



**WESTERN REGION
HAZARDOUS SUBSTANCE RESEARCH CENTER**

1990 ANNUAL REPORT

Stanford University
Oregon State University

December 1990

Sponsored by the U.S. Environmental Protection Agency

WESTERN REGION HAZARDOUS SUBSTANCE RESEARCH CENTER

ADMINISTRATION

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

Kenneth J. Williamson
Director, Training and Technology Transfer
Department of Civil Engineering
Oregon State University
Corvallis, OR 97331
(503) 737-2751

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 non-chlorinated 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. Currently, the Center is overseeing 23 research projects, eight of which are concerned with chlorinated solvents, four involve halogenated aromatic compounds such as pentachlorophenol and PCBs, three address problems with non-halogenated aromatics including petroleum derivatives such as gasoline and ordnance wastes such as TNT, two are directed towards solution of heavy metal problems, and six evaluate factors affecting movement and fate of the above chemicals in the environment or address design and management issues for site cleanup in general. Technology transfer and training activities are broad and include sponsorship of sessions at several major conferences, technical workshops directed towards technology transfer, development of a major training program in Oregon, sponsorship of a national meeting of environmental engineering educators to address hazardous substance education, and numerous presentations of research information and technology transfer at conferences, workshops, and seminars for regulators, industry, consulting firms, and university faculty and students.

The faculty and staff who are directing the Center's research, training, and technology transfer activities are listed in Table 1. They collectively represent an integrated research team representing four different schools (engineering, earth sciences, medicine, and veterinary medicine), and many different disciplines (microbiology, chemistry, hydrogeology, hydrology, chemical engineering, civil engineering, and medicine). Perry L. McCarty is Director of the overall Center and of the research program. Kenneth J. Williamson serves as Associate Director in charge of training and technology transfer and coordinates the Center's overall activities in Oregon. Lewis Semprini is an Assistant Director who coordinates technology transfer and research activities in California. Martin Reinhard is Assistant Director in charge of the Center's analytical program. Marilyn C. King is the Center's Administrative Assistant.

The Center's Science Advisory Committee and Training and Technology Transfer Committee members are listed in Tables 2A and 2B, respectively, and represent federal and state governments, industry, consulting firms, and universities. The budgets for the past year and the total since the Center's inception are summarized in Table 3.

CENTER DIRECTOR'S REPORT

The goal of the Western Region Hazardous Substance Research Center is to develop alternative and advanced processes for treatment of hazardous substance contamination of soil and groundwater, which collectively represents the subsurface environment. The selected subsurface contaminants being addressed are the most prevalent ones throughout the country, and the focus of most national and state cleanup efforts. These include chlorinated solvents and their derivatives, both halogenated and non-halogenated aromatic compounds, and heavy metals. Development of a greater understanding of processes governing the movement and fate of these contaminants in groundwater, and the development and evaluation of schemes for groundwater remediation represent the principal emphasis of the Center's research and educational activities. There are several

reasons for this focus. One is that groundwater contamination is one of the major and most costly environmental problems both within the western region and the nation as a whole. Also, the faculty team assembled for the Center have a long history of research on groundwater contamination, and so are in an excellent position to address this important problem. This team represents several different disciplines, the combined expertise of which is vital for successfully resolving the complex physical, chemical, biological, geological, and engineering facets of the subsurface contamination problem.

During this past year, the Center added four new members to help direct the Center's activities. Dr. Abduhl Matin, a new faculty member from Stanford's Department of Microbiology and Immunology, is evaluating the performance of special microorganisms that have been engineered to degrade trichloroethylene (TCE) under conditions of starvation, which is the usual state of organisms in the environment. Another new member is Dr. Morrie Craig from Oregon State's School of Veterinary Medicine, who discovered a unique degrading ability of microorganisms contained in the rumen of sheep. These natural organisms offer excellent potential for degrading a variety of biologically resistant aromatic compounds including pesticides and ordnance wastes such as TNT. Dr. Lynn Hildemann, a new member of Stanford's Department of Civil Engineering, is a specialist in air pollution, and complements the other faculty who are addressing surface and subsurface environments. She will help insure that in addressing problems of groundwater or soil contamination, we do not simply transfer the problem to another media. Dr. Lewis Semprini, another addition this year, will not only coordinate some of the Center's administrative functions, but will add his expertise as well in process modeling associated with the field studies being conducted.

The Center's primary emphasis on groundwater and soil contamination complements very well the focus of the other four EPA hazardous substance research centers. By carefully focusing on a small set of the several hazardous substance problems of significance, a better possibility for solving important, but complex problems, results. The Center's studies on groundwater are helping to define new processes that have good potential for application in surface treatment systems as well. For example, studies on groundwater processes have led to the finding of naturally occurring microorganisms with the capability to destroy man-made organic chemicals that were previously believed to persist in the natural environment. Several laboratory and field studies are underway to take advantage of the potential of these organisms for in-situ bioremediation. In addition, because of the great potential, efforts are being made to capture this natural ability in above-ground engineered systems where the reaction rates can be greatly increased and the overall process can be better controlled. Such research on surface processes is a natural extension of the Center's research since most approaches to resolving subsurface contamination involve some form of surface treatment. The development of both in-situ and surface advanced treatment systems for handling the problem compounds being researched by the Center 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.

In addition to research, the Center fosters training and technology transfer activities, both by Center personnel and others. Through Dr. Kenneth Williamson, Associate Director of

the Center and 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 development of an annual hazardous substance conference in the Northwest region, similar to programs presently in operation in California and elsewhere. Another is a series of seminars and workshops to present results of research that has direct application in the field. Finally, presentations by all Center faculty of research findings at international, national, and regional conferences and publication in widely-read and peer-reviewed journals is essential for the dissemination of results to potential users. The Center has been highly active in all these areas. These various training and technology transfer initiatives 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.

The Center was initiated in the Spring of 1989 with 14 separate research projects. An additional 12 research projects have since been added, and three have been completed. While most projects are funded by the EPA Center's program, five of them have been supported by industry, two are supported by the U.S. Department of Navy, two are financed by the U.S. Department of Energy, and one is jointly supported by EPA and industry. In addition, gift support from industry, consulting engineering firms, and municipalities has helped expand the overall efforts of the Center greatly, and at the same time has helped insure that we are addressing environmental problems of significance to the country.

HIGHLIGHTS FOR 1990

This second year of Center activity has seen significant growth in the number of research projects being conducted, ranging from basic to applied, as well as in the education of practitioners in hazardous substance cleanup and in transfer of research findings to those in need. Among the new projects funded this year are four that are concerned with bioremediation of chlorinated solvents, the major groundwater contaminants in the country, and range from basic studies in genetic engineering to design for application of bioremediation at a Superfund site. This increases the number of projects being conducted in this area to eight. Another major focus has been anaerobic processes for biotransformation of both halogenated and nonhalogenated aromatic compounds. In the past these compounds were believed to be resistant to biotransformation in the absence of oxygen, but field observations just a few years ago suggested this was not the case. The aromatic compounds were found to be transformed under natural conditions in the absence of oxygen. This has important implications for site remediation. These studies are being extended into a third class of aromatic compounds that contain nitro groups through a new Center project. Heavy metal contamination of soils and groundwaters is growing in significance in the western region of the country, and so a new project has been added here. This is an area that we would like to see increase within the Center, both because of its importance and because we have experienced researchers at both Center universities to carry out the needed studies.

Training and technology transfer activities have increased significantly this past year, and range from numerous presentations at seminars, workshops, and conferences for industry, the consulting profession, and regulators. Sponsorship of two major conferences and several sessions in the western region this year, and another in the coming year, have contributed to the technology transfer activities. In addition, the initiation of a hazardous substance training program in Oregon has been undertaken. More details of these highlights are contained in the following.

Biodegradation of Chlorinated Solvents

Chlorinated solvents and their transformation products (chloroaliphatics) are the most prevalent priority contaminants found in groundwater in the United States. They include trichloroethylene (TCE), dichloroethylene (DCE), 1,1,1-trichloroethane (TCA), dichloroethane (DCA), and vinyl chloride (VC). These chemicals are characterized by their relatively high mobility in groundwater and their resistance to biological degradation. However, in recent years transformation both in the presence and absence of molecular oxygen has been found possible. Here, microorganisms are fed a primary substrate for energy and growth such as methane during which they produce enzymes or coenzymes that fortuitously transform the chlorinated compounds. This process termed cometabolism has not been used in the past, but it now offers new possibilities for environmental restoration.

Most of the Center's biotransformation studies with chloroaliphatic compounds involve cometabolism by methanotrophs, or microorganisms that consume methane. Methane monooxygenase (MMO) is the enzyme used by methanotrophs for the initial step in methane oxidation, and this enzyme fortuitously oxidizes the chloroaliphatics. Through previous studies in the laboratory and at the Moffett field site in Mountain View, California, a team of Center researchers demonstrated that native methanotrophic bacteria would indeed degrade TCE, DCE, and VC when methane and oxygen were dissolved in water and injected into the ground. Compounds such as VC with less chlorine atoms per molecule were much more rapidly degraded than ones with more chlorine atoms per molecule such as TCE.

A Superfund site at St. Joseph, Michigan, has now been found that appears ideal for the first application of this technology at full scale, and an initial feasibility study was conducted this past year through support from the Allied Signal Corporation and EPA. Here, a relatively uniform fine-sand unconfined aquifer about 10 meters below ground surface has been contaminated with mg/l concentrations of TCE. In addition, both DCE and VC are present at similar concentrations, and were perhaps formed from TCE by anaerobic biological reductive processes in the groundwater. Because of the promise indicated by the feasibility study, funds have been received from EPA to initiate the design of a full scale system. Cooperating in this study is the Gas Research Institute which is providing additional funds for evaluating an alternative method for subsurface mixing of methane and oxygen with groundwater so that the groundwater need not be brought to the surface for this purpose. The St. Joseph site will allow an evaluation of the methanotrophic process at full scale, and also provides an opportunity to explore alternative technologies for introduction and mixing of required bacterial substrates and

nutrients with contaminants. The latter is one of the more difficult unresolved problems with in-situ bioremediation.

The St. Joseph project is a cooperative venture between the federal government, industry, consultants and the the Center to bring innovative technology to practice. We believe there is a great need for such activity and hope that more such opportunities can develop in the future.

While in-situ treatment by methanotrophs is attractive, it is likely that groundwater at most sights will be pumped to the surface and treated there. Two other Center projects are concerned with the development of technology for biological treatment of chloroaliphatic compounds in surface reactors where the process can be better controlled. These studies are being jointly sponsored by EPA and the Gas Research Institute. Considerable progress has been achieved this past year in understanding the basic mechanisms involved in cometabolism, appropriate reaction rate models have been developed, and a two-stage bioreactor for treatment is currently under evaluation.

Most Center studies on biotransformation of chloroaliphatics have involved methanotrophs, but other researchers have found other microorganisms that oxidize propane, ethylene, toluene, or ammonia also produce oxygenases that can cometabolize chloroaliphatic compounds. Particularly promising here is organisms with toluene monooxygenase (TMO), which is a better understood enzyme than MMO. TMO has been genetically characterized and is available for evaluation through genetic engineering. One new current project with Drs. Abduhl Matin and Dunja Grbic-Galic as principal investigators is concerned with incorporation of TMO genes into *E. coli* in such a way that the enzyme can be produced only when the microorganism is growing under starvation conditions, which is the normal state of microorganisms in the environment. In addition, funds have been received from the Department of Energy to conduct at the Moffett field site a comparative evaluation between the MMO and TMO enzyme systems so that the relative advantages and disadvantages of these two systems under natural conditions with native organisms can be determined.

Aromatic Compounds

The Center is also studying the second most prevalent groundwater contaminants, the soluble components of gasoline, which include the aromatic hydrocarbons: benzene, ethylbenzene, toluene, and xylene (BETX). In addition, the Center has under evaluation several other aromatic compounds, some of which sorb strongly to soil and thus tend to be more associated with surface contamination. These include polynuclear aromatics (PAHs), and halogenated aromatic compounds such as the wood preservative pentachlorophenol (PCP), and polychlorinated biphenols (PCBs).

Research activities at Stanford University are focused primarily on BETX and PAHs, while Oregon State University's primary focus is PCP and PCBs. In addition, a new Center project with Dr. A. Morrie Craig of the Oregon State Department of Veterinary Medicine as principal investigator, is exploring the potential of the microflora associated with sheep rumen to degrade ordnance hazardous compounds such as trinitrotoluene

(TNT). Considerable knowledge is available on the degradation of aromatic compounds in the presence of oxygen (aerobic), and applications of biodegradation here is common. However, aromatic compounds have recently been found to be degraded in the absence of oxygen (anaerobic) conditions as well. The Center faculty at both Stanford and Oregon State have been instrumental in the development of knowledge of anaerobic aromatic biodegradation, and so continue to study this important area through support from the Center. Anaerobic conditions often occur in the subsurface environment where the availability of oxygen is limited, and for this reason, better understanding of the conditions required, the organisms involved, and the additional compounds formed from degradation are of great significance.

During this past year at Oregon State faculty Dr. Sandra Woods and her students have elucidated the different pathways by which PCBs are degraded under anaerobic conditions. They are working with a consortium of bacteria that convert organic compounds into methane (methanogenesis), and have found that of the five chlorine atoms on the PCB molecule, those in the number one and three positions on the ring generally are removed first, with some preference for the former. While chlorine atoms in the number two position are less favored, they too are sometimes removed initially. The fact that these different pathways are all operative to some degree leads to the formation of mixtures of intermediate compounds of great complexity and susceptibility to further transformation. However, they all lead to the formation of less halogenated compounds which can then be more readily destroyed by aerobic activity. The development of a combined anaerobic-aerobic treatment system in which the overall destruction of these compounds is favored is also under study at Oregon State University.

An additional area of research support by the Center is on movement, fate, and treatment for heavy metals. One element of particular concern in the region is chromium (CrVI), which is a major groundwater contaminant. Research at both Stanford University under Dr. James Leckie and Oregon State University under Dr. Peter Nelson is addressing this issue.

During this past year the research group working with Dr. James Leckie has developed a data base that will permit development of a model for describing mass transport limited adsorption in porous metal oxide particles. The experimental work indicated that porous particles can be designed with the physical size and strength appropriate for engineered processes and with a pore size distribution to allow a large adsorption capacity (internal) and a time dependency appropriate for engineered systems (uptake and regeneration within 1-2 hours). Thus it now appears feasible to consider applications where it is practical to reuse trace metals and the adsorbent oxide particles. Concentration ratios of 1000 or greater may be possible for dilute waste streams where the adsorbed metals can be eluted off in concentrated form. Potential users of such an engineered system are the electronics industry (rare earth metals), metal finishing industries (toxic trace metals), power industry waste streams (fly ash pond waters), and agricultural areas with elevated concentrations of metalloids such as selenium and arsenic.

Training and Technology Transfer

During the first year of Center activity, a survey was made of hazardous substance training and technology transfer needs in EPA Regions 9 and 10. California was found to have an excellent training program in place at the nine campuses of the University of California, but this did not exist in several of the other eight states in the region pair. Also a need for better transfer of research findings to regulators and consulting engineers existed, especially in California. A cooperative venture was established between the Center and the California University Extension program to extend their experience in training courses to other states in the region pair, and to initiate seminars and workshops for technology transfer. In addition, several conferences within the region have been cosponsored by the Center, and programs for individual workshops and sessions have been developed in order to foster better transfer of technology. These activities are in addition to the numerous presentations by Center researchers on findings of their studies at local, state, and national conferences, seminars, and workshops.

A program in hazardous waste training has now been established in Portland, Oregon, to be operated by the Portland Community College System.

Last year, the Center was a joint sponsor of an International Conference on Processes Affecting the Movement and Fate of Contaminants in the subsurface environment. This, year, the Center cosponsored with Idaho State University and the Idaho Association of Commerce and Industry the 1990 Regional Conference on Hazardous Materials and Wastes in Pocatello, Idaho. The Center also cosponsored the 1990 Responsible Hazardous Materials Management Conference in Portland, and organized six seminars on subjects ranging from methodology for groundwater monitoring to remediation of heavy metal contamination in groundwater and bioremediation of chlorinated solvents. Each seminar was attended by 30 to 60 individuals.

Two one-day workshops were conducted in northern and southern California on Chlorinated Solvents in Groundwater, and cosponsored with the University of California extension service. There were over 160 in attendance at the northern California meeting, and a full house of 110 individuals at the southern California workshop. Because of the success of this workshop, plans are underway to present it elsewhere in California, and perhaps other region states as well. Other similar workshops are also being planned. This cooperative venture with the University of California Extension service is working well. The Center is also a cosponsor of an International Conference on In-Situ and On-Site Bioreclamation that was initiated by Batelle, and will be held in San Diego, California, March 19 to 21, 1991. This meeting has attracted much interest and will have several foreign participants. The Center has been responsible for organizing a session on chlorinated aliphatic compounds.

A final but important activity that the Center is sponsoring next year is a meeting of the Association of Environmental Engineering Professors (AEEP) to discuss educational issues. AEEP represents about 100 universities that educate environmental engineers and scientists throughout the country, and has educational meetings about once every four to five years. One of the three main topics at this meeting will be how best to incorporate hazardous substance issues into the curriculum. Environmental education at the undergraduate level will also be a major theme at this meeting. Oregon State University

was selected as the site for this important conference because of the focus of the WRHSRC and its relevance to the topics of the Conference.

RESEARCH PROJECT DESCRIPTIONS

CHEMICAL MOVEMENT, FATE, AND TREATMENT

Treatment of Complex Mixtures: Martin Reinhard, Dunja Grbic-Galic, J. O. Leckie, P. L. McCarty, and P. V. Roberts, Stanford University.

Goal: The goal of this project is to apply a computer-aided information system to the problems of hazardous waste treatment.

Rationale: When designing treatment processes and assessing the risk of complex hazardous wastes, numerous complex and interrelated factors must be considered, foremost the biodegradability and the physico-chemical characteristics of the contaminants. However, such data is not available except for the most common contaminants. Using computer-based property estimation techniques and process simulation, pilot studies can be designed with considerable cost savings.

Approach: An information system is being used to analyze in detail the performance of single and multi-step treatment plants for which the removal efficiencies of a broad range of contaminants have been characterized. In these cases, substance properties relevant to treatment of contaminated waters, such as aqueous solubility and n-octanol/water partition coefficients as a function of treatment conditions, are being correlated with observed removal rates during air-stripping, activated carbon and reverse osmosis. Biological properties will also be considered.

Status: Detailed analysis of air-stripping and activated carbon treatment should be complete by March 1991. Analysis of multi-process treatment trains including reverse osmosis and biological process is about to begin with completion expected in March 1992.

Client/Users: Consultants, educators and regulators interested in treatment plant design for complex mixtures, and researchers studying the relationship between properties and environmental fate of contaminants.

Design of Reliable and Cost-Effective Mitigation Schemes: Steven M. Gorelick, Stanford University

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 ensure capture of contaminant plumes. Reliable designs must be based on reliable predictive models. Quantifying both model parameter uncertainty and consequent prediction uncertainty is a major research goal.

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. 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, and focuses on the Gloucester Special Waste Compound in Ontario, Canada. In 1989 design began for pump-and-treat remediation to remove hazardous organic solvents. The best remediation design requires optimal well selection and the determination of optimal pumping rates. The problem is being approached by developing stochastic simulation models based upon available field data. Then these models are combined with nonlinear optimization methods in order to identify reliable design strategies. Model parameter uncertainty is considered to be a key indicator of design reliability. In this approach, model parameters are first described statistically. This quantification of uncertainty in model input is then translated into confidence bounds on model predictions of contaminant transport. The reliability indicated by the predictive model is then used to over design the remediation system to the extent necessary to insure success.

Status: Analysis of the hydraulic and chemical field data for the Gloucester site has been completed. Geologic characterization and hydrogeologic conceptualization are also complete. A large scale two-dimensional finite- element simulation model was developed which simulates the hydraulic head distribution and solute migration. Using a coupled-process approach, both the hydraulic head and solute concentration data were jointly used to estimate parameter values and their uncertainties. This simulation-regression model proved to be a powerful tool to reduce parameter uncertainty and consequent prediction uncertainty. Currently, a stochastic optimization formulation, based on the parameter estimates, is being used to establish reliable remediation design alternatives. Completion is expected by 3/92.

Client/Users: Engineers and hydrogeologists involved in aquifer remediation design. Groundwater modelers interested in parameter estimation methods.

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

Goal: The objective of this study is to gain a better understanding of the factors which control the efficiency of vapor phase stripping of volatile contaminants from the vadose (unsaturated) zone.

Rationale: Vapor stripping is becoming an increasingly popular method of removing nonaqueous liquids from the unsaturated zone. However, there is no basis for assessing when conditions are favorable for this process, nor is there any way of predicting the rate and extent of removals.

Approach: This investigation is divided into three areas. The first is the measurement of organic vapor sorption isotherms for trichloroethylene on a range of different solids. The second involves measuring the rate at which the organic solvents desorb from the soils under vapor stripping conditions. The third encompasses computer modeling of the stripping process using the isotherm and kinetic data obtained in the other two phases of the project.

Status: A novel methodology has been developed to measure adsorption isotherms under conditions of the unsaturated subsurface environment. Three aquifer materials have been characterized, and adsorption isotherms have been measured for TCE. Desorption rates have been measured and models are being evaluated to rationalize the observed removal rates.

Client/Users: Consultants and educators interested in ground water and soil remediation technology.

Detection and Assessment of Subsurface Contamination: Peter K. Kitanidis, Stanford University.

Goal: The thrust is the development of better techniques for characterizing contaminated sites. Objectives include the development of better computational 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 at field scales.

Rationale: There is seldom enough information to determine with certainty the precise values of all parameters for characterizing a contaminated site, 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, however, determination of 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, is sufficient and is what is sought by this study.

Approach: The approach combines measurements, mechanistic models describing the transport and fate of pollutants, and statistical methods. Because of spatial variability and incomplete knowledge, the parameters which determine the transport and fate of solutes, such as conductivity, retardation, and reaction coefficients, are characterized in statistical terms. The mathematical formalism of random functions is used to describe spatially variable quantities through statistical moments, such as mean and covariance functions. These moments are obtained from data and other (such as geological) information using geostatistical techniques. Then, through the governing flow and mass transport equations, the statistics of solute concentration are determined. These methods are applied to two problems of practical interest: the evaluation of the macroscopic, or field-scale, flow and transport parameters and the conditioning of predictions on measurements.

Status: Initial efforts 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. The second year produced a numerical spectral method for carrying out computations of interest.

Clients/Users: Groundwater modelers; engineers working in the characterization of hazardous-waste sites; regulators; and policy makers interested in evaluating the worth of data.

FASTCHEM Applications and Sensitivity Analysis: Peter K. Kitanidis and David L. Freyberg, Stanford University.

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) quantifying the sensitivity and uncertainty of predicted chemical distributions (in time and space) to variations in input parameters; (2) developing a set of computer programs which apply state-of-the-art estimation methods for the interpolation of parameters from sparse measurements; and (3) evaluating the literature and developing new techniques for optimal decontamination strategies at utility hazardous waste sites under uncertainty.

Rationale: Amendments to the Resource Conservation and Recovery Act in 1984 and reauthorization of the Safe Drinking Water Act 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. There is a need now to determine the applicability of the model and for incorporating subroutines for the utilization of data.

Approach: The model's sensitivity and uncertainty is evaluated through application to specific case studies. Methods for incorporating available measurements are being based on linear estimation methods.

Status: The computer codes have been installed and tested and recommendations for model improvement have been made. The model is currently being applied to six case studies representing typical problems of ash disposal from coal-fired plants. The sensitivity of the results to the input parameters is being evaluated.

Clients/Users: The electric utility industry; regulators; policy makers.

Dispersion Modeling of Volatile Organic Emissions from Ground-Level Treatment Systems: Lynn M. Hildemann and Paul V. Roberts, Stanford University

Goal: Treatment to remove organic substances present in contaminated groundwater can result in the emission of hazardous volatile organics into the atmosphere. This project

will develop a detailed model for the dispersal of emissions from a ground-level area source into the atmosphere, with the goal of accurately predicting concentration levels near the source as well as further away.

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

Approach: A detailed model capable of predicting the near-source dispersion of emissions from a ground-level area source will be developed. Accurate theoretical expressions for the variation of wind speed and eddy diffusivity with vertical height will be incorporated in order to accurately model dispersion in the surface layer regime. This model will be linked to an already-developed model predicting emission rates resulting from aerobic biological treatment of wastewaters. The model predictions then will be compared with published measurements of concentrations downwind of treatment sites.

Status: Since the project began in October 1990, a review of the literature to identify recent work dealing with the characterization of fluid mechanical behavior in the surface layer of the atmosphere has been undertaken. The next step will be to begin development of the atmospheric diffusion model.

Client/Users: Industries and regulators involved in the treatment of contaminated groundwater, and researchers concerned with risk assessment with such treatment.

CHLORINATED SOLVENTS

Oxidation of Chlorinated Solvents by Methanotrophs: Perry L. McCarty and Paul V. Roberts, Stanford University

Goal: Methanotrophic bacteria, which oxidize methane for energy, can also oxidize chlorinated solvents such as TCE by co-metabolism. The goals of this project are: (1) to evaluate competitive inhibition effects between methane and chlorinated compounds, (2) to assess mass transfer limitations to treatment-reactor design, and (3) to optimize the design for an above ground treatment system.

Rationale: There have been several studies of treatment systems for degrading chlorinated solvents and related compounds by cometabolism. However, knowledge of reaction kinetics are poorly understood so that little scientific basis currently exists for optimizing treatment reactor design. In addition, since the substrates and contaminants of concern are all poorly soluble in water, mass transfer is of great significance and must be considered.

Approach: It is hypothesized that oxidation rates for methane and chlorinated contaminants can be described by a competitive inhibition model. To evaluate this hypothesis, reaction coefficients for methane and TCE alone are being evaluated using a mixed methanotrophic culture derived from the Moffett Field aquifer. Reaction rates when they are used in combination are then being predicted and measured in order to test the hypothesis. In mass transfer studies, model calculations that consider mass transfer effects and biological reaction kinetics are being made for a variety of reactor configurations. The model results will guide reactor design and will help to determine important knowledge gaps for further research.

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

Client/Users: Researchers interested in co-metabolism, and industry, consulting engineers, and state and EPA regulators who are evaluating treatment options for chlorinated solvents.

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

Goal: The goal is to determine how compound sorption onto solid surfaces affects the rates of degradation of chlorinated solvents by methanotrophic bacteria.

Rationale: Rates of biodegradation of organic compounds are affected by sorption onto surfaces, but the nature of this effect 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 is needed in order to better predict fate of chemicals, and to devise treatment schemes where sorption is involved.

Approach: The availability of sorbed trichloroethylene (TCE) to biological degradation by methanotrophic bacteria which use methane as primary substrate for growth is being evaluated. Biotransformation kinetics for TCE by non-fed (resting) methanotrophic bacteria, and parameters associated with sorption kinetics of TCE on a well-defined synthetic media (silicalite) are being determined. A numerical model for experimental evaluation is being developed to relate desorption and biotransformation kinetics, using the hypothesis that transformation rates are directly related to solution concentration of TCE.

Status: Studies of TCE transformation by resting cells have been completed. Experiments on the effect of sorption onto silicalite on reaction rates have been completed. Progress is on schedule.

Client/Users: Researchers interested in co-metabolism, and industry, consulting engineers, and state and EPA regulators who are evaluating treatment options for chlorinated solvents.

Long-Term Chemical Transformation of 1,1,1-Trichloroethane (TCA) and Freon 113 Under Aquifer Conditions: Martin Reinhard, Stanford University

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

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

Approach: This work involves a long-term (5-year) study of the rates and pathways of reaction of TCA and Freon 113 in aqueous solution in the presence, as well as the absence of aquifer material. Because under ambient conditions, the half-life of TCA is on the order of a year and several different products may form, substrate disappearance and product formation will be monitored over several years in order to make obtain mass balances..

Status: The test systems have been in operation for 10 months, and several products of TCE transformation are now being detected and quantified. The study is expected to be completed in 1994.

Client/Users: Consultants, regulators, and researchers interested in natural processes affecting the long-term fate of TCA and Freon 113 in the subsurface environment.

Use of Starvation and Stress Promoters for Biodegradation of Hazardous Wastes: Abdul Matin, Dunja Grbic-Galic, Stanford University

Goal: The goal of this project is to use bacterial starvation and stress promoters to create recombinant strains that maintain high biodegradation activity under typical environmental stress conditions.

Rationale: Biodegradation activity in the environment is typically limited by nutrient deficiencies or other stresses, including carbon, nitrogen, or phosphorus starvation. Bacterial strains that maintain high degradation activity in the face of typical environmental stresses would be very useful in treatment of hazardous waste sites.

Approach: Bacterial stress promoters are genetic elements that turn on in response to specific stress conditions. Our laboratory has isolated and characterized genetic promoters that turn on under carbon starvation conditions. We have also obtained other

stress promoters that respond to more general stress conditions. Our approach is to splice the toluene monooxygenase (TMO) gene (responsible for trichloroethylene (TCE) degradation) under control of these stress promoters, and to characterize the degradation activities of these recombinant strains.

Status: The TMO gene has been cloned under control of two carbon starvation promoters and a stress promoter in *E. coli*, which has permitted the organism to maintain TCE degradation activity for several hours after the onset of starvation. The degradation ability under a variety of stress conditions is now being evaluated.

Client/Users: Researchers, consultants, and regulators interested in understanding environmental factors affecting biotransformation, and potential methods for improving biotransformation rates.

Subsurface Mixing of Nutrients and Groundwater for In-Situ Bioremediation: P. L. McCarty, P. K. Kitanidis, P. V. Roberts, and L. Semprini, Stanford University

Goal: A scheme by which gases such as methane and oxygen are introduced directly into groundwater for mixing with contaminants is proposed for evaluation in order to avoid bringing contaminants to the surface for this purpose.

Rationale: In-situ bioremediation of chlorinated solvents in groundwater with methanotrophic bacteria requires that the primary substrate, methane, and oxygen for its oxidation be introduced into the groundwater and mixed with the contaminants. This is difficult to accomplish, especially when the contaminants do not sorb strongly to the soil. Bringing contaminated groundwater to the surface for this purpose poses a health hazard, and so a method for accomplishing the introduction and mixing of gases without removing groundwater is desirable.

Approach: A subsurface mixing system is proposed which consists of a series of submerged wells with intake screens at the bottom and top. A pump permits drawing groundwater into the well through the bottom screen and pumping it back into the aquifer through the top screen, or vis versa. In the well, oxygen and methane are introduced and mixed with the groundwater. Model analysis is being conducted to determine the effect of design parameters on the degree of mixing of dissolved gases with contaminated groundwater, and to predict the effect of these operating parameters on the degree of in-situ bioremediation that can be achieved. Alternative methods for introduction of gases into the submerged wells are also being evaluated.

Status: Funds to begin this one-year study were received in October 1990, and the proposed analysis has begun.

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

Test-Bed Evaluation of In-Situ Bioremediation of Chlorinated Aliphatic Compounds by Toluene: P. L. McCarty, P. V. Roberts, L. Semprini, and G. Hopkins, Stanford University

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

Rationale: Recent research has indicated that microorganisms containing the toluene monooxygenase (TMO) or toluene dioxygenase (TDO) enzyme can oxidize chlorinated aliphatic compounds such as trichloroethylene (TCE) by cometabolism, similar to biodegradation by methanotrophs with methane monooxygenase (MMO). In order to obtain a comparison between the relative advantages and disadvantages of the TMO or TDO and the MMO enzyme system, an evaluation will be conducted at the Moffett Naval Air Station field site in Mountain View, California, where a four-year evaluation of the MMO system has been completed.

Approach: The field study with TMO- or TDO-producing bacteria will be conducted similar to the previous study in which methane was used as a primary substrate so that the results can be directly compared. Here, phenol and oxygen will be dissolved in recycled groundwater along with TCE, dichloroethylene (DCE), and vinyl chloride (VC) for introduction into a confined aquifer about four meters below the surface that is about 1.2 m deep and 6 meters long. The growth of a native phenol degrading population, and the rate and extent to which the introduced chlorinated compounds are removed will be monitored. The extent of transformation will be evaluated through comparison of concentration decreases using conservative tracers for reference.

Status: Funds to begin this study were received in October 1990, and preparation of the test-bed for beginning of this evaluation has just begun.

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

Demonstration of In-Situ Bioremediation of Chlorinated Aliphatics by Methanotrophs at St. Joseph: P. L. McCarty, P. V. Roberts, S. M. Gorelick, P. K. Kitanidis, and L. Semprini, Stanford University

Goal: This project is for the evaluation of alternative technologies leading to the design of a full-scale system for in-situ cometabolic biodegradation of chlorinated solvents and related compounds by methanotrophic bacteria.

Rationale: Bioremediation of groundwaters offers great promise because it results in destruction of contaminants. However, application of promising techniques requires research and demonstration at full scale. Field and laboratory studies at Stanford University have helped develop a basic understanding of the processes involved in methanotrophic treatment of chlorinated aliphatic compounds; the next step towards application is an evaluation of potential technologies for the process through research and demonstration at full scale.

Approach: The St. Joseph, Michigan, Superfund site has contamination of a relatively homogeneous fine-sand aquifer with mg/l concentrations of trichloroethylene, dichloroethylene, and vinyl chloride. Laboratory, field, and modeling studies conducted

by the WRHSRC indicated that conditions were ideal for evaluating in-situ bioremediation at this site. In order to develop an appropriate treatment system design, additional site characterization is required, alternative technologies need to be researched, modeling studies for alternatives need to be evaluated, and a system design needs to be developed for evaluation by the responsible industries, their engineers, and state and EPA regulators. These tasks will be carried out by a team of researchers at Stanford University in cooperation with the interested parties.

Status: Funding for this study was received in September 1990. The team of researchers has agreed on a division of tasks, and evaluations have been started, with the expected design recommendation scheduled for summer 1991.

Client/Users: State and EPA regulators, industries, and consulting engineers interested in the removal and degradation of chlorinated solvents and related compounds present in groundwaters.

Determining and Modeling Diffusion-limited Sorption and Desorption Rates of Organic Contaminants in Heterogeneous Soils: Paul V. Roberts, Stanford University

Goal: The overall goal of this project is to advance the understanding of the basic processes governing the uptake and release of aqueous phase organic contaminants in a heterogeneous porous medium.

Rationale: Aquifer remediation strategies, such as pump-and-treat or bioremediation, can be greatly prolonged by the diffusion limitations on sorption and desorption from the soil matrix. Equilibrium models, which are the most commonly used solute transport models, do not account for these effects. There is presently little basis for assessing when mass transfer conditions are favorable for pump-and-treat and/or bioremediation strategies, nor is there an accepted method for predicting the required duration of remediation efforts.

Approach: Long-term batch experiments for measuring the uptake and release rates of several contaminants from solids obtained from an experimental aquifer restoration site are being conducted. The data will be used to evaluate and parameterize existing transport models.

Status: Batch sorption rate data have been used to study the breakthrough of several compounds in the experimental aquifer. A purge-and-trap method for studying desorption rates is being developed. The completion of sorption/desorption studies, and related modeling efforts, is expected 3/92.

Client/Users: Researchers interested in mass transfer limitations on the transport or biodegradation of organic contaminants; state and EPA regulators, industry, and consultants concerned with site remediation.

AROMATICICS

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

Goal: The goal is to develop and verify a mathematical model for anaerobic biotransformations in the presence of competing electron acceptors, and to measure process kinetic constants. Electron acceptor interactions between chlorophenols and their dechlorinated metabolites and interactions between chlorophenols and sulfate are examined.

Rationale: Reductive dechlorination of chlorinated aromatic compounds appears to progress such that parent compounds are almost completely removed before degradation of metabolic products begins. To evaluate this hypothesis, the kinetics of pentachlorophenol biotransformation is evaluated in the presence of varying quantities of alternate electron acceptors (metabolic products and sulfate).

Approach: Organisms acclimated to pentachlorophenol or pentachlorophenol and sulfate are grown in continuous flow anaerobic reactors. The reactors are allowed to reach steady-state and then used as a source of organisms for subsequent batch experiments. Progress curves for chlorophenol, sulfate and acetate degradation are generated from the batch experiments. From the results the effect of alternate electron acceptors on the rate of chlorophenol biotransformation are determined.

Status: Several batch experiments have been conducted that indicate acclimated cultures carry out transformations by several routes compared to a single route by unacclimated cultures. Biotransformation rates have been measured individually for each chlorophenol congener, and in the future will be used to measure chlorophenol transformation rates under varying initial conditions.

Clients/Users: Consultants and regulators concerned with site characterization for bioremediation or above-ground biological treatment of pentachlorophenol, and researchers interested in biotransformation reaction kinetics in a complex system.

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

Goal: The goal is to develop and verify a mass transport and biokinetics model of the sorption and biological degradation of pentachlorophenol and its degradative products by an anaerobic and aerobic biofilms on 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 to occur of toxic compound by the attached biofilms. Haloaromatic compounds undergo different biodegradation pathways under anaerobic and aerobic conditions. Anaerobic pathways typically result in metabolic products that cannot undergo further metabolism in that environment. By sorbing these compounds to GAC and then moving the GAC to an aerobic environment, complete and rapid degradation may be possible.

Approach: Anaerobic and aerobic biofilms will be developed on GAC maintained in upflow expanded beds with recycle with acetate as the primary substrate. Pentachlorophenol will be fed as a secondary substrate to the anaerobic column, and should rapidly dechlorinate to a series of tri- and di-chlorophenols which are primarily sorbed to the GAC. The GAC will be moved from the anaerobic column to the aerobic column with a solid retention time of 30 days. The tri- and di-chlorophenols slowly desorb in the aerobic reactor and should undergo degradation by the aerobic biofilms.

Status: Experiments have been conducted to determine substrate removal rates for pentachlorophenol and its metabolic products under aerobic and anaerobic conditions. Adsorption isotherms have been conducted on GAC. The column reactors have nearly achieved steady-state and data collection is underway. The project began in February 1989 and is expected to be completed in January 1992.

Client/Users: Researchers and consulting engineers interested in developing treatment technologies for chlorinated aromatic and aliphatic compounds.

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

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

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

Approach: A mathematical model was developed based on the processes of advection, dispersion, diffusion, sorption, and anaerobic degradation for pentachlorophenol and its metabolites, an electron donor (acetate), and biomass. Monod kinetics and a "macroscopic bulk concentration" concept are used to describe degradation and 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. Dispersion coefficients and sorption parameters were measured in miscible displacement experiments in packed soil columns (30.0 cm long by 5.38 cm in diameter). Comparisons between predicted and measured effluent concentrations will be made during miscible displacement experiments in inoculated soil columns.

Status: Batch experiments to measure equilibrium sorption coefficients and degradation rates have been completed. Model verification in the soil tanks will be completed by February 1992.

Clients/Users: Consultants and regulatory agencies concerned with site characterization for bioremediation and understanding of pentachlorophenol fate and transport.

Anaerobic Microbial Transformation of Homocyclic and Heterocyclic Polynuclear Aromatic Hydrocarbons: Dunja Grbic-Galic, Stanford University

Goal: While monoaromatic hydrocarbons such as benzene have been shown to undergo anaerobic microbial degradation, information on anaerobic biodegradability of polynuclear aromatic hydrocarbons (PAH) is scarce. The goal of this project is to seek anaerobic microbial activity towards PAH and complex nitrogen, sulfur, and oxygen heterocycles (NSO) under sulfate-reducing and methanogenic conditions. Once such activity is found the transformation routes will be evaluated.

Rationale: Environmental contamination by PAH and NSO compounds, which are chemically stable and potential carcinogens, is widespread. Frequently, oxygen is not present so that anaerobic transformation is the only possibility for destruction of PAH and NSO. Thus, it is important to know whether such transformation can occur, and if so, what are the microorganisms involved, what is the degree of transformation (partial chemical change versus mineralization), what intermediates and products are formed, and what interactions occur in mixtures of PAH and NSO.

Approach: Saturated batch microcosms with aquifer solids from several contaminated sites in the country and with prerduced defined mineral medium are being amended with single PAH (indene, naphthalene, acenaphthene) or NSO compounds (indole, quinoline, benzothiophene, benzofuran), or with mixtures of these chemicals. In some cases, benzoate or lactate are added to examine the possibility of cometabolic transformation. Additionally, sulfate is being added as an alternative electron acceptor. Once transformation is observed, enrichments will be developed for isolation of individual strains with the ability to transform aromatic hydrocarbons. In an alternate approach, mixed methanogenic cultures (originally obtained from sewage sludge), shown to degrade toluene, benzene, naphthalene, and acenaphthene, are being evaluated.

Status: To date, only the Pensacola, Florida, aquifer solids have exhibited activity towards PAH (indene, naphthalene) and NS compounds. Ongoing studies are evaluating the adaptation times required, pathways, and environmental factors affecting transformation rates. Attempts are being made to isolate pure cultures of bacteria from naphthalene- and acenaphthene-degrading methanogenic consortia.

Client/Users: EPA regulators, industries, and consultants concerned with clean-up of sites contaminated by petroleum or creosote.

In-Situ Biological Treatment of Aromatics in Groundwater: Martin Reinhard and Perry L. McCarty, Stanford University.

Goal: The objective of this study is to develop and characterize microbial consortia capable of transforming aromatic hydrocarbon compounds under anaerobic conditions with emphasis on methanogenic, sulfate- and nitrate-reducing conditions, and to understand the effect of environmental factors on the transformation processes.

Rationale: Although most gasoline constituents are readily degraded in aerobic surface water systems, the groundwater environment associated with hydrocarbon spills is typically anaerobic, thus precluding aerobic degradation pathways. In the absence of oxygen, degradation of gasoline components can take place only with the utilization of alternate electron acceptors such as nitrate, sulfate, carbon dioxide, and possibly ferric iron or some other metal oxides. Neither the potential for transformation of these compounds under field conditions using alternate electron acceptors, nor the rate of such transformations has yet been assessed.

Approach: Microbial consortia from aquifer solids and other sources are being enriched for anaerobic biotransformation of benzene and selected alkyl-substituted monoaromatic compounds. The different media for the enrichments are formulated to favor consortia that use selected electron acceptors (nitrate, sulfate, and carbon dioxide), and mixtures of aromatic compounds are being used to ascertain multicomponent effects on acclimation. Fundamental kinetic constants of the individual microbial consortia will be determined using substrate utilization and biological growth experiments. Results of laboratory studies will be compared with degradation rates determined in bioreactors placed into a gasoline contaminated aquifer at the Seal Beach site in Southern California. The field research is being developed and carried out in cooperation with research staff of the Orange County Water District (Dr. Harry F. Ridgway and Don Phipps).

Status: The hydrodynamic characteristics of the three in situ bioreactors at Seal Beach have been determined and experiments are underway to assess biotransformation rates under prevailing anaerobic conditions. Beginning in 1991, different redox regimes will be induced at the field site, and contaminant removal will be assessed.

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

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

Goals: The objectives are to determine trinitrotoluene (TNT) degradation rates and transformation products with anaerobic metabolism by sheep ruminal microorganisms utilizing ¹⁴C radiolabel.

Rationale: Pilot trials have shown that a new source of bacteria capable of degrading aromatic compounds have been found in sheep's rumen. The uniqueness of these microorganisms is the time rate in which total degradation of the toxic molecules occur. Few anaerobes from sediments can degrade TNT; however, preliminary evidence has shown that sheep microorganisms can degrade 100mg/ml within 96 hours. Commercializations of these bacteria in bioremediation of munitions sites for the Navy and other branches of the armed forces would be highly desirable.

Approach: A three-fold approach will be used: 1) The ruminal microorganisms will be enriched for TNT degradation, and a partially purified bacterial consortia will be defined,

2) Degradation of radiolabelled TNT will be used to identify the metabolic transition and end products of TNT metabolism, 3) Optimum growth parameters and degradation rates utilizing this consortia will be determined.

Status: The grant was initiated October 1, 1990. Sheep have been fistulated to obtain ruminal fluid. Anaerobic hoods have been calibrated and checked for optimum efficiency. Primary cultures are currently degrading TNT at a 96 hour rate. Different select media are being tried to enhance growth of detoxifying organisms and degradation rates.

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

The Effect of Surfactants on Biodegradation of Chlorinated Biphenyls in Soils: Martin Reinhard, Stanford University

Goal: The goal of this project is to explore the effect of surfactants on the aerobic biodegradation of strongly sorbing compounds, such as polychlorinated biphenyls (PCBs), in the presence of soils. Solubilization using surfactants has been proposed as a means of facilitating biodegradation of these compounds which are recalcitrant due to strong sorption onto soils and sediments.

Rationale: Sorption is thought to be one of the primary factors limiting the biotransformation of PCBs in soils and sediments. By increasing the bioavailability through the addition of solubilizing agents, biotransformation of PCBs could be enhanced and soil and sludge decontamination by microbial processes could be accelerated.

Approach: This feasibility investigation includes the following: (1) a test of 4-chlorobiphenyl desorption using several commercial surfactants, (2) a test of surfactant toxicity to 4-chlorobiphenyl degrading organisms, (3) determination of the solubilizing effect of surfactants in soils, and (4) a test of the rate of 4-chlorobiphenyl degradation in the presence of solids and surfactant at various concentrations.

Status: The experimental work using a 4-chlorobiphenyl desorbing surfactant is underway, with completion expected by December 31, 1990.

Client/Users: Researchers interested in PCB degradation; regulators concerned with controlling levels of toxic/carcinogenic compounds in the environment, and industry with contaminated sites to remediate .

HEAVY METALS

Trace Metal Removal Processes: James O. Leckie, Stanford University

Goal: The goal is development of an experimental data base and mathematical model for mass transfer limited adsorption of trace metals in porous particles. Experimental results

and the mathematical model will facilitate the design of removal process utilizing porous metal oxide particles.

Rationale: Previous experimental work with porous, high-surface-area oxide particles has demonstrated a dramatic increase in adsorption capacity of the porous material relative to non-porous particles. From an engineering perspective, porous particles with high internal surface area are appropriate for treating large volumes of dilute metal bearing wastewaters and allowing regeneration and recycling of the adsorbent. Reactions within porous particles can be severely limited by intraparticle diffusion. Investigation of diffusional limitations is an objective of this project. Choice of particles with a suitable pore size distribution will provide the high surface area desired without imposing severe pore diffusion limitations.

Approach: The approach involves the design and implementation of a parametric study of adsorption of an oxyanion (selenite) and a cation (cadmium) on porous, amorphous alumina particles. Samples of three different porous aluminum oxide particles were obtained from ALCOA for the study. The first phase of the experimental work involved the physical-chemical characterization of the adsorbent (particle morphology, particle size distribution, pore size distribution, surface area, solid structure, surface site density, acidity constants, electrolyte binding constants, and trace element binding constants). The second and main phase of the experimental work explores the role of mass transfer on trace element adsorption/desorption in the porous alumina particles. The parametric study includes experiments at variable pH values, solid and trace element concentrations, solid/solution ratios, and ionic strengths. Based on particle characterization and data developed in the second experimental phase, a time-dependent mathematical model will be developed coupling diffusion processes with adsorption. The modeling task is difficult because of the inability to measure experimental parameters directly associated with trace metal adsorption inside the particles

Status: The physical characterization of the adsorbent has been completed and chemical characterization is being carried out. Equilibrium experiments with selenite have confirmed the high adsorptive capacity of the porous alumina. Rate experiments indicate that the approach to equilibrium depends on the solid-to-liquid ratio, as expected for diffusion limited adsorption, and desorption rates were found comparable to adsorption rates. The next phases will involve modeling of equilibrium and rate experiments.

Client/Users: Researchers interested in trace metal removal processes; electronics, electroplating, and power industries; areas with high trace metal concentration problems (e.g. Kesterson reservoir).

Hexavalent Chromium Sorption and Desorption in Natural Soils and Subsoils: Peter O. Nelson and Jonathan D. Istok, Oregon State University

Goal: The intent of this research is to gain a better understanding of the chemical behavior of hexavalent chromium, Cr(VI), in natural soils. Emphasis will be placed on determination of reaction kinetics and the effects of competing solute anions on Cr(VI)

sorption and desorption. Results will be used to improve transport modeling of the fate of Cr(VI) and to better design remediation schemes for chromium-contaminated soils.

Rationale: Remediation schemes for chromium contaminated sites give strong consideration to soil flushing, or pump-and-treat technology. Pump-and-treat has been selected for at least one Region 10 site (United Chrome Products), and is being considered for many others around the country. The efficacy of pump-and-treat is highly dependent on chromium sorption and desorption kinetics and on the influence of competing solute anions. Models to predict the transport of Cr(VI) in soils must therefore incorporate these effects.

Approach: A controlled laboratory investigation is proposed in which Cr(VI) sorption and desorption reactions with natural soils and subsoils are studied. Batch reactor experiments will be used to determine equilibrium sorption parameters for chromate and sorbing co-solutes on soil and to study sorption and desorption kinetics over extended time periods (weeks to months) that are relevant to soil contamination sites. Soil column studies will be used to more closely simulate field conditions of porous media flow for investigation of diffusion-limited sorption and desorption kinetics. This latter is necessary for transport modeling and the preliminary design of in situ chemical extraction- remediation processes.

Status: This two-year project began on 3/1/90. Design of laboratory experiments for batch and soil column reactors has been completed, and experimental work is in progress. Expected project completion date is 2/28/92.

Client/Users: Practitioners selecting remediation processes for sites with hexavalent chromium contamination will benefit from the methodology developed in this research.

TRAINING AND TECHNOLOGY TRANSFER PROJECT DESCRIPTIONS

Hazardous Waste Training: Kenneth J. Williamson, Oregon State University and Gilbert Albelo, Mt. Hood Community College

Goal: The goal is to develop a comprehensive and coordinated program of hazardous substance training in the State of Oregon involving the community colleges and Oregon State University.

Rationale: A coordinated education program in Oregon was not available, but was found to be necessary to train and educate individuals for careers in the hazardous substance field.

Approach: A consortium of higher education, regulatory, and industrial representatives was developed to plan a multiple-level curriculum for hazardous substance management. The University of California extension program was used as a model. The curriculum would be implemented by the Oregon community college and university system.

Status: A curriculum has been developed and is being adopted at four community colleges and at Oregon State University. A proposal has been developed to the Oregon Legislature to adopt statutory requirements of certification for all employees with hazardous substance responsibilities. The levels in the certification are tied directly to various educational levels in the developed curriculum. The project began in January 1990 and is expected to be complete in June 1991.

Advanced Topic Workshops: Lewis Semprini, Stanford University

Goal: The goal is to give advanced topic workshops to transfer results of basic and applied research being performed at the Center to regulators, consultants, industry, and researchers, illustrating how the research findings pertain to problems encountered in practice.

Rationale: There is an expressed need among the community working on hazardous substance problems for the most recent available research findings in the field together with a theoretical foundation on which the research findings are based.

Approach: The Center is presenting these workshops primarily in California where the expressed need has been the greatest. They are being provided in conjunction with the University of California Extension Program in Environmental Hazard Management to complement the basic training program which they already provide. The one to two day workshops are presented by a group of Center researchers to provide a broad range of expertise on central contaminant problems of concern in EPA Regions 9 and 10.

Status: Two workshops entitled "Biological Transformations of Chlorinated Solvents in Subsurface Systems - Natural Processes and In-situ Bioremediation" were given on June 22, 1990, at Stanford University, and on June 28, 1990, at the University of California Irvine. They were attended by over 200 professionals from industry, governmental agencies, and consulting firms. This workshop may be given again this coming year. A new workshop on "Biological Transformations of Chlorinated and Non-Chlorinated Aromatic Compounds" is also being planned for the coming year.

Continuing Education Program: Kenneth J. Williamson, Oregon State University

Goal: The goal of this activity is to provide continuing education courses for professionals in the hazardous substance field.

Rationale: There is a need by regulators, consultants, and industrial personnel who are working in the hazardous substance field to obtain greater knowledge about hazardous chemical management and treatment, and to keep abreast of current developments. Extension courses provide greater breadth and depth of knowledge in given areas than can be obtained from conferences, seminars, or workshops alone. A need for such courses existed in Oregon.

Approach: A series of extension courses is being given by the Oregon State University Center faculty at the Tektronix Learning Center, Beaverton, Oregon, which is near the Portland area, where the need is large.

Status: This past year three courses were given entitled: Hazardous Substance Management, Hazardous Substance Legislation, and Hazardous Substance Minimization. For this coming year, two courses are currently being planned: Groundwater Contaminant Transport, and Hazardous Substance Legislation.

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

Goal: The goal is for the Center to actively participate in the cosponsorship of conferences held in EPA Regions 9 and 10 that address technical aspects of hazardous substance problems.

Rationale: Conferences are a highly efficient and cost-effective way to achieve the transfer of technology from research, and thus the Center should be active in sponsoring them, and organizing and participating in sessions, seminars, and workshops associated with them.

Status: This year the Center cosponsored, organized sessions, and participated in two conferences: the 1990 Idaho Regional Conference on Hazardous Materials and Wastes in Pocatello, Idaho, and the 1990 Responsible Hazardous Materials Management Conference in Portland. In addition to these conferences next year, the Center is also cosponsoring the International Symposium on In Situ and On-Site Bioreclamation, San Diego, and the Association of Environmental Engineering Professors Educational Conference at Oregon State University.

PUBLICATIONS

A. Refereed Journal Articles

Gorelick, S.M; "Large Scale Nonlinear Deterministic and Stochastic Optimization: Formulations Involving Simulation of Subsurface Contamination", *Mathematical Programming*, 48, 19-39 (1990).

Kitanidis, P. K., Effective Hydraulic Conductivity for Gradually Varying Flow, *Water Resources Research*, 26(6),1197-1208 (1990).

Chrysikopoulos, C. V., P. K. Kitanidis, and P. V. Roberts, "Analysis of One-Dimensional Solute Transport through Porous Media with Spatially Variable Retardation Factor", *Water Resources Research*, 26(3), 437-446 (1990).

B. Articles Submitted or in Press

Alvarez, L. M. and P. L. McCarty, "TCE Transformation by a Mixed Methanotrophic Culture: Effects of Toxicity, Aeration, and Reductant Supply," *Applied and Environmental Microbiology*, (accepted 1990).

Alvarez-Cohen, L. and P. L. McCarty, "A Cometabolic Biotransformation Model for Halogenated Aliphatic Compounds by Resting Microbial Cells," (submitted 1990).

Alvarez-Cohen, L. and P. L. McCarty, "Two-Stage Dispersed-Growth Treatment of Halogenated Aliphatic Compounds by Cometabolism," (submitted 1990).

Chrysikopoulos, C. V., P. K. Kitanidis, and P. V. Roberts, "Macrodispersion of Sorbing Solutes in Heterogeneous Porous Formations in Spatially-Periodic Retardation and Velocity Field," (submitted 1990).

Chrysikopoulos, C. V., P. K. Kitanidis, and P. V. Roberts, "Generalized Taylor-Aris Moment Analysis of the Transport of Sorbing Solutes through Porous Media with Spatially Periodic Retardation Factor," (submitted 1990).

Dykaar, C. B., and P. K. Kitanidis, "Determination of Effective Hydraulic Conductivity in Heterogeneous Porous Media," (submitted 1990).

Grbic-Galic, D., S.M. Henry, E. M. Godsy, E. Edwards, and K.P. Mayer, "Anaerobic Degradation of Aromatic Hydrocarbons and Aerobic Degradation of Trichloroethylene by Subsurface Microorganisms," (submitted 1990).

Grbic-Galic, D., "Degradation of Aromatic Hydrocarbons and Phenols in Methanogenic Environments," (submitted 1990).

Harmon, T.C., L. Semprini, and P.V. Roberts; "Simulating Groundwater Solute Transport Using Independently Determined Sorption Parameters," (submitted 1990).

Henry, S.M., and D. Grbic-Galic, "Trichloroethylene (TCE) Oxidation by Methanotrophic Cultures from a Ground Water Aquifer: Endogenous and Exogenous Electron Donors and TCE Oxidation Toxicity, *Appl. Environ. Microbiol.*, (accepted 1990).

Istok, J. D., S.B. Lee, and S.L. Woods, "A Numerical Model for Interpreting Results of Column Transport Experiments with Nonlinear, Nonequilibrium Sorption," (submitted 1990).

C. Books and Bound Proceedings

K.J. Dawson and J.D. Istok, *Aquifer Testing: A Manual for the Design and Analysis of Pumping Tests*, Lewis Publishers, Inc, Chelsea, Michigan (accepted, 1990).

McCarty, P. L. and P. V. Roberts, editors, "Contaminants in the Subsurface Environment," *Water Science and Technology*, 22(6), 110 pp. (1990).

D. Chapters in Other Books or Bound Proceedings

Grbic-Galic, D., "Anaerobic Microbial Degradation of Aromatic Hydrocarbons," Proceedings, Conference on Microbially Enhanced Oil Recovery, Norman, Oklahoma, (submitted 1990).

Gailey, R.M. and S.M. Gorelick, "Coupled Process Parameter Estimation: The Combined Worth of Concentration and Head Data", International Conference on Calibration and Reliability in Groundwater Modelling, The Hague, The Netherlands, (submitted 1990).

E. Project Reports

McCarty, P. L., L. Semprini, M. E. Dolan, T. C. Harmon, S. Just, C. Tiedeman, S. M. Gorelick, and P. V. Roberts, "Evaluation of In-Situ Methanotrophic Bioremediation for Contaminated Groundwater, St. Joseph, Michigan," Technical Report No. WR-1, WRHSRC, Department of Civil Engineering, Stanford University, Stanford, CA (1990).

F. Theses/Dissertations

S.B. Lee, A Numerical Model for the Fate and Transport of Chlorinated Phenols in Groundwater, Ph.D. thesis, Department of Civil Engineering, Oregon State University, Corvallis, Oregon (1990).

K.J. Dawson, Aquifer Testing: A Manual for the Design and Analysis of Pumping Tests, M.S. thesis, Department of Civil Engineering, Oregon State University, Corvallis, Oregon (1990).

G. Conferences and Workshops Held

McCarty, P. L. P. V. Roberts, D. Grbic-Galic, and L. Semprini, "Biological Transformations of Chlorinated Solvents in Subsurface Systems - Natural Processes and In-situ Bioremediation," One day workshops held June 22, Stanford University, and June 28, 1990, University of California Irvine, California.

Western Region Hazardous Substance Research Center, Idaho State University, and the Idaho Association of Commerce and Industry, "Regional Conference on Hazardous Materials and Wastes," Pocatello, Idaho,

Western Region Hazardous Substance Research Center, Associated Oregon Industries, Department of Environmental Quality, Oregon Council, American Electronics Association, and Semiconductor Safety Association, "Responsible Hazardous Materials Management Conference," Portland, Oregon, October 9 and 10, 1990.