to be naturally present at the field site, and when stimulated to grow by the addition of methane and oxygen dissolved in water, they degraded TCE, DCE, and VC. The latter were degraded faster and more completely than the former. Because of the success of this research, several Center projects are now underway to obtain greater fundamental understanding of the several processes involved, and to speed the application of this in-situ bioremediation method at contaminated sites.

An industrial site has been located in Michigan that has good potential for an initial full-scale application of the methanotrophic process. The engineering and economic feasibility of applying the process here is being evaluated through a Center project funded with an industrial contract with the company involved and additional EPA

support. Through natural biological processes, TCE at this site has been transformed in the ground water into DCE and VC, compounds that are degraded faster than TCE itself by the methanotrophic process. Subsurface samples have been obtained with the aid of the EPA Ada, Oklahoma, laboratory in order to determine whether the methanotrophic bacteria of interest are naturally present in this system, and their respective rates of chemical transformations. A computer model is being used in order to evaluate alternative ways for adding methane and oxygen, and to select the best operating procedures for the system.

One of the significant findings from past studies is the important effect of sorption of contaminants onto ground water minerals on their rate of movement. A new finding is the relatively slow rate that some chemicals desorb from ground water minerals, a fact that has important implications for any engineered solution to a contamination problem as well as for in-situ biodegradation. The sorptive properties of aquifer material at the Michigan site is being studied because of this need. In addition, two Center projects are specifically addressing the question of just how sorption affects the rates of biological degradation.

In many subsurface clean-up schemes, contaminated water is pumped to the surface, and volatile organic compounds such as TCA, TCE, DCE, and VC and air stripped and transferred either to the air or onto sorbing material such as activated carbon. Vapor extraction is another process used. Biodegradation of the contaminants so removed in an above ground surface reactor could lead to their destruction, thus achieving a permanent remedy. Toward this end, one industrially-funded Center project is developing basic information on mass transfer and kinetics of biodegradation of chlorinated solvents for application in surface reactors. As already indicated, contaminant degradation by methanotrophs is a co-metabolic process. In the usual biological treatment process, bacteria use the organic contaminants directly for energy and growth, and in so doing, the contaminants are destroyed. However, in the co-metabolic process, the organism gains no advantage from co-metabolism of the compound. A separate energy source, such as methane, must be supplied. The co-metabolized compound competes for the enzyme used by the organism to oxidize the energy source, and this complicates the resulting reaction kinetics. Understanding of how best to take advantage of co-metabolism in treatment systems and of the limitations involved is very primitive, but the practical implications of being able to do so is great. By learning how to capture the co-metabolic abilities of organisms, we may be able to biologically degrade many of the xenobiotic chemicals that are creating such environmental problems today. Thus, this area of research has great potential for the future.

In order to implement engineered systems to reduce ground water contamination, strategies are needed to detect and assess the presence of ground water contaminants and to design reliable and cost-effective mitigation schemes. Two Center projects are directed towards satisfying these needs. The projects are directed specifically to consider the great uncertainties involved in ground water remediation because of the complexity and variability of subsurface geology. These studies will aid in the design of in-situ bioremediation schemes, such as methanotrophic oxidation, as well as other clean-up approaches.

Such studies by the WRHSRC cover short-term and long-term needs for the remediation of contaminated groundwaters and for treatment of contaminated water supplies as well. The approach we are taking is to develop a basic understanding of the physical, chemical, and biological processes involved, and to develop as rapidly as possible engineered applications that make use of these processes. The new approach of using co-metabolism for degradation appears very promising for permanent disposal of chlorinated solvents, which are among the most prevalent, difficult, and costly hazardous substance problems before the country.

Anaerobic Biological Transformations of Aromatic Compounds

Leakage of gasoline and other petroleum hydrocarbons represents another major source of subsurface contamination. Of the many components in gasoline, the compounds benzene, ethyl benzene, toluene, and xylene (BTX) are the most soluble in water and thus are the ones most commonly found as ground water contaminants. These aromatic compounds, so named because they all contain the benzene ring structure, are readily degraded by bacteria when oxygen and other inorganic nutrients required for bacterial growth are present. However, oxygen often is deficient in ground water because of lack of contact with air, and for this reason, aromatic compounds often persist for years. Just 10 years ago, biotransformation of aromatic hydrocarbons was not considered possible under these anaerobic conditions. Recently, however, through research conducted Center faculty and others, it has been clearly demonstrated that natural microorganisms exist that can degrade aromatic hydrocarbons such as BTX in the absence of oxygen. The rates are slow, and very little is known about the microorganisms involved or of their biochemistry. Through previous studies by Center faculty and their students, disappearance of BTX under anaerobic conditions was first observed at landfill leachates from North Bay, Canada, and was confirmed through laboratory studies.

Aromatic hydrocarbons are also common contaminants in wood preservatives, such as creosotes, and in wastes from consumer-gas production plants, widely used in the past. Recent studies by Center faculty have demonstrated some of the aromatic hydrocarbons in these wastes are also slowly degraded in ground water under some conditions. Anaerobic degradation of pentachlorophenol, which is another important wood preservative, has also been found. The recent observations that other highly chlorinated aromatic compounds such as polychlorinated biphenyls (PCBs), can be transformed in the absence of oxygen as well, has led to considerable interest in the anaerobic process. Indeed, chlorine atoms from highly chlorinated compounds are often removed faster under anaerobic conditions than aerobic conditions.

These very recent and important findings indicate that under the proper conditions, some ground water contaminants of concern will naturally disappear with time so that no costly remediation will be required. If we had the ability to predict when and where such degradation would occur, then scarce financial resources could be used elsewhere to solve more intractable problems. Also, the potential exists for engineered approaches to speed along these natural processes. This requires a much better scientific understanding

of the microorganisms involved, pathways of degradation, and factors affecting rates of reaction. Several of the Center projects have this objective in mind.

In aerobic systems, bacteria use oxygen to oxidize organic compounds for energy. In the absence of oxygen, there are bacteria that can use alternative oxidants (electron acceptors) such as nitrate, sulfate, or carbon dioxide. The bacteria capable of using these different oxidants are themselves quite different as is their biochemistry. A potentially important group of anaerobic bacteria are the sulfate reducers for sulfate is commonly found in ground water. However, knowledge about their ability to degrade aromatic compounds is almost non-existent. For this reason, three Center projects are concerned with biotransformation of aromatic compounds under sulfate reducing conditions. One is directed towards evaluating the degradation of chlorinated aromatic compounds in pulp mill bleaching effluent, and the other is directed towards the polycyclic compounds (PAHs) that are commonly present at creosote sites and consumer gas plants. Another Center project funded by the U.S. Navy and the Orange County Water District is directed towards understanding factors affecting rates as well as nutrient requirements in BTX destruction by the different groups of bacteria that use nitrate, sulfate, or carbon dioxide as oxidants. These studies are difficult because of the necessity to exclude oxygen from the cultures, and the slow rate of organism growth and adaptation to these newer compounds. However, because of the long residence times of ground waters, transformation processes that are very slow can be quite significant, and thus are worth understanding. In spite of the slow and complex nature of this research, significant progress is being made.

International Symposium

A significant event co-sponsored by the Center this year was the International Symposium on Processes Governing the Movement and Fate of Contaminants in the Subsurface Environment. This three-day meeting, held at Stanford University on July 23 to 26, 1989, was also sponsored by the International Association on Water Pollution Research and Control, with financial support from EPA, the National Science Foundation, and the U.S. Geological Survey. The purpose of the meeting was to bring together leading research scientists and engineers from around the world to evaluate the current knowledge about the processes that affect the way in which chemicals interact with the soil, move with the flow of water and air through the subsurface environments, and are transformed or degraded by both abiotic and biotic processes. A total of 175 individuals attended the meeting, including 28 foreign participants from 14 different countries. Included were 35 oral and 40 poster presentations.

The symposium focused on the physical, chemical, and biological processes that are most important to chemical migration and transformation in both the saturated and unsaturated zones. There was considerable scientific interaction at this meeting, and it helped considerably in sharpening the focus of the Center faculty, staff, and students on the important issues requiring further research. The symposium was highly successful in meeting its objectives.

VI. SUMMARY OF ONGOING PROJECTS

A listing of the research and training programs is provided in Table 3. A summary description of each project follows.

Table 3

**WESTERN REGION HAZARDOUS SUBSTANCE RESEARCH CENTER
PROGRAM SUMMARY**

(Dates shown indicate estimated date of final reports)

RESEARCH PROGRAM SUMMARY

Above Ground Treatment Systems

Reinhard, McCarty, Roberts, Grbic'- Galic', Leckie	1992	Treatment of Complex Mixtures
McCarty, Roberts	1992	Oxidation of Chlorinated Solvents by Methanotrophs
Woods	1992	Interactions between Electron Acceptors in the Treatment of Wastewaters Containing Sulfate, Chlorophenols and Acetate
Williamson, Nelson	1991	Enhancing Biodegradation with Sorption and Alternating Aerobic/Anaerobic Environments

Subsurface Assessment and Treatment

Kitanidis	1992	Detection and Assessment of Subsurface Contamination
Gorelick	1992	Design of Reliable and Cost-Effective Mitigation Schemes
Roberts, Kitanidis	1992	Spatial Distribution and Mass Transfer of an Organic Liquid Contaminant in a Porous Medium
Reinhard, Roberts	1992	Gaseous Stripping of Nonaqueous Liquids from the Vadose Zone

Istok, Woods	1992	Development and Verification of a Numerical Model to Predict the Fate and Transport of Chlorinated Phenols in Groundwater
McCarty, Reinhard	1992	In-Situ Biological Treatment of Aromatics in Groundwater
McCarty, Roberts	1990	In-Situ Bioremediation of Chlorinated Aliphatics with Methanotrophs
Reinhard, McCarty	1990	The Effect of Surfactants on Biodegradation of Chlorinated Biphenyls in Soils
Kitanidis, Freyberg	1990	FASTCHEM© Applications and Sensitivity Analysis
Reinhard, McCarty	1993	Long-Term Chemical Transformation of 1,1,1-Trichloroethane (TCA) and Freon 113 under Aquifer Conditions

Mechanistic Studies

Grbic'-Galic'	1992	Anaerobic Microbial Transformation of Homocyclic and Heterocyclic Polynuclear Aromatic Hydrocarbons
McCarty, Roberts	1992	Effects of Sorption on Biodegradation of Halogenated Organics
Leckie	1992	Trace Metal Removal Processes
Reinhard	1989	Abiotic Dehalogenation of Haloaliphatic Compounds in Aqueous Solutions Containing Hydrogen Sulfide

TRAINING AND TECHNOLOGY TRANSFER PROGRAM SUMMARY

Symposiums

McCarty, Roberts	1989	International Symposium on Processes Governing the Movement and Fate of Contaminates in the Subsurface Environment
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Courses

Williamson, Nelson	1989	Fundamentals of Chemistry of Hazardous Substances
Williamson, Nelson, Istok, Woods	1989	Fundamentals of Hazardous Substances

Workshops

Grbic'-Galic', McCarty, Roberts, Semprini	1989	Biological Transformation of Chlorinated Solvents in Subsurface Systems
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RESEARCH PROJECT DESCRIPTIONS

Treatment of Complex Mixtures: Martin Reinhard, Perry L. McCarty, Paul V. Roberts, Dunja Grbic'-Galic', and James O. Leckie, Stanford University (funded by EPA).

Goal: The long term goal of this project is to develop a computer based information system which can be used to develop criteria for choosing appropriate treatment combinations for complex wastes.

Rationale: Waste streams and waters containing complex mixtures generally cannot be treated using a single treatment process. Depending on the types of contaminants present and their physical, chemical and biological properties, combinations of several different processes must be employed.

Approach: Our approach is to develop a computerized data base which may be used to retrieve or to estimate the compound properties that are relevant for assessing their behavior in treatment systems, such as physico-chemical properties of contaminants, energetics concepts for evaluating the thermodynamic feasibility of biotransformations, and correlations for estimating mass transfer rate coefficients.

Status: Presently, we are implementing two chemical information systems, EICHEM and SECHEM, which were previously developed at the Technical University in Munich. Dr. Drefahl, the developer of the two systems, has joined the Center and is currently in the process of setting them up at our laboratory. EICHEM is capable of estimating a range of environmentally relevant substance properties, such as n-octanol/water partition coefficients, vapor pressure, and heat of evaporation, on the basis of substituent constants. SECHEM is designed to evaluate contributions of substructures based on discriminant analysis techniques and a test set of data. Work during this project period will focus on the implementation of algorithms which consider the effect of solution

variables, such as cosolutes, temperature, pH, ionic strength, on solute properties. In future work we will develop programs for the evaluation of contaminant behavior in treatment processes.

Oxidation of Chlorinated Solvents by Methanotrophs: Perry L. McCarty and Paul V. Roberts, Stanford University (funded by the Gas Research Institute)

Goal: Methanotrophic bacteria, which oxidize methane for energy, have been found capable of oxidizing chlorinated solvents by co-metabolism. The goals of this project are: (1) to obtain a better basic understanding of the relationship between the relative concentrations of methane and chlorinated compounds, and the overall chlorinated solvent degradation rate, (2) to assess the importance of mass transfer limitations to methanotrophic reactions, and (3) to use the knowledge gained about reaction kinetics and mass transfer limitations to determine the most suitable reactor design for enhancing chlorinated solvent degradation.

Rationale: There are many current attempts to devise treatment processes for degrading chlorinated aliphatic compounds. However, there is a lack of basic understanding of the factors affecting reaction rates for co-metabolized compounds. In addition, since the energy substrates, methane and oxygen, and the contaminants are all poorly soluble in water, mass transfer properties of treatment systems becomes of great significance.

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

Status: Preliminary laboratory studies have been conducted to determine basic reaction coefficients for methane and trichloroethylene utilization alone by methanotrophs. Model calculations have been carried out for a fluidized bed reactor, and results are being evaluated to determine where knowledge gaps may exist.

Interactions between Electron Acceptors in the Treatment of Wastewaters Containing Sulfate, Chlorophenols and Acetate: Sandra L. Woods, Oregon State University (funded by EPA)

Goal: The goal of this project is to develop and verify a mathematical model for anaerobic biodegradation in the presence of competing electron acceptors. Biodegradation constants will be measured to describe sulfate reduction, acetate fermentation and reductive dechlorination. Resulting kinetic expressions and constants will be used (1) to develop an effective anaerobic biological treatment process for wastewaters from the pulp and paper industry; (2) to model sequential reductive dechlorination of chlorophenols in soils; and (3) to model the anaerobic/aerobic treatment of chlorophenols in biological wastewater treatment systems.

Rationale: A better understanding of biodegradation in the presence of multiple substrates is needed. Additionally, kinetic constants for biodegradation are necessary to understand the fate of hazardous wastes in soils and to develop bioremediation or wastewater treatment systems.

Approach: Progress curves for compound biotransformation are generated in batch reactor systems, and biodegradation constants are determined by fitting a mathematical model to the progress curves generated under varying initial conditions (concentrations of acetate, sulfate and chlorophenols). The initial biomass is held constant. The reactor system has been designed and constructed to permit strictly anaerobic transfers. The system consists of two 9 liter mother reactors and 2 liter batch reactors. The mother reactors are operated at a 10 hour hydraulic retention time. The first reactor is fed a solution of pentachlorophenol, acetate and nutrients. The second reactor is fed a similar solution except for the addition of sulfate. Progress curves are developed with the 2 liter batch reactors.

Status: Several batch experiments have been conducted. Reductive dechlorination of pentachlorophenol has been observed in the presence and absence of sulfate. Experimental work is continuing to evaluate biodegradation kinetics under varying initial conditions. Completion of the project is expected in February, 1992.

Enhancing Biodegradation with Sorption and Alternating Aerobic/Anaerobic Environments: Kenneth J. Williamson, Peter O. Nelson, Oregon State University (funded by EPA)

Goal: The overall goal of this project is to develop and verify a mass transport and biokinetic model of the sorption and biological degradation of chlorophenols by an aerobic-anaerobic layered biofilm on granular activated carbon.

Rationale: Granular activated carbon (GAC) has been shown useful for enhancing biological treatment of toxic organic compounds by adsorption, resulting in reduced aqueous concentrations to below inhibitory levels. This enables biological degradation by both suspended bacteria and the biofilm attached to the GAC. Haloaromatic compounds undergo different biodegradation pathways under anaerobic and aerobic conditions. Either anaerobic or aerobic pathways may result in the production of metabolites that cannot undergo further metabolism in that particular pathway. It may be possible to increase the potential for biodegradation of these compounds and their

metabolites by alternating their exposure to aerobic and anaerobic conditions. GAC will serve as an adsorbing media for the halogenated organic compounds and their metabolic products that do not undergo rapid biodegradation. GAC will also serve as a support media for the biofilm to allow physical separation from the liquid stream and transfer between aerobic and anaerobic environments with a controlled frequency.

Approach: The project has been broken down into several individual tasks to meet the overall project goal. The tasks are: 1. determine the aerobic biodegradation kinetics of chlorophenols in batch biological reactor experiments; 2. determine the anaerobic biodegradation kinetics of chlorophenols in batch biological reactor experiments; 3. measure the sorption and desorption kinetics and equilibria of chlorophenols on granular activated carbon in complete-mix batch reactors; and 4. investigate the combined sorption-biodegradation of chlorophenols sorbed on GAC in alternating aerobic-anaerobic complete-mix flow reactors; and 5. develop a combined kinetic model.

Status: Experiments are in progress for the first three tasks identified above. Reactors are being designed for the experiments in task four. Individual components of the combined kinetic model are under development for representing the results of aerobic biodegradation, anaerobic biodegradation, and sorption experiments. Expected completion date for the project is February 1991.

Detection and Assessment of Subsurface Contamination: Peter K. Kitanidis, Stanford University (funded by EPA).

Goal: The thrust of this project is the development of better techniques for contaminated-site characterization. Objectives include the development of better methods for the detection and assessment of groundwater contamination and the determination of the mechanisms and parameters which govern the transport and fate of pollutants. Another important objective of this project is to develop practical methods for the determination of the effective properties of heterogeneous media from measurements of the local parameters.

Rationale: There is seldom enough information to determine with certainty the precise values of all parameters, especially at the local scale. Measurements of some critical transport parameters, such as hydraulic conductivity, indicate variability over orders of magnitude over short distances. Other parameters, such as thermodynamic constants and rate coefficients, are quite variable too. In many cases, one is interested in the "effective" parameters of the heterogeneous formation, i.e., those which govern the net or "macroscopic" rate of advection, dispersion, and chemical attenuation, rather than the highly variable local rates.

Approach: The developed approach combines measurements, mechanistic models describing the transport and fate of pollutants, and statistical methods.

Status: Since the project was initiated, we have focused on the determination of the relation between the measurable but highly erratic local parameters and the effective

parameters which govern the flow and solute transport at macroscopic scales of interest. Significant progress was achieved in the problem of effective conductivities. Consider the problem of flow in a porous medium with hydraulic conductivity which fluctuates locally about a mean value. The flow is unsteady but gradually varying, i.e., the scale of head fluctuations is larger than the scale of hydraulic-conductivity fluctuations. We have derived the equations which must be satisfied by the effective conductivity tensor under general conditions using a method of volume averaging and spatial moments. The effective conductivity is defined as the conductivity of a fictitious homogeneous medium which would effect the same rate of spreading on a pressure mound as the actual heterogeneous medium. The key result of the analysis was that the effective conductivity matrix of the hydraulically heterogeneous medium is given by solving a well-defined boundary value problem and carrying out an integration. Even if those have to be performed numerically, this approach is potentially a significant improvement over other numerical methods. We are currently experimenting with a numerical method which takes advantage of the structure of the problem at hand. We are also working on the problem of effective dispersion coefficients.

Design of Reliable and Cost-Effective Mitigation Schemes: Steven M. Gorelick, Stanford University (funded by EPA).

Goal: The aim of this project is to develop and test methods for design of pump-and-treat aquifer remediation systems. These methods can target reliable strategies that identify the best well locations and pumping rates to successfully capture contaminant plumes. Reliable strategies also must be made cost effective by determining the lowest pumping rates that assure contaminant capture.

Rationale: Simulation models can be powerful tools for designing aquifer remediation schemes. Unfortunately, there is tremendous uncertainty associated with our predictive models of subsurface contaminant transport, even for substances whose chemical behavior is well understood. This uncertainty stems from the spatial variability of aquifer properties which dictate flow. Given this uncertainty, one must over design any pump-and-treat system. Knowledge of the nature of simulation model uncertainty and the development of risk-based design strategies are therefore essential.

Approach: The project is being conducted in cooperation with Environment Canada. Our efforts focus on the Gloucester Special Waste Compound in Ontario, Canada. In 1989 work began to design a pump-and-treat remediation scheme for this research site which contains hazardous organic solvents. The best remediation design requires optimal well selection and the determination of optimal pumping rates. We approach the problem by developing stochastic simulation models based upon available field data. Then we combine these models with nonlinear optimization methods in order to identify reliable strategies. Model parameter uncertainty is considered as an indicator of design reliability. In this approach model parameters are first described statistically and these statistical measures of uncertainty are then used to over design the remediation system.

Status: Preliminary analysis of the hydraulic and chemical field data for the Gloucester site has been completed. A stochastic simulation model of the site is currently under development. The model is a two-dimensional plan view finite-element simulation model in which the transmissivity, porosity, and dispersivity are considered the critical uncertain parameters. Geologic characterization is complete and calibration of the model is underway. Completion is expected by 3/92.

Spatial Distribution and Mass Transfer of an Organic Liquid Contaminant in a Porous Medium: Paul V. Roberts and Peter Kitanidis, Stanford University (funded by EPA).

Goal: The goal of this project is to improve understanding of the physical processes that govern the distribution and mass transport of residual organic liquid contaminants in the subsurface, in particular the effects of mass transfer limitation and heterogeneity.

Rationale: These phenomena are believed to influence significantly the design and economics of groundwater quality restoration efforts in situations where immiscible organic liquids have contaminated the subsurface.

Approach: This project will proceed by formulating a conceptual model for the distribution of the residual liquid, applying interphase mass transfer models to the situation of a uniform medium, testing the models against the results of laboratory experiments, and developing mathematical models to simulate behavior in nonuniform media.

Status: The evaluation of mass transfer of residual liquid contaminant phases has commenced with the development of a simple conceptual model which envisions the residual contaminant as being held in the form of pendular rings in the narrow spaces surrounding the solid contact points. We have calculated the relationship between the relative saturation and the interfacial area for various packing geometries under these idealized conditions. A manuscript in preparation summarizes the basic theory and results of the preliminary computations, and points out the implications for groundwater contamination problems. Also, we have succeeded in developing a new modeling approach for simulating transport of a sorbing solute under conditions of spatially variable retardation; a closed-form analytical solution was obtained using the method of small perturbations (Chrysikopoulos, Kitanidis, and Roberts, 1989).

Gaseous Stripping of Nonaqueous Liquids from the Vadose Zone: Martin Reinhard, Paul V. Roberts, Stanford University (funded by EPA).

Goal: The goal of this project is to develop an understanding of the basic processes which govern the behavior of organic vapors in the unsaturated zone.

Rationale: Vapor stripping has become a widely used method for removing volatile organics from the subsurface. However, there is no basis for assessing when conditions

are favorable for this procedure, nor is there any way of predicting the rate of contaminant removal.

Approach: Chromatographic columns packed with aquifer material and model sorbents are being used to simulate vapor phase sorption in the vadose zone. The data will be used to evaluate the existing transport models.

Status: Two similar vapor sorption systems consisting of a soil column connected to a gas chromatographic detector have been constructed and tested. Work with two aquifer materials and several model solids is expected to be completed 3/1992.

Development and Verification of a Numerical Model to Predict the Fate and Transport of Chlorinated Phenols in Groundwater: Jonathan D. Istok and Sandra L. Woods, Oregon State University (funded by EPA)

Goal: The objectives are to develop a numerical model to predict the fate and transport of 2,4-dichlorophenol, pentachlorophenol and their primary anaerobic degradation products in field soils and groundwater aquifers, and to verify the model using laboratory and field experiments.

Rationale: Predictive models are needed for site characterization and to design effective biological remediation strategies.

Approach: A preliminary mathematical model was developed based on processes of advection, dispersion, diffusion, sorption, and anaerobic degradation for each solute species in the anaerobic degradation pathway for pentachlorophenol, an electron donor (acetate), and biomass. Monod kinetics and a "macroscopic bulk concentration" concept is used to describe growth. The resulting set of nonlinear differential equations are solved by the finite difference method. Experiments are conducted using a Chehalis soil in batch reactors, columns, and in large soil tanks consisting of an aluminum box (2 m wide x 4 m long x 20 cm deep) supported by a steel framework. The tanks each hold 1500 kg of soil and are designed to provide controlled temperature, atmosphere, and water pressure and flow rate during long-term (many months) experiments. The tanks are instrumented with pressure and temperature sensors and sampling ports for liquid, solid and gas phases.

Status: Verification of the model in the soil tanks will be completed in February, 1992

In-Situ Biological Treatment of Aromatics in Groundwater: Perry L. McCarty and Martin Reinhard, Stanford University (funded by the U.S. Department of the Navy and the Orange County Water District).

Goal: This project attempts to evaluate the rate of aromatic hydrocarbon biotransformation under methanogenic, sulfate and nitrate reducing conditions under

field and laboratory conditions, and to assess the potential of these processes for aquifer remediation.

Rationale: Although most gasoline constituents are readily degraded under aerobic conditions, the groundwater environment impacted by the gasoline spills is typically anaerobic, thus precluding aerobic degradation pathways. In the absence of oxygen, there is the potential that alternate electron acceptors, such as nitrate, sulfate and carbon dioxide may be utilized.

Approach: This study is a combined field and laboratory study. The laboratory study concerned with anaerobic biotransformation is being conducted at the Center. Laboratory studies concerned with aerobic conditions are being conducted at the Laboratory of the Orange County Water District (OCWD) in Southern California under the direction of Dr. Harry F. Ridgeway. The field study is being conducted at the Seal Beach field site which is near the OCWD laboratory. In the field studies, degradation rates will be determined in 30 L bioreactors which will be emplaced in the ground at the site. Both aerobic and anaerobic conditions will be studied.

Status: The laboratory studies have focussed on the growth conditions of denitrifying microorganisms which utilize aromatic hydrocarbons as their sole carbon and energy source. At the field site, a mobile laboratory is being developed and within the next few months, we will install and instrument the reactors.

In-Situ Bioremediation of Chlorinated Aliphatics with Methanotrophs: Perry L. McCarty and Paul V. Roberts, Stanford University (funded by Bendix Automotive)

Goal: To evaluate the feasibility of remediating a groundwater contaminated with trichloroethylene (TCE), dichloroethylene (DCE), and vinyl chloride (VC) through stimulation of the growth of indigenous methane oxidizing bacteria (methanotrophs).

Rationale: A four-year field study of in-situ biodegradation of chlorinated solvents by methanotrophs at the U.S. Navy Moffett Field site, funded by EPA and conducted by Stanford University, demonstrated the potential of this process for aquifer clean-up. Stimulation of the growth of indigenous methanotrophs at this site by injection of water containing dissolved methane and oxygen resulted in in-situ degradation of chlorinated aliphatic compounds injected into the aquifer. The next step in application to full-scale is a technical and economic evaluation of the feasibility of the process, as is being conducted here.

Approach: A contaminated ground water site in Michigan was found to have suitable conditions of aquifer homogeneity and permeability, distribution of TCE, DCE, and VC contaminants, and access to make in-situ bioremediation attractive. Aseptic samples of aquifer material from two separate wells were obtained from this site through the assistance of the EPA Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma. The possible presence of indigenous methanotrophic bacteria, and their rates of chlorinated chemical transformation is being determined through laboratory studies

with these materials, as is their sorptive properties. Computer simulation models will be used to help design a treatment strategy that will be used by the engineering firm involved in a comparative evaluation of in-situ bioremediation with other treatment alternatives.

Status: Aquifer samples have been obtained, and laboratory studies have been initiated. The feasibility study should be completed within six months.

The Effect of Surfactants on Biodegradation of Chlorinated Biphenyls in Soils:

Martin Reinhard and Perry L. McCarty, Stanford University (funded by Chemical Waste Management, Inc.).

Goal: The goal of this study is to develop a data base which can be used to judge the feasibility of surfactant treatment of PCB contaminated soils, and to study the effect of surfactants on the aerobic biotransformation of PCBs.

Rationale: Addition of surfactants has been proposed as a means to desorb and solubilize hydrophobic contaminants in groundwater aquifers and from contaminated soils. Because sorption of PCBs onto solids may slow or prevent biotransformation, solubilization using surfactants followed by biotransformation is a potential treatment scheme to purify PCB contaminated soils.

Approach: First PCB sorption onto a sorbent such as diatomaceous earth will be studied using a single PCB congener, such as para-chlorobiphenyl (pCB). Then, a microbial culture will be developed (derived from the Palo Alto Sewage Treatment Plant) which is capable of degrading pCB. Finally, the effect of surfactant on the biotransformation rate will be studied with and without solids added.

Status: Currently, analytical quality assurance and control protocols are being developed and current models of the solubilization process are being reviewed. Expected completion date is 9/1990.

FASTCHEM Applications and Sensitivity Analysis: Peter K. Kitanidis and David L. Freyberg, Stanford University (funded by Electric Power Research Institute).

Goal: FASTCHEM is a collection of computer programs which can be used to predict the advection, dispersion, and geochemical transformation of chemicals emanating from utility waste disposal sites. The objectives of the work to be performed include: (1) To quantify the sensitivity and uncertainty of predicted parameters; and (2) to develop a set of computer programs which apply state-of-the art estimation methods for the interpolation of parameters from sparse measurements.

Rationale: Amendments to RCRA in 1984 and reauthorization of SDWA in 1986 have prompted the formulation of several new regulations to protect groundwater quality. In response to new regulations and to develop a capability to assess the potential success of remedial actions, the Electric Power Research Institute (EPRI) has supported the

development of the interim hydrogeochemical modeling package FASTCHEM. This package of codes can be used to simulate the advection, dispersion, and chemical attenuation of inorganic chemicals that may be leached from electric utility waste disposal sites. EPRI is interested in determining the applicability the model and in incorporating subroutines for the utilization of data.

Approach: The model's sensitivity and uncertainty will be evaluated using first-order analysis and Monte Carlo simulations. Methods for incorporating available measurements will be based on linear estimation methods.

Status: Since the project was initiated in September 1989, the computer codes have been installed and tested. Next, the sensitivity and uncertainty of predictions will be evaluated.

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

Goal: This project is designed to determine the transformation rate of TCA and Freon 113 under conditions closely simulating those of a contaminated aquifer.

Rationale: It is generally difficult to determine transformation rates occurring at contaminated field sites from field data because of uncertainty about the input, the variability of the data, and the lack of mass balances. Moreover, extrapolation of laboratory data obtained in pure water to field conditions is fraught with uncertainty, because environmental factors, such as the role of sorption and nucleophilic and redox active reagents, are not considered in pure water experiments. Therefore, laboratory experiments are needed which simulate the natural conditions, and which allow us to determine products, accurate mass balances, and rates.

Approach: TCA and Freon 113 will be added to flame sealed vials which contain groundwater and sediment from the site and the organic contaminants at realistic concentrations. The glass vials will be incubated at ambient temperature and disappearance and product formation will be analyzed at regular intervals over a period of four years.

Status: All quality assurance and control protocols have been developed, the soil and the water have been characterized and the rate experiment will be set up in the near future. Completion date is 1993.

Anaerobic Microbial Transformations of Homocyclic and Heterocyclic Polynuclear Aromatic Hydrocarbons: Dunja Grbic'-Galic', Stanford University (funded by EPA)

Goal: Recently, we demonstrated that monoaromatic hydrocarbons such as toluene and benzene, and some of the nitrogen- and sulfur-heterocyclic polynuclear aromatics such as quinoline or benzothiophene, could be anaerobically degraded by complex microbial

communities derived from ground water aquifers or from municipal sludge, under the conditions of methanogenic fermentation. The goal of this project is to investigate the capabilities of bacteria under two types of strictly anaerobic conditions -- sulfate-reducing and methanogenic -- to transform polynuclear aromatic hydrocarbons (PAH), more complex nitrogen and sulfur heterocycles, and oxygen heterocycles (NSO-compounds). The transformation routes, intermediates, and products are to be studied for single compounds of interest, as well as for mixtures of compounds, such as occur in real contamination incidents.

Rationale: PAH and NSO which are constituents of fossil fuels and creosote, and are also formed through incomplete combustion processes, are common environmental pollutants characterized by relative chemical stability, toxicity, and potential carcinogenicity. These compounds had been shown to efficiently biodegrade due to the activity of aerobic microorganisms, in the presence of molecular oxygen which serves as a reactant for the PAH or NSO oxygenation and also as an ultimate electron acceptor for the microorganisms. However, oxygen is frequently limited -- and sometimes completely absent -- in certain contaminated habitats, such as numerous ground water aquifers. Therefore, it is of interest to learn how significant the anaerobic microbial processes may be in determining the fate of PAH and NSO in anoxic environments, how complete the anaerobic transformations of these compounds are, and whether the intermediates and products of these transformations are more or less hazardous than the parent compounds.

Approach: It is hypothesized that relatively small PAH and NSO molecules (such as naphthalene, acenaphthene, acridine, dibenzothiophene, etc.) are amenable to anaerobic microbial transformations, and that the transformation routes are similar to those determined for monoaromatic hydrocarbons and simpler heterocycles under identical conditions. It is not known how PAH and NSO influence the transformation of one another in complex mixtures, where the interactions may range from transformation inhibition, over sequential transformation, to acceleration (through cometabolism, or other mechanisms) of transformation of certain compounds by other compounds in the mixture. In order to evaluate the hypothesis and answer these questions, batch microcosms containing single PAH or NSO or mixtures thereof as substrates, and sulfate or carbon dioxide as electron acceptors, are being studied. These microcosms contain microbial inocula derived from PAH- and NSO-contaminated ground water aquifers, or from stable methanogenic cultures degrading aromatic hydrocarbons, which had been developed in this laboratory. Several different analytical techniques (gas chromatography [GC], high performance liquid chromatography, and GC/mass spectrometry) and ¹⁴C-labeling of the substrates, are used to detect and identify the intermediates and products of transformation, and to follow the degradation of substrates over time. The most active microcosms will be used to inoculate larger-size microcosms (batch-fed glass columns containing saturated aquifer material) in which the transformation processes on a larger scale can be evaluated. They will be used also to attempt to enrich stable suspended cultures of the active microorganisms, in which details of the transformation pathways and mechanisms of interactions in mixtures can be studied.

Status: Batch microcosm studies are underway and the tested microbial inocula have been shown to transform some of the model substrates under anaerobic conditions.

Degradation routes for these compounds are being determined. Upon completion of this stage of research, the scale-up of microcosms to column size, as well as enrichment of suspended microbial cultures, will be undertaken.

Effects of Sorption on Biodegradation of Halogenated Organics: Perry L. McCarty and Paul V. Roberts, Stanford University (funded by EPA).

Goal: The goal of this project is to determine how compound sorption onto solid surfaces such as soil and sorption media (e.g., activated carbon) affects the rates of biological degradation of organic compounds.

Rationale: Rates of biodegradation of organic compounds are known to be affected by sorption onto surfaces, but the nature of the effects is not well understood. Whether it enhances or reduces transformation rates appears to depend upon properties of the sorbed compound, the surface to which it is sorbed, and the biological process involved. Greater knowledge of the affect of sorption is needed in order to better predict fate of chemicals in the environment, and to devise treatment schemes where sorption is involved.

Approach: An experimental approach is being used to determine the availability to biological degradation of trichloroethylene (TCE) by methanotrophic bacteria. First, biotransformation kinetics for methanotrophic oxidation of TCE are being determined, using existing laboratory cultures derived from the Moffett Field site, and then parameters associated with sorption kinetics of TCE on a well-defined synthetic media (silicalite) as well as aquifer solids is being determined. A numerical model is also being developed to relate desorption and biotransformation kinetics, using the hypothesis that transformation rates are directly related to solution concentration of TCE. If this hypothesis does not prove correct, than alternative hypotheses that are consistent with experimental results will be sought and tested.

Status: Preliminary kinetic studies of methanotrophic transformation of TCE have been completed, as has been the development of sorption isotherms on aquifer material and silicalite. Preliminary biodegradation rate studies have also been conducted with sorbing solids present. Progress is on schedule.

Trace Metal Removal Processes: James O. Leckie, Stanford University (funded by EPA)

Goal: The long term goal of this project is to develop a mathematical model of mass transport limited adsorption of toxic trace metals in porous particles. The premise is that hydrous metal oxide particles with the proper pore structure can be used to concentrate and remove the trace metals in engineered processes.

Rationale: Previous experimental work with both porous and nonporous particles indicates that the porous particles can dramatically increase the capacity for removal of the trace toxic metals from solution. The engineering application of particles with

tailored pore size distributions could provide a means of removing the trace metals in a sufficiently concentrated form to allow economic recycle where appropriate.

Approach: The approach taken on this project involves the design and implementation of a parametric study of the adsorption of cadmium and selenite onto porous amorphous alumina particles. The first phase of the project involves the physical-chemical characterization of the alumina particles, including particle size distribution, pore size distribution, site density, specific surface area, surface acidity constants and the surface complexation constants for the trace elements. The second, and longest phase, will be the experimental work evaluating the mass transfer limited adsorption process. On the basis of the data developed in the second phase, a mathematical model describing the overall physical-chemical process will be developed to allow simulations over a range of operational variables such as pH, solid to liquid ratio, and adsorbate and adsorbent concentrations.

Status: Experimental work is underway, with completion expected 3/92.

Abiotic Dehalogenation of Haloaliphatic Compounds in Aqueous Solutions Containing Hydrogen Sulfide: Martin Reinhard, Stanford University (funded by EPA and the Shell Companies Foundation).

Goal: The goal of this project has been to study the reactivity of hydrogen sulfide towards simple haloaliphatic compounds.

Rationale: Relatively little research has been directed towards studying the rates and pathways of abiotic reactions that may be significant under anaerobic conditions. Recent research of this as well as of other laboratories has shown that hydrogen sulfide may promote the dehalogenation of haloaliphatic contaminants at rates that are significantly faster than the competing reactions with water, i.e. hydrolysis and dehydrohalogenation.

Approach: 1,2-Dichloroethane and 1,2-Dibromoethane (EDB) were reacted in glass ampules under anaerobic and aseptic conditions for periods of months to years. Products and rates were analyzed using chromatographic techniques.

Status: The project has been completed and the results will be published in Environmental Science and Technology in 1989.

TRAINING AND TECHNOLOGY TRANSFER PROJECT DESCRIPTIONS

International Symposium on Processes Governing the Movement and Fate of Contaminants in the Subsurface Environment: Perry L. McCarty and Paul V. Roberts, Co-Chairman, Stanford University

Goal: The goal of this symposium, cosponsored by the Center and the International Association on Water Pollution Research and Control, was to bring together leading scientists and engineers from around the world to evaluate the current knowledge about the processes that affect the way in which chemicals interact with the soil, move with the flow of water and air through the subsurface environments, and are transformed or degraded by both abiotic and biotic processes.

Rationale: Basic understanding of such processes is necessary in order to develop realistic models for the movement and fate of contaminants in the environment.

Approach: The symposium was held at Stanford University from July 23 to 26, 1989. There were presentations on eight special topics by invited speakers, twenty seven additional oral presentations, and forty four poster presentations. The symposium focused on the physical, chemical, and biological processes that are most important to chemical migration and transformation in the unsaturated zones above aquifers as well as in the groundwater zone. This includes information regarding both equilibrium and rate processes, and the various environmental variables that affect them. Among the processes of importance that were emphasized at the symposium were sorption, dissolution, volatilization, diffusion, multi-phase flow, and abiotic and biotic transformations. Experimental investigations were stressed, but presentations were also included that were oriented toward simulation of transport if they emphasized fundamentals of processes affecting the transport and fate of contaminants. The meeting was partially supported financially by EPA, the U.S. Geological Survey, and the U.S. National Science Foundation.

Status: The symposium went very well, with much valuable interchange of information. From all indications, the meeting was highly successful in meeting its objectives.

Fundamentals of Chemistry of Hazardous Substances, Training Course, Portland Metropolitan Area, Kenneth Williamson and Peter Nelson

Goal: The goal of this course was to meet a need for training hazardous waste personnel in the electronics industry.

Rationale: Basic understanding of chemical processes are necessary for personnel to further their professional development in the hazardous waste field.

Approach: The class was held in six 4-hour sessions in the spring, 1989. A total of 34 individuals completed the course. The class focused upon chemical nomenclature, hazardous waste identification, and chemical processes including oxidation, reduction, acid-base hydrolysis, and precipitation. One session involved a series of laboratory exercises.

Status: The class provided strong educational development to most of the participants. The greatest difficulty proved to be meeting the wide variety of interests and abilities of the students.

Fundamentals of Hazardous Substances, Training Course, Portland Metropolitan Area, Kenneth Williamson, Peter Nelson, Jonathan Istok, and Sandra Woods

Goal: The goal of this course was to provide professional level education concerning the fate and transport of hazardous materials to hazardous waste managers, regulatory personnel, and professional engineers.

Rationale: A need exists for professional-level training of hazardous waste managers and regulators.

Approach: The class consisted of 10 three-hour sessions in the spring, 1989. Twenty-one persons attended the sessions. The approach was to focus on fate and transport mechanisms including biodegradation, volatilization, precipitation, oxidation-reduction, and sorption. A wide variety of organic and inorganic hazardous substances were described. For each fate and transport mechanism, an example problem was developed and an above-ground treatment process was described.

Status: The class successfully provided professional-level development for the students. Student evaluations were excellent.

Biological Transformation of Chlorinated Solvents in Subsurface Systems, Workshop, Portland Metropolitan Area, Perry L. McCarty, Paul V. Roberts, Dunja Grbic'-Galic', and Lewis Semprini.

Goal: The goal of this workshop was to provide information on the current knowledge concerning chemical movement and fate, and bioremediation of subsurface environments contaminated with chlorinated solvents.

Approach: The workshop was offered at Intel Corporation in Hillsboro, Oregon, on April 18, 1989, to a variety of attendees including hazardous substance managers, regulatory personnel, professional engineers, academic personnel, and graduate students. The information included physical transport processes, biological reaction rates and pathways, sorption and desorption processes and rates, and mathematical modelling of a field application. Information was provided on a variety of small-molecular-weight chlorinated solvents.

Status: The workshop was well received. It was decided to repeat the workshop at other locations within EPA Regions 9 and 10 during 1990.

VII. PUBLICATIONS:

A. Refereed Journal Articles

Celorie, J. A., S. L. Woods, T. S. Vinson, and J. D. Istok. 1989. A comparison of sorption equilibrium distribution coefficients using batch and centrifugation methods. *Journal of Environmental Quality*. Vol. 18, No. 3, pp. 307-313.

Celorie, J. A., S. L. Woods, T. S. Vinson, and J. D. Istok. 1989. Modeling solute transport by centrifugation. *Journal of Environmental Engineering*. Vol. 115, No. 3, pp. 513-526.

B. Articles Submitted or in Press

Lee, S.B., J.D. Istok, and S.L. Woods. 19xx. A Numerical Model for Interpreting Results of Column Transport Experiments with Nonlinear, Nonequilibrium Sorption. Submitted to *Computer & Geosciences*.

Kitanidis, P. K., Effective hydraulic conductivity for gradually varying flow, *Water Resources Research*, submitted, 1989.

C. Books and Bound Proceedings

International Symposium on Processes Governing the Movement and Fate of Contaminants in the Subsurface Environment, Abstracts, Stanford University, July 23 to 26, 1989.

Istok, J.D. 1989. Groundwater Flow and Solute Transport Modeling by the Finite Element Method. *Water Resources Monograph No. 13*. American Geophysical Union. IN PRESS.

D. Chapters in Other Books or Bound Proceedings

Gorelick, S.M., "Incorporation of Uncertainty Analysis Into Management of Groundwater Quality," Report from the SCOPE Workshop on Groundwater Contamination, Stanford University, Stanford, California, July 27-28, 1989.

Gorelick, S.M. and R.M. Gailey, "The Relationship Between Model Calibration and Engineering Overdesign for Heterogeneous Aquifers," Proceedings of International Conference on Calibration and Reliability in Groundwater Modelling, The Hague, The Netherlands, September 3-6, 1990.

Moore, J.A. and J.D. Istok. 1990. Chapter 7, Agricultural Waste Management Field Manual. *Geologic and Groundwater Quality Considerations in Waste Management*. Soil Conservation Service. IN PRESS.

E. Project Reports

F. Conferences and Workshops Held

International Conference on Processes Governing the Movement and Fate of Contaminants in the Subsurface Environment, Stanford University, July 23 to 26, 1979.

SCOPE Workshop on Groundwater Contamination, Stanford University, July 27 to 29, 1989.