

**WESTERN REGION  
HAZARDOUS SUBSTANCE RESEARCH CENTER**

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**2003 ANNUAL REPORT**

Oregon State University  
Stanford University

December 2003

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**Table Of Contents**

**Administration..... 3**

**The Center At A Glance..... 3**

**Director's Report..... 8**

**Project Highlights Of The Year ..... 8**

**Training And Technology Transfer..... 11**

**TOSC And TAB Programs..... 12**

**Center Annual Research Meeting..... 13**

**Research Project Reports ..... 13**

**Outreach Project Reports..... 27**

**Western Regional Lead Training Center--Hazardous Waste Training..... 38**

**Technology Demonstrations of In Situ CAH Treatment..... 39**

**New Center Projects..... 42**

**2003 WRHSRC Publications..... 43**

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## Administration

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## The Center at a Glance

The Western Region Hazardous Substance Research Center (WRHSRC) is a cooperative activity between Oregon State University and Stanford University that was established in October 2001. The center is a continuation of the original center established in 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. The objectives of the center are

1. To develop innovative technologies for the in situ treatment of volatile organic chemicals (VOCs) in groundwater, especially chlorinated solvents.
2. To increase the number, speed, and efficiency of available treatment options for both high concentration source zones and diffuse contamination plumes.
3. 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 treatments that use microbes or chemical catalysts to transform VOCs into harmless substances, represent the major focus of center activities. Research projects include biological (biotic) and physical and chemical (abiotic) treatment processes, as well as in situ characterization methods for monitoring the progress of both intrinsic and the enhanced remediation. In combination with basic laboratory and field studies, physical and mathematical models are being used to study these processes and to provide a bridge between theory and practice. The technology transfer program involves the process of taking new technologies from the laboratory to the field. Center researchers are working with other federal agencies such as the Department of Defense (DoD)

and the Department of Energy (DoE) and private industry, in conducting field evaluations of new technologies. Technical Outreach Services for Communities (TOSC) is a technical assistance program designed to aid communities confronted with environmental contamination by hazardous waste sites. TOSC provides interested community groups with technical information and assistance that can enable early and meaningful public participation in decisions that affect health and welfare. The center's Technical Assistance to Brownfields Communities (TAB) Program provides assistance to communities attempting to address cleanup and redevelopment of properties whose reuse has been prevented by real or perceived contamination. TAB attempts to improve involvement of all affected parties in cleanup and redevelopment process through education and training.

Table 1 lists the 24 OSU and Stanford faculty members who are involved in the center. Seventeen of these are directing the center's research, training, and technology transfer activities. They collectively represent an integrated research group of many different disciplines, including biochemistry, chemistry, environmental engineering, environmental chemistry, geosciences, hydrogeology, molecular biology, microbiology, public health, and sociology. Lewis Semprini is director of the center and of the research program. Kenneth J. Williamson serves as associate director in charge of training, technology transfer and community outreach. Martin Reinhard, the assistant director, is in charge of the center's quality control program. Garrett Jones is the center's administrative assistant.

The center has two major advisory groups to guide its activities. The Science Advisory Committee (SAC) has oversight for all center research activities and technology transfer activities, and the Outreach Advisory Committee (OAC) oversees the center's TOSC and TAB programs. The members of the SAC and OAC during this past year are listed in Tables 2 and 3, respectively. They represent federal and state governments, industry, consulting firms, and universities. Experts with a broad range of expertise are included in the SAC and the OAC.

The center budgets for the 2003 fiscal year and since the center's inception are listed by category of support in Table 4. During the second year of operation, core funding totaled \$1,125,000. The distribution of the center's \$900,000 of base EPA funding is shown in Figure 1. Over 59% of the funds go directly to the research program.

The education of students interested in careers directed toward finding solutions to environmental problems is another important goal. The number of students supported through WRHSRC funds is listed in Table 5. Sixteen graduate students have been supported during the second year of the center, with fourteen of these being Ph.D. students. Over 50% of the center core funds are being directed toward the graduate training of students through the center's research and outreach projects.

**Table 1. Key Personnel at the WRHSRC**

<u>Stanford University/Discipline</u>	<u>Oregon State University/Discipline</u>
Craig C. Criddle, Environmental Engineering	Daniel J. Arp, Biochemistry
Peter K. Kitanidis, Hydrogeology	Peter Bottomley, Microbiology
James O. Leckie, Environmental Chemistry	Lynda Ciuffetti, Microbiology
Dick Luthy, Environmental Engineering	Mark Dolan, Environmental Engineering
Perry L. McCarty, Environmental Engineering	Jennifer Field, Environmental Chemistry
Martin Reinhard, Environmental Chemistry	Steve Giovannoni, Molecular Biology
Alfred Spormann, Microbiology/Biochemistry	Anna Harding, Public Health
	Roy Haggerty, Geosciences
	James D. Ingle, Chemistry
	Jonathan D. Istok, Hydrogeology
	Denise Lach, Sociology
	Peter Nelson, Environmental Engineering
	Lewis Semprini, Environmental Engineering
	Stephanie Sanford, Sociology
	John C. Westall, Chemistry
	Kenneth J. Williamson, Environmental Engineering
	Brian Wood, Environmental Engineering

**Table 2. Science Advisory Committee**

<u>Member</u>	<u>Affiliation</u>	<u>Expertise</u>
Dr. Richelle M. Allen-King (Vice-Chair)	Department of Geology, University at Buffalo, Buffalo, NY	Geochemistry; Hydrogeology
Dr. Harold Ball	U.S. EPA Region 9, San Francisco, CA	Environmental Engineering
Dr. Roseanne Ford	Chemical Engineering Department, University of Virginia, Charlottesville, VA	Microbial Processes; Chemical Engineering
Dr. Joe Hughes (Chair)	Department of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA	Bioremediation; Environmental Engineering
Dr. Andrea Leeson	SERDP/ESTCP Program Office, DoD, Arlington, VA	Bioremediation; Environmental Engineering
Dr. Kirk O'Reilly	ChevronTexaco Research and Technology Company, Richmond, CA	Biochemistry; Microbial Processes
Dr. Gregory D. Sayles	USEPA Office of Research and Development, Cincinnati, OH	Microbial Processes; Bioremediation
Dr. Jim Spain	Air Force Research Laboratory, Tyndall AFB, FL	Microbiology

**Table 3. Outreach Advisory Committee**

<u>Member</u>	<u>Affiliation</u>	<u>Expertise</u>
Mr. Tim Brincefield	U.S. EPA, Region 10, Seattle, WA	Superfund cleanup and brownfields
Mr. Alan Kiphut	Oregon Department of Environmental Quality, Portland, OR	Policy/law of environmental regulations
Mr. Brooks Koenig	Veritas, Vizslas, & Velos, Portland, OR	Policy/law of environmental regulations
Mr. Luis Rivera	North Coast Regional Water Quality Board, Santa Rosa, CA	Regulations
Ms. Vicki Rosen	U.S. EPA, Region 9, San Francisco, CA	Superfund community involvement
Mr. Lenny Siegel	Center for Public Environmental Oversight, Mountain View, CA	Policy/guidance for cleanup and reuse
Ms. Kathleen Veit	U.S. EPA, Region 10, Seattle, WA	Community involvement

**Table 4. Center Funding**

<u>Funding Sources</u>	<u>FY 2001*</u>	<u>FY 2002*</u>	<u>Funds to Date</u>
EPA: Centers Program	\$900,000	\$885,000	\$1,785,000
EPA: Brownfields	150,000	150,000	300,000
Oregon State University	<u>90,000</u>	<u>90,000</u>	<u>180,000</u>
TOTAL	\$1,140,000	\$1,125,000	\$2,265,000

\*Oct. 1, 2002- Sept. 30, 2003

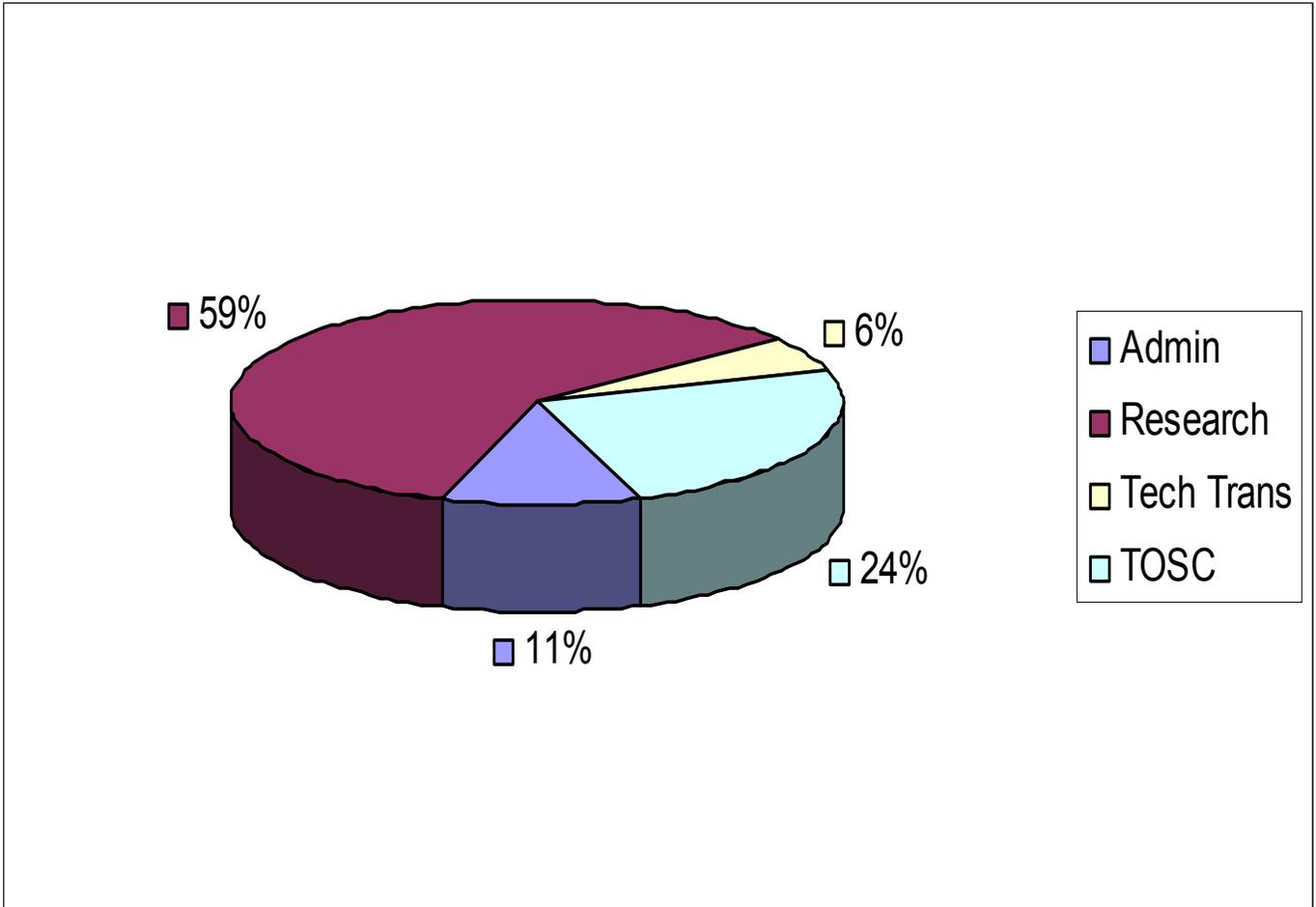
**Table 5. Student Support**

<u>Student Support</u>	<u>FY 2001</u>	<u>FY 2002</u>	<u>Funds to Date†</u>
M.S.	2	2	\$ 160,000
Ph.D.	9	14	1,030,000
Post Doctoral	<u>0</u>	<u>0</u>	<u>-</u>
TOTAL	11	16	\$1,190,000

\*Total numbers in researcher-years participating on center Projects since 2001

† Includes tuition, stipends travel, supplies, etc.

**Figure 1.**



# Director's Report

## Project Highlights of the Year

The major focus of research activities for the OSU-Stanford WRHSRC, and indeed its major mission, has been the conduct of basic research related to the in situ treatment of VOC subsurface contamination. During the past year research has continued in seven research projects associated with the in situ remediation of chlorinated solvents. The projects and the researchers are summarized below.

**Table 6. RESEARCH PROJECT SUMMARY**

<b>Project</b>	<b>Title</b>	<b>PI Co-PIs</b>	<b>Year 1 Budget</b>	<b>Year 2 Budget</b>
1-SU-01	Strategies for Cost-Effective In situ Mixing of Contaminants and Additives in Bioremediation	Peter K. Kitanidis, PI; Craig S. Criddle, Co-PI	\$75,001	\$74,999
1-OSU-01	Developing and Optimizing Biotransformation Kinetics for the Bioremediation of Trichloroethylene at NAPL Source Zone Concentrations	Lewis Semprini, PI; Mark E. Dolan, Co-PI	\$70,224	\$51,501
1-OSU-02	Aerobic Cometabolism of Chlorinated Aliphatic Hydrocarbon Compounds with Butane-Grown Microorganisms	Peter Bottomley, PI Daniel J. Arp Lynda Ciuffetti, Stephen Giovannoni, Lewis Semprini, Ken Williamson, Mark Dolan, Co-PIs	\$156,348	\$163,486
1-SU-02	Chemical, Physical and Biological Processes at the Surface of Palladium Catalysts under Groundwater Treatment Conditions	Martin Reinhard, PI; John Westall, Co-PI	\$84,427	\$86,870
1-SU-03	Effects of Sorbent Microporosity on Multicomponent Fate and Transport in Contaminated Groundwater Aquifers	Martin Reinhard, PI	\$56,026	\$41,329
1-OSU-03	Development of the Push-Pull Test to Monitor Bioaugmentation with Dehalogenating Cultures	Mark E. Dolan, PI Jennifer A. Field, Jonathan D. Istok, Co-PIs	\$45,627	\$47,656
1-OSU-04	Development and Evaluation of Field Sensors for Monitoring Bioaugmentation with Anaerobic Dehalogenating Cultures for In Situ Treatment of TCE	James D. Ingle, PI	\$47,400	\$48,900

Research projects include biological (biotic) and physical and chemical (abiotic) treatment processes, as well as in situ characterization methods for monitoring the progress of both intrinsic and the enhanced remediation. Four project PIs are at OSU and three are at Stanford University.

Project 1 (1-SU-01), which is being conducted at Stanford University by Peter Kitanidis and Craig Criddle, is focused on developing strategies for cost-effective in situ mixing of contaminants and additives in bioremediation. Such methods will employ recirculation units, pairs of extraction-injection wells, sparging systems, biocurtains, and time- and space-sequenced operations. Over the past year the researchers have focused on the design of an effective chemical delivery and mixing scheme for in situ bioremediation of Uranium (VI) at Oak Ridge National Laboratory (ORNL). Mathematical models of flow, transport and biogeochemistry have been developed and predictions compared with the results of experiments and field tests. Software has been developed for the delineation of injection, extraction, and recirculation zones; the efficient determination of breakthrough curves; the application of travel-time methods of modeling transport; and biogeochemical modeling using PHREEQC in conjunction with hydrogeological modeling within the MATLAB computational environment.

Project 2 (1-OSU-01), which is being conducted at OSU by Lewis Semprini and Mark Dolan, aims at developing a mixed anaerobic culture that is effective at transforming PCE and TCE via halorespiration at elevated concentrations representative of those associated with NAPL contamination. The specific objectives of this project are to (1) develop a culture with the ability to reductively dechlorinate TCE to ethylene at very high concentrations (above 1,000  $\mu\text{M}$ ) and in the presence of DNAPL; (2) characterize microbial growth and measure maximum substrate utilization rates and half velocity coefficients for successive dechlorinations of TCE to ethylene; and (3) characterize the microbial consortium by investigating molecular methods to evaluate the diversity of the mixed culture developed in the kinetic studies. Over the past year kinetic parameters were determined for each step in the dehalogenation process, with two mixed cultures and a binary culture (a mixture of the two cultures) to describe the reductive dechlorination of chlorinated ethylenes. Kinetics of the inhibition of the CAHs was also studied. Model simulations of the sequential transformation of PCE and TCE to VC and ethene matched well the results of batch kinetic experiments over a factor of 30 change in concentration, using the independently determined kinetic parameters. Molecular characterization of the two cultures was also performed.

In project 3 (1-OSU-02), which is being conducted at OSU by a number of investigators headed by Peter Bottomley and Dan Arp, the CAH degrading properties of several individual strains of butane-oxidizing bacteria and fungi that are known to possess distinctly different butane monooxygenases is being examined. The work is directed towards the aerobic cometabolism of a broad range of CAHs and CAH mixtures. Research on three sub-projects has continued during the past year. Research by Peter Bottomley and Dan Arp examined the CAH degrading properties of several individual strains of butane-oxidizing bacteria, *Pseudomonas butanovora*, *Nocardioides* CF8, and *Mycobacterium vaccae* JOB5, that are genotypically distinct from each other, and that are known to possess distinctly different butane monooxygenases (BMO). Their studies focused the inactivation of the butane monooxygenases, the BMO, resulting from transformation of different CAHs as well as the potential from BMO induction upon exposure

to CAHs. Research by Lew Semprini and Mark Dolan is evaluating 1,1,1-TCA and 1,1-DCE cometabolism by a *Rhodococcus* sp. that has been bioaugmented into the continuous flow laboratory column packed aquifer solids from the Moffett Air Field In-Situ Test facility. Studies have shown effective and long term removal of 1,1,1-TCA in the column upon bioaugmentation and growth butane. Molecular based PCR probes have detected the bioaugmented microorganism in the column groundwater effluent after bioaugmentation and throughout the column test. Studies directed by Ken Williamson and Lynda Ciuffetti are evaluating the ability of a fungi, *Graphium* sp., to degrade a range of volatile organic compounds including chlorinated aliphatic hydrocarbons (CAHs), trichloromethanes and polyaromatic hydrocarbons (PAHs). The study also aims to demonstrate that these reactions are catalyzed by an alkane inducible cytochrome P450 monooxygenase through heterologous expression assays with yeast. The investigators are using cloning techniques to study the P450 monooxygenase in different types of fungi. In another related project, supported by an EPA STAR fellowship, the alkane monooxygenase activity will be conferred to plants, and the kinetics and fate of environmentally significant compounds (fuel oxygenates, chlorinated solvents and PAHs) in these transgenic plants will be determined.

Project 4 (1-SU-02) is an investigation of the chemical, physical, and biological processes at the surface of palladium catalysts under groundwater treatment conditions by Martin Reinhard and Stanford University and John Westall at Oregon State University. This project approaches optimization of the abiotic process for CAH reduction using Pd catalysts. The project aims at obtaining a through understanding of changes in the catalyst surface during treatment and correlating these to changes in catalytic activity. Research conducted during the second year of this project demonstrated that deactivation of the catalyst was consistent with sulfide poisoning. Treatment with sodium hypochlorite was able to fully regenerate the catalyst. The research is being undertaken in collaboration with a field study at Edwards Air Force Base (EAFB) near Lancaster, California.

In project 5 (1-SU-03), conducted by Martin Reinhard at Stanford University, the effects of sorbent microporosity on multicomponent fate and transport in contaminated groundwater aquifers is being studied. This project is investigating the importance of one of the most fundamental processes of organic sequestration on porous sorbents—micropore sorption. The impacts of the environmental variables affecting micropore sequestration is being quantified. The competitive sorption/desorption of multiple contaminants on the natural soils is being studied to elucidate the interactions among molecules with different properties during micropore sequestration. The kinetics of contaminant uptake and release from micropores is being measured and compared with other sorption/desorption pathways. Over the past year an apparatus has been developed specially for measuring slow sorption and desorption kinetics of VOCs on solid materials packed in columns. This design has expanded the investigative capabilities in several ways: data are acquired in real-time with high resolution over the entire contaminant desorption profile, contaminant detection is extremely sensitive, and sorption and desorption of multiple volatile organic contaminants can be studied. The initial experimental results suggests that the property of micropores in geosorbents, rather than the total volume of the micropores, plays key role in controlling contaminant sequestration and desorption.

In project 6 (1-OSU-03), being conducted by Mark Dolan, Jennifer Field and Jonathan Istok at OSU, the push-pull test to monitor the bioaugmentation with dehalogenating cultures is being developed. The overall goal is to modify the single-well push-pull groundwater test as a means

for obtaining quantitative information on in situ dechlorinating activity before and after bioaugmentation. Two cultures characterized in Project 2 (Evanite and Pt. Mugu) that transform TCE to ethene are being used in this study. The transport of the culture(s) is being determined during injection into anaerobic physical aquifer models (PAMs). Spatial distributions of dechlorinating activity and redox are determined from a suite of assays conducted at sampling ports and at the injection/extraction well. Push-pull tests are being conducted at the injection/extraction well to assess changes in reductive dechlorination activity resulting from bioaugmentation. The investigators are currently evaluating the survivability of the cultures in groundwater/sediment microcosms and studying basic transport behavior in columns. Molecular methods, using *Dehalococcoides* sp. group-specific PCR primers are being used to track the dehalogenators. Serial dilutions of the Evanite culture were extracted and analyzed using *Dehalococcoides* group-specific PCR and dilutions down to  $10^{-4}$  were detectable by this process. Future work includes expanding this testing to real-time quantifiable PCR analyses to attain better enumeration of *Dehalococcoides* sp.

In project 7 (1-OSU-04), directed by Dr. Jim Ingle at OSU, field sensors are being developed and evaluated for determining redox conditions during in situ treatment of TCE. This study aims to refine and use redox sensors based on redox indicators as monitoring tools for assessing and optimizing redox conditions for treatment of TCE and PCE with dehalogenating cultures. Flow sensors based on redox indicators are being deployed in two primary collaborate situations for calibration and demonstration of their applicability: 1) continuous monitoring of redox conditions of cultures inside bioreactors or microcosm bottles as a tool for the optimizing conditions for effective dechlorination of PCE or TCE with enriched halorespiratory cultures, and 2) on-line monitoring of the redox status of the material in a physical aquifer model (PAM) bioaugmented with the developed dehalogenating cultures. Research in the second year evaluated the dechlorinating culture (Project 2) in bioreactors and microcosm bottles to calibrate the response of the redox indicators to the dechlorination of PCE. The indicator data support the concept that the dechlorinating process is increasingly reduced as PCE is dechlorinated, with the most reducing step in the process being the dechlorination of vinyl chloride to ethene. Research has also focused on the development of a hydrogen sensor on membranes with platinum embedded membranes.

## **Training and Technology Transfer**

The education of graduate students in the research focus area of the center is one of our main training activities. The students who have been funded through our center research grants are shown in Tables 5 and 7. Two M.S. students and fourteen Ph.D. students received center funds through graduate research assistantships over the past year. Two of the students have been funded through the center outreach program and fourteen through the different research projects. Through center funding, students are being trained to do fundamental research at the Ph.D. level in a broad range of disciplines. As shown in Table 5, over half of the center funding is devoted to the training of graduate students, with the funding going directly in tuition, stipends, travel to conferences, and supplies and materials for research.

Technology transfer is a important component of the WRHSRC. The goals of the training and technology transfer program are to 1) promote teamwork and information exchange among

researchers using web pages and seminars; 2) provide information transfer with practitioners using web pages, electronic newsletter, video workshops, faculty presentations and publications; 3) test new technologies through pilot-scale testing, and developing online project databases; and 4) implement full-scale demonstration projects. The WRHSRC web site developed and maintained at OSU receives about 700 visitors per month. Some of the information contained on the web site includes descriptions of research focus areas and projects; a database of WRHSRC publications and previous projects, 1989-2002; descriptions of center outreach programs and links to the separate websites for the Western Region TOSC/TAB programs; and a News and Events page with regular postings. The website address is <http://wrhsrc.orst.edu>. The web site features center publications and a searching capability, research briefs, demonstration projects for Technical Outreach Services for Communities, and a page that walks clients through the process of obtaining help from TOSC. Interested clients and individuals can subscribe to the new e-mail newsletter (launched in spring 2003) for WRHSRC and TOSC (started in fall 2002). Three Research Briefs, focusing on the Center Research Projects, were distributed through e-mail in 2003.

The WRHSRC also houses a program to promote training activities related to lead paint contamination and disposal. The Western Regional Lead Training Center at OSU (WRLTC-OSU), originally established with U.S. EPA grant funding in 1992, is an accredited non-profit training provider of lead-based paint abatement workshops for U.S. EPA and the State of Oregon certification programs. It is the only Oregon-accredited lead-based paint (LBP) training center and provides all of the federal LBP curricula. WRLTC-OSU is also accredited in Washington, Alaska, and Idaho, as well as the all of the Pacific Northwest Indian Tribes. In 2003, over 200 students attended 22 workshops and received 242 certificates. Accredited workshops included Lead Inspector, Lead Risk Assessor, Combined Lead Inspector & Risk Assessor Refresher, Lead Abatement Worker, Lead Abatement Supervisor, Combined Lead Abatement Worker and Supervisor Refresher, and Lead Project Designer.

## **TOSC and TAB Programs**

The two outreach programs of importance are Technical Outreach Services for Communities (TOSC) and Technical Assistance to Brownfields (TAB). These programs are directed by Ken Williamson and Denise Lach at Oregon State University.

TOSC provides interested community groups with technical information and assistance that can enable early and meaningful public participation in decisions that affect health and welfare. The TOSC program provides a viable alternative strategy for communities that do not qualify for a Technical Assistance Grant (TAG) from the US Environmental Protection Agency. The TOSC team is comprised of university faculty and students, as well as contracted environmental professionals with specialization in environmental engineering, risk communication, public health, information transfer, environmental justice, and community relations. Currently the TOCS program is actively working with communities in, Oregon (2), Washington (1), Arizona (2), and California (12) (the number following the state designates the number of communities in each state).

The TAB program provides assistance to communities attempting to address cleanup and redevelopment of properties whose reuse has been prevented by real or perceived

contamination. TAB attempts to improve involvement of all affected parties in cleanup and redevelopment process through education and training. The TAB program is currently working in Oregon, Washington, California, and Nevada. They have worked with the cities of Portland, OR, Spokane, WA, East Palo Alto, CA, and Richmond, CA, on various issues related to brownfields redevelopment. The TAB program helps coordinate an annual Brownfields conference in partnership with Oregon Department of Environmental Quality and Oregon Economic and Community Development Department.

## **Center Annual Research Meeting**

In August 2003, center researchers, graduate students, outreach specialists, and Science Advisory and Outreach Advisory Committee members met for the second annual meeting of the WRHSRC. The meeting goal was to discuss the progress of the center's research projects over the past year, and for the SAC committee to review and rank new proposals for the third and fourth years of Center funding. In the morning and afternoon researchers from Oregon State University (OSU) and Stanford gave presentations highlighting five of the center's research projects and two community outreach programs. A student poster session on the center's research projects and outreach programs was held in the afternoon. On the second day of the meeting the SAC and OAC reviewed the progress of the center's research and outreach programs. The SAC committee also reviewed research proposals for center funding. The SAC ranked five new center projects (discussed later) for funding.

## **Research Project Reports**

Summary reports are presented below for each of the center's projects and outreach and technology transfer activities.

### **1-SU-01: Strategies for Cost-Effective In Situ Mixing of Contaminants and Additives in Bioremediation**

Peter Kitanidis, Stanford University, PI; Craig Criddle, Stanford University, Co-PI

*Goal:* (1) To develop and critically evaluate principles and strategies for mixing, using recirculation units, pairs of extraction-injection wells, sparging, biocurtains, combined systems and operations that are sequenced in time and space. (2) To develop methods for cost-effective chemical delivery and mixing, prevention of clogging, and hydraulic control. (3) To define the range of application of these methods and compare them on the same basis in terms of effectiveness and cost. (4) To synthesize available knowledge and previous experience on flow, transport, and biochemical reactions using results from field-scale studies. (5) To advance and test theories for subsurface mixing at field scales through hydrodynamic dispersion, partitioning, fingering, etc. (6) To develop a set of tools and guidelines for the design of cost-effective in situ delivery and mixing systems.

*Rationale:* Effective mixing and chemical delivery schemes is essential in the success of in situ remediation methods. This is because these methods usually require the injection of growth promoters (in situ bioremediation), chemical additives (e.g., surfactant-enhanced remediation),

or cells (bioaugmentation). To achieve successful mixing and chemical delivery at the field-scale, we need to (1) create a sufficiently large in-situ reactor, and (2) regulate residence times.

*Approach:* In this research, principles of mixing and the performance of mixing schemes are studied, and a broad range of existing and new full-scale mixing and chemical delivery schemes are evaluated through comprehensive mathematical, technical, and economic analysis. Research is guided by case studies.

*Status:* The design of an effective chemical delivery and mixing scheme for in situ bioremediation of Uranium (VI) at Oak Ridge National Laboratory (ORNL) was the focus. This is a challenging site, characterized by complex hydrogeology and biogeochemistry. The subsurface material is highly weathered saprolite. In addition to high uranium concentration, the pH is exceptionally low, at about 3.5, and nitrates are exceptionally high, at about 10 g/L. Nitrate needs to be removed and the pH needs to be raised in a controlled fashion, e.g., to prevent clogging of the porous medium from precipitation of aluminum. The speciation of U(VI), and thus its mobility, is controlled strongly by the pH. An elaborate on-site treatment plant has been designed and will be combined with a multi-step in situ treatment experiment. We have developed mathematical models of flow, transport and biogeochemistry and are comparing predictions with the results of experiments and field tests. We have developed software for the delineation of injection, extraction, and recirculation zones; the efficient determination of breakthrough curves; the application of travel-time methods of modeling transport; and biogeochemical modeling using PHREEQC in conjunction with hydrogeological modeling within the MATLAB computational environment. These modeling tools are currently being implemented at the ORNL site to extract information from data and to assist in the design of new experiments. The project is nearing completion.

### **1-OSU-01: Developing and Optimizing Biotransformation Kinetics for the Bioremediation of (Trichloroethylene at NAPL Source Zone Concentrations**

Lewis Semprini, Oregon State University, PI; Mark Dolan, Oregon State University, Co-PI

*Goal:* This project aims to: (1) develop a culture with the ability to reductively dechlorinate TCE to ethylene at very high concentrations (above 1,000  $\mu\text{M}$ ) and in the presence of DNAPL; (2) characterize microbial growth and measure maximum substrate utilization rates and half velocity coefficients for successive dechlorinations of TCE to ethylene; (3) characterize the microbial consortium by investigating molecular methods to evaluate the diversity of the mixed culture developed in the kinetic studies; (4) provide kinetic information and cultures in support of the center projects “Development of the Push-Pull Test to Monitor the Bioaugmentation of Dehalogenating Cultures,” and “Development and Evaluation of Field Sensors for Monitoring Bioaugmentation with Anaerobic Dehalogenating Cultures for In-Situ Treatment of TCE.”

*Rationale:* While TCE reductive dechlorination has been demonstrated under a variety of conditions, most laboratory and field projects have been conducted at TCE concentrations of 100 mg/L or less. However, near NAPL sources, concentrations of chlorinated aliphatic hydrocarbons approach their solubilities (>1,000 mg/L for TCE and >150 mg/L for PCE). Studies with different enrichment cultures isolated from contaminated sites have shown good potential for treatment of high concentrations of PCE and TCE. The cultures have different dehalogenation kinetic properties, which indicate that a more effective enrichment culture might

be obtained by combining cultures. Research is needed to optimize the transformation kinetics for the consortium that has the ability to reductively dechlorinate high concentrations of TCE and PCE to stoichiometric quantities of ethylene. This project will prove useful for the remediation of chlorinated aliphatic compounds in the NAPL source zone.

*Approach:* A culture is being developed that can rapidly degrade high concentrations of PCE and TCE to ethylene by mixing two enrichment cultures. The Point Mugu enrichment (PM) rapidly transforms TCE to VC, and slowly transforms VC to ethylene at very high PCE and TCE concentrations. The Evanite enrichment (EV), rapidly transforms PCE to *c*-DCE, and vinyl chloride to ethylene. By mixing both cultures, we hope to achieve rapid transformation of PCE and TCE to ethylene. We will use batch reactor studies to determine transformation kinetics for both cultures, and then when both cultures are combined. Inhibition among the CAHs will also be evaluated. Models will be constructed to simulate the results of the sequential transformations over a broad range of concentrations up to the solubility limits of PCE and TCE.

*Status:* Kinetic studies were conducted with two mixed cultures and a binary culture (a mixture of the two cultures) to describe the reductive dechlorination of chlorinated ethylenes. Inhibition of the CAHs was also studied. The EV culture and the PM obtained from different contaminated sites showed different patterns of reductive dechlorination. The simple batch kinetic method was developed that was easy to implement and produced very reproducible kinetic values. The  $k_{max}$  (based on the total protein content of the culture) for *c*-DCE of the EV culture was about two times lower than that of the PM culture, reflecting the slower *c*-DCE biotransformation of the EV culture. The  $k_{max}$  and  $K_S$  values for VC ( $2.44 \pm 0.36$   $\mu\text{mol}/\text{mg}$  of protein/day and  $602 \pm 7.06$   $\mu\text{M}$ , respectively) of the PM culture were very different from those of the EV culture ( $8.08 \pm 0.94$   $\mu\text{mol}/\text{mg}$  of protein/day and  $62.6 \pm 2.37$   $\mu\text{M}$ , respectively). Inhibition studies were performed on the inhibition of the CAH on the transformation of each other. Inhibition studies show the more chlorinated ethylenes inhibit reductive dechlorination of the less chlorinated. PCE inhibited reductive TCE dechlorination, but not *c*-DCE dechlorination, while TCE strongly inhibited *c*-DCE and VC dechlorinations. *c*-DCE strongly inhibited the transformation of VC. Inhibition constants of each chlorinated ethylene,  $KI$  ( $\mu\text{mol}/\text{L}$ ), were comparable to their respective half-velocity coefficients, when a competitive inhibition model was applied.

Batch tests to study the sequential transformation of PCE to ETH were also performed over a factor of 30 change in concentration of PCE, up to its solubility limit in water ( $1128$   $\mu\text{M}$ ), with the EV, PM, and a 50/50 mixture of both cultures to yield a binary culture (BM). Additional studies were performed with TCE up to a concentration of  $4173$   $\mu\text{M}$  ( $550$   $\text{mg}/\text{L}$ ), which represents 50% of its solubility limit in water. Simulations of the successive transformations of PCE to ETH, and TCE to ETH using the independently derived kinetic parameters matched well the results of batch kinetic tests for initial PCE concentration up to around  $317$   $\mu\text{M}$ . The simulations included the growth on the chlorinated solvents, and Monod kinetics including competitive inhibition. Above this concentration simulations deviated from the experimental observations, and predicted more rapid transformation of VC than was observed. The results suggest potential toxicity or inhibition at the higher concentrations of PCE and TCE. Simulations have been performed with Halden kinetics incorporated into the transformation models, where high concentrations of a contaminant inhibit its transformation. In order to explain the experimental observations Halden kinetics for TCE transformation were required for

both the EV and the PM cultures and for c-DCE and VC transformation by the EV culture. The EV culture appears to be more inhibited at higher CAH concentrations. TCE concentrations, up to 4173  $\mu\text{M}$  (550 mg/L) were transformed by both the EV and PM culture, with the PM culture more rapid transforming the TCE to VC and ethene. The results indicate less inhibition of the PM culture at higher concentrations. Batch experimental results indicate that the BM culture, which represent a mixture of both cultures, has better transformation abilities than either of the single cultures. Simulations for the BM culture, using individual transformation abilities of each culture support the experimental observations of more diverse dechlorination ability than either of the single mixed cultures.

Molecular methods analysis using PCR reactions with *Dehalococcoides*-specific primers and *Desulfuromonas*-specific primers, found *Dehalococcoides*-like microorganisms in both the cultures, but not *Desulfuromonas*-like microorganisms. The molecular methods could not distinguish between the *Dehalococcoides* species of the EV and the PM cultures. Future work will include the creation of clone libraries to characterize the cultures. We also plan to perform kinetic measurements at high concentrations of the CAHs to determine whether Halden kinetics are observed, which are consistent with the results obtained from model simulations.

### **1-OSU-02: Aerobic Cometabolism of Chlorinated Aliphatic Hydrocarbon Compounds with Butane-Grown Microorganisms.**

Peter Bottomley, Oregon State University, PI; Dan Arp, , Lynda Ciuffetti, Mark Dolan, Lewis Semprini, Kenneth Williamson, Oregon State University, CoPIs

The following project has three subprojects dealing with evaluating how to maximize the CAH degrading potential of individual strains and mixed communities of hydrocarbon degrading bacteria and fungi. Specific sub-objectives include (1) identifying growth conditions that maximize reductant flow to cometabolism and the cellular mechanisms that minimize the toxic effects of cometabolism and sustain the process; (2) understanding the relationship between community dynamics of hydrocarbon oxidizing bacteria and the kinetics of cometabolism in bioremediatory situations; and (3) evaluating the performance of cultures in laboratory column studies; and (4) applying improved cometabolic transformation models to the results of laboratory studies.

#### **Project 1**

Investigators: Peter Bottomley and Dan Arp

*Goal:* The project aims to evaluate how to maximize the CAH degrading potential of individual strains and mixed communities of hydrocarbon degrading bacteria. Specific sub-objectives include identifying growth conditions that maximize reductant flow to cometabolism and the cellular mechanisms that minimize the toxic effects of cometabolism and sustain the process.

*Rationale:* Studies conducted under laboratory and field conditions have shown that hydrocarbon-oxidizing bacteria cometabolize a wide range of CAHs. Nonetheless, there is considerable variability in the properties of cometabolism shown by different types of bacteria both in terms of the range of CAHs degraded and in their transformation capacities. More research is needed to better understand the microbiological reasons for the range of efficiencies observed, and to use this information to improve the biotechnology of bioremediation under cometabolism conditions.

*Experimental Approaches:* We have examined the CAH degrading properties of several individual strains of butane-oxidizing bacteria that are genotypically distinct from each other, and that are known to possess distinctly different butane monooxygenases (BMO). We have examined the impact of cometabolism of different CAHs on monooxygenase activity, and assessed the effect of cometabolism on cell viability. We are focused upon a comparison of TCE degradation in three different butane-oxidizing bacteria, *Pseudomonas butanovora*, *Nocardioides* CF8, and *Mycobacterium vaccae* JOB5. In addition, we are also conducting an examination of the cometabolism of the lesser-chlorinated DCEs by *P. butanovora*, because they are often persistent products of reductive dechlorination at field sites.

*Status:* While co-oxidation of TCE by *P. butanovora*, and *Nocardioides sp.* CF8 results in 96% inactivation of the butane monooxygenases, the BMO of *M. vaccae* was more resistant to inactivation, and 34% of activity remained. In *P. butanovora* and *Nocardioides* CF8, respiratory activity declined to two-thirds of the control value after TCE degradation, whereas it was virtually unaffected in *M. vaccae*. At high TCE concentrations (165  $\mu\text{M}$ ) the rates of TCE transformation by *P. butanovora* increased substantially relative to the other two strains, but cell viability was reduced to 17% of the control. Viability of *M. vaccae* and CF8 were unaffected because their rates of TCE transformation did not increase in response to TCE concentrations increasing  $> 22 \mu\text{M}$ . These findings indicate that situations might be identified where the use of strains (such as *M. vaccae*) possessing slower rates of CAH degradation without cell toxicity, might be more appropriate bioremediatory agents than strains that show high rates of TCE degradation that are transitory, and accompanied by substantial loss of cell viability.

Butane-grown *P. butanovora* co-oxidizes cis-DCE, 1,2, trans-DCE, and 1,1-dichloroethene (1,1-DCE). When *P. butanovora* was exposed to each of the three DCEs, and residual BMO activity measured by ethylene-dependent ethylene oxide formation, BMO activity was reduced in a time-dependent manner that varied with the specific DCE. BMO activity decreased by 50% after 15 min exposure to cis-DCE, after 6 min exposure to trans-DCE, and after 30 sec exposure to 1,1-DCE. In addition, cooxidation of the DCEs had different cytotoxic effects on *P. butanovora*. Although cooxidation of cis-DCE and trans-DCE inactivated the majority of BMO activity, cells retained lactate-dependent  $\text{O}_2$  consumption but they were unable to grow normally after removal of the DCEs. In contrast, cooxidation of 1,1-DCE caused a rapid decrease in both BMO activity and lactate-dependent  $\text{O}_2$  consumption within three min of exposure, and cells lysed. Treating cells with acetylene to inactivate BMO could eliminate the effects of 1,1-DCE, and lactate-grown cells (in which BMO was not expressed) were also unaffected.

We compared the efficiency of induction of BMO gene expression by TCE and DCEs in wild type and in a *LacZ/ BMO* reporter strain of *P. butanovora*. The relative induction characteristics of the three DCEs differed from their substrate properties. Trans-DCE induced BMO activity in both the wild type and in the *Lac Z* reporter strain, while cis-DCE only induced enzyme activity in the wild type, implying that products of cooxidation of cis-DCE were probably the major inducer(s). Enzyme activities in wild type cells were induced to  $\leq 25$  and 45% of the butane control by cis-DCE and trans-DCE, respectively, whereas *LacZ* expression was induced to 80% of maximal by trans-DCE in the reporter strain implying that the latter compound is an excellent inducer and that the products of its oxidation are not involved in the induction process. In the case of trans-DCE, BMO induction could be detected in the reporter strain at lower concentrations (5 to 10  $\mu\text{M}$ ) than

could be detected by ethylene-dependent ethylene oxide formation in the wild type (30  $\mu\text{M}$ ). The possibility exists that 1,2 trans-DCE could be a useful model compound for gaining a better understanding of the mechanism behind gene regulation of butane monooxygenase, and might serve as a surrogate inducer of BMO in the absence of butane in naturally attenuating sites downstream of zones of reductive dechlorination where DCEs might persist.

## **Project 2**

Investigators: Lewis Semprini and Mark Dolan

*Goals:* Evaluate the potential for bioaugmentation of butane-utilizing culture that is effective in transforming mixtures of 1,1,1-trichloroethane (1,1,1-TCA), 1,1-dichloroethane (1,1-DCA), and 1,1-dichloroethene; use molecular tools that have been developed to track the culture upon its addition to a continuous flow laboratory column; develop kinetic parameters for butane-utilization and CAH transformation for use in a modeling analysis of the column tests; and model the results of the column experiment with a numerical model that includes kinetic terms for the microbial processes that have been determined independently in the laboratory.

*Rationale:* Laboratory and microcosm studies have shown different abilities of butane-utilizing microorganisms to cometabolize CAHs. Of particular interest is 1,1,1-TCA, 1,1-DCE, and 1,1-DCA. A *Rhodococcus* sp. culture has been sequenced and obtained in pure culture that effectively transforms these compounds. This culture has been bioaugmented to the subsurface at the Moffett Field tests zone in a collaborative research grant funded through the DoD SERDP program. The Center project is performing continuous flow column experiments, like those performed in the field, for direct comparison with the field results, and to permit more detailed evaluation of the of processes and conditions that cannot be performed in the field. Transformation rate parameters for the *Rhodococcus* culture, including maximum utilization rate ( $k_{\text{max}}$ ) and half-saturation coefficients ( $K_s$ ) values are also being determined, and compared with previously determined values obtained with the mixed culture from which the pure culture was derived.

*Experimental Approach:* Continuous flow column studies are being performed with groundwater and aquifer material from the Moffett Airfield experimental test site. The 30-cm long column is being operated with an average groundwater velocity of  $2.6 \times 10^{-3}$  cm/s, to yield a hydraulic residence time of 3.2 hours. The transport time is in the range of that achieved in the field for the first monitoring well observation point. The column system has been constructed to permit the feed of two separate groundwater solutions that are amended with either oxygenated groundwater or groundwater containing butane. Both groundwater solutions contain the CAHs of interest. A clock timing system permits the alternate pulsed injection of two different groundwater amended solutions, consisted with the operation of the field tests. Bromide has also been added as a conservative tracer to determine transport characteristics of the column.

Resting cell transformation kinetic tests have also been performed with the *Rhodococcus* sp culture for butane-utilization, and 1,1,1-TCA and 1,1-DCA transformation. Studies are also being performed in a constant injection batch reactor to compared kinetic constants generated at constant butane and contaminant concentrations. Modeling analysis is being performed and compared with the results obtained from the reactor experiments.

*Status:* Transport, bioaugmentation, and biotransformation experiments have been performed in the continuous flow column experiment. A porosity of 0.26 and a dispersion coefficient of  $1.96 \times 10^{-3}$  cm<sup>2</sup>/s were obtained from a 1-D transport model analysis of bromide transport tests. The transport of 1,1,1-TCA was observed to be retarded, with a retardation coefficient of 3.1, and no evidence of 1,1,1-TCA transformation was observed prior to bioaugmentation and biostimulation of the column. Oxygen and butane were transported through the column prior to biostimulation, and butane mass balances indicated that no butane was consumed. Upon bioaugmentation of 0.3 mg (dry mass) of the *Rhodococcus* culture to the column, rapid biostimulation was achieved as indicated by decreases in dissolved oxygen, butane, and 1,1,1-TCA concentrations. Decreases in 1,1,1-TCA concentration were correlated with decreases in oxygen and butane concentrations. After 10 days of bioaugmentation, 1,1,1-TCA concentrations in the column effluent gradually decreased to 20 to 30 µg/L, represented over a 85 % reduction in the injection concentrations of 200 µg/L. Steady-state removals of over 85% were achieved over a 15 day period. When 1,1,1-TCA concentrations were increased to 500 µg/L, about 40% removal was achieved. Upon decreasing the influent concentration to 200 µg/L, effluent concentrations of reached steady-state levels of 80 µg/L representing about 70% removal. Transient tests were performed where butane addition was stopped and 1,1,1-TCA continued. Upon the removal of butane, 1,1,1-TCA concentrations increased to the influent value, indicating transformation quickly ceased upon the removal of butane. Upon starting butane addition, 1,1,1-TCA removals of about 70% were achieved. Thus far, 1,1,1-TCA removal has been maintained for a period of 80 days since the column was bioaugmented. The results are consistent with those obtained those obtained in the field demonstration. Some of the loss of activity of 85% removal to 70% may be related to indigenous microorganisms being stimulated.

Molecular-based PCR probes have detected the bioaugmented microorganism in the column groundwater effluent after bioaugmentation and throughout the column test. Currently, a Real Time PCR method is being developed to quantify the concentration of microorganisms in the column effluent. At the end of the column experiments we will also determine the concentrations of the bioaugmented microorganisms distributed spatially throughout the column.

Laboratory batch kinetic tests are being performed to determine maximum degradation rates and the half saturation coefficients of butane, 1,1,1-trichloroethane and 1,1-dichloroethane with resting cells of the *Rhodococcus* culture. A cell yield (Y) for growth on butane of 0.01 mg protein/µmol of butane was obtained. The  $k_{max}$  and  $K_s$  obtained thus far are as follows: Butane: 4.3 µmol/hr/mg protein; 7.9 µM; 1,1,1-TCA: 0.44 µmol/hr/mg protein; 9 µM ; 1,1-DCA: 0.46 µmol/hr/mg protein; 15 µM. The kinetic parameters were in the range of values previously determined for the mixed culture from which the culture was isolated.

Future studies in the continuous column will evaluate the transformation of CAH mixtures including 1,1-DCE and 1,1,1-TCA. A modeling analysis will be performed of the results from the column test using independently measured kinetic parameters. At the end of the column test a molecular analysis of the aquifer solids will be performed to determine and spatial distribution of the bioaugmented culture.

### **Project 3**

Ken Williamson and Lynda Ciuffetti

*Goals:* This project has two main goals. The primary objective of this project is to describe the ability of *Graphium* sp. to degrade a range of volatile organic compounds including chlorinated aliphatic hydrocarbons (CAHs), trichloromethanes and polyaromatic hydrocarbons (PAHs). The study also aims to demonstrate that these reactions are catalyzed by an alkane inducible cytochrome P450 monooxygenase through heterologous expression assays with yeast.

*Rationale:* Volatile organic compounds including trichloroethylene (TCE), 1,1-dichloroethylene (1,1-DCE), 1,2-dichloroethylene (1,2-DCE), carbon tetrachloride (CT) and chloroform (CF), a trichloromethane, are important soil and groundwater contaminants. The ability of microorganisms to degrade these compounds represents a promising avenue for the attenuation of polluted sites.

*Status:* *Graphium* sp., a filamentous fungus, is one of the few eukaryotes known to grow on gaseous *n*-alkanes. The initial enzymatic step by which *Graphium* sp. oxidizes *n*-alkanes for energy and growth is initiated by a highly nonspecific and alkane-inducible cytochrome P450 monooxygenase. Previous studies have suggested that this enzyme also enables *Graphium* sp. to cometabolically degrade CAHs, trihalomethanes, and PAHs. More specifically, evidence suggests that *Graphium* sp. can degrade numerous CAHs including all 4 trihalomethanes, chloromethane, dichloromethane, chloroethane, 1,2-DCE and 1,1,2,2-tetrachloroethane. This fungus can also reductively dechlorinate CT to CF in the absence of oxygen and then consume CF when aerobic conditions are reestablished. However, neither the substrate range nor the rates of these *Graphium* sp. mediated reactions have been determined. The primary aim of this project is to more quantitatively describe both the substrate range and the rate of these reactions. Although preliminary evidence suggests that a cytochrome P-450 monooxygenase catalyzes the initial steps of these reactions, the role of this enzyme has not been conclusively established. The study also aims to demonstrate the role of this enzyme in cometabolic degradation of environmentally significant pollutants.

*Progress:* The cytochrome- p450 alkane monooxygenase (GRSPALK1) cDNA was amplified from propane-grown *Graphium* sp. mRNA and cloned into the expression vector, ppicz $\beta$ . The resulting plasmid was sequenced and used to transform *Pichia pastoris*, a methylotrophic yeast. Sequence analysis revealed that PCR amplification introduced various errors into the cDNA cassette, which resulted in key amino acid mutations. Therefore, colorimetric assays used to monitor for GRSPALK1 activity were negative. This study will be repeated with a higher-fidelity copy of GRSPALK1.

### **1-SU-02: Chemical, Physical and Biological Processes at the Surface of Palladium Catalysts under Groundwater Treatment Conditions**

Martin Reinhard, Stanford University, PI; John Westall, Oregon State University, Co-PI

*Goal:* This project aims to (1) evaluate the impacts of groundwater on catalyst activity; (2) elucidate the chemical and physical mechanisms responsible for changes in catalyst activity; (3) investigate potential biofouling issues that may result from biological activity expected in long-term treatment applications; (4) develop convenient and economical methods to regenerate catalysts in situ.

*Rationale:* Batch studies with supported palladium catalysts have demonstrated the potential of the palladium/hydrogen process for treating groundwaters or effluent streams that are contaminated by halogenated compounds. These studies yielded virtually complete reductive dehalogenation of chlorinated ethylenes to ethane at room temperature in short contact times, with reaction rates that are orders of magnitude higher than zero-valent iron. Other batch studies have shown the ability of palladium to catalyze the reaction of a range of compounds: all six species of chlorinated ethylenes, carbon tetrachloride, chloroform, 1,2-dibromo-3-chloropropane, Freon 113, chlorobenzene, naphthalene and lindane. However, laboratory column studies and field tests have indicated that catalyst activity may decline over time, thereby potentially affecting the economic competitiveness of this process. Research is needed to optimize the catalyst and operating parameters for the field, by determining the causes of activity loss and the means for preventing or minimizing such effects.

*Approach:* This project approaches optimization of the Pd process through (1) testing the catalyst kinetics and response during operation in a laboratory-scale version of the field system and (2) observing changes in the catalyst surface during treatment. Laboratory reactors have been constructed and used to remove trichloroethylene (TCE, a model substrate) from water sources of varying quality, e.g., deionized (DI) water or groundwater; various regenerants are being compared. The kinetic experiments use a column reactor with a dispersed catalyst, which is typical of catalysts used in field applications. The surface studies use a batch reactor with a model catalyst, which is more amenable to spectroscopic analyses and therefore should yield more insight into surface phenomena; samples are removed from the reactor periodically over the course of treatment for spectroscopic characterization. The research is undertaken in collaboration with a field study at Edwards Air Force Base (EAFB) near Lancaster, California.

*Status:* The laboratory reactor system with the dispersed Pd catalyst successfully removed TCE from EAFB groundwater. Observed deactivation was consistent with sulfide poisoning, and sodium hypochlorite was able to fully regenerate the catalyst. The sulfide was attributed to sulfate-reducing bacteria, whose growth was promoted by storing the reactor feed water under hydrogen pressure. As a result, the system was modified so that feed water was stored under helium, i.e., conditions were more representative of the aerobic field site and less favorable for the growth of sulfate-reducing bacteria. This modified system successfully removed TCE from DI water for four months with no deactivation. The catalyst was then deactivated with a solution of roughly 0.04 mg/L of sulfide, and several regenerants were compared: sodium hypochlorite, hydrogen peroxide, and air-saturated water. Air-saturated water and a 20 mM hydrogen peroxide solution both resulted in 50% recovery of the catalyst activity; further exposure of the catalyst to 200 mM hydrogen peroxide yielded no additional recovery. As in the case of the groundwater, 20 mM sodium hypochlorite fully regenerated the catalyst.

X-ray photoelectron spectroscopy (XPS) was performed on the model catalyst after exposure to EAFB groundwater and sodium hypochlorite. Preliminary analyses are consistent with earlier experiments with dispersed catalyst; those experiments indicated that organics accumulate on the catalyst surface upon exposure to water, but there was no strong correlation to activity. The preliminary data also suggest that sulfide may bind to the Pd surface, and may be oxidized to sulfate with hypochlorite treatment. However, the sulfide/sulfate data were not cleanly reproduced in a concurrent replicate system, possibly due to differences in catalyst handling; more experiments are needed to verify accuracy and reproducibility.

Future work will confirm the above XPS data and will correlate chemical changes in the model catalyst to activity. In addition, regeneration will be optimized with respect to concentration, exposure time, and total dose. Finally, results will be compared with kinetic data from the field study. This study commenced January 1, 2002, and is authorized for a two-year period terminating December 31, 2003.

### **1-SU-03: Effects of Sorbent Microporosity on Multicomponent Fate and Transport in Contaminated Groundwater Aquifers**

Martin Reinhard, Stanford University, PI

*Goal:* The overall goal of this project is to develop a better understanding of organic contaminant sequestration by geosorbents. Specific project goals are to (1) develop a method to characterize microporosity in geological solids in the presence of moisture, (2) determine how micropore hydrophobicity/hydrophilicity and contaminant properties influences contaminant sequestration and desorption, and (3) quantify the interactions among multiple contaminants during uptake in and release from micropores. Information gained from this research will allow us to better predict contaminant bioavailability, the rate of natural attenuation processes, and the time scale of contaminant release from natural sorbents.

*Rationale:* Micropores are pores (less than 2 nm in diameter) that are comparable in size to small organic contaminant molecules, and the sorption potential inside these pores are significantly enhanced due to the proximity of the opposite pore walls. Understanding contaminant sequestration in micropores is essential for predicting the long-term fate of contaminants in groundwater aquifers, and for assessing the significance of natural attenuation processes. Most natural solids contain micropores that form due to weathering, cracking, material imperfections, or turbostratic stacking. Previous work has demonstrated that sorption of hydrophobic organic compounds in micropores can be a significant sequestering process. Sorption in micropores is reversible but rates are very slow and difficult to quantify, especially in the field. Our understanding of geosorbent microporosity and its effect on contaminant sorption is limited because conventional microporosity characterization methods used (vacuum piezometric and gravimetric techniques) employ only a single “model” sorbate and are not sensitive enough to detect the low volumes of micropores typically present in geological solids. Furthermore, our understanding of sorption in micropores is inadequate to predict solid-contaminant interactions based on pore volume and pore size distribution data obtained with these methods.

*Approach:* A methodology is being developed and validated for measuring slow uptake and release rates of volatile organic compounds (VOCs) by microporous solids. To validate the method, the sorption and desorption of simple sorbates, such as methane, carbon tetrachloride, and trichloroethylene on model sorbents, such as silica gel are being studied. Subsequently, the methodology will be applied to study contaminant sorption and desorption on natural sorbents and characterize their microporosity under environmentally relevant conditions.

The focus of this investigation is to study how contaminant properties (e.g., molecular size, structure, and polarity) and environmental variables (such as relative humidity and temperature) affect micropore sequestration. Sorption and desorption kinetics of model contaminants on

microporous engineered solids and natural solids under different conditions are measured with an apparatus developed in our laboratory. The interactions between contaminant molecules and microporous sorbents and the influence of the sorbate and sorbent properties will be elucidated by comparing contaminant sorption and desorption kinetics under these conditions.

*Status:* An apparatus has been developed specially for measuring slow sorption and desorption kinetics of VOCs on solid materials packed in columns. A HP 5890 II GC equipped with FID and ECD detectors is used to analyze gas phase compositions at the inlet and outlet of the column in rapid sequence. Samples of the gas stream that enters and leaves the column are alternatively injected into the GC column (through an valve injector), and the contaminant mixtures are subsequently separated in GC column and detected by both FID and ECD. This design has expanded our investigative capabilities in several ways: data are acquired in real-time with high resolution over the entire contaminant desorption profile, contaminant detection is extremely sensitive (0.1 nmol/L), and sorption and desorption of multiple volatile organic contaminants can be studied. Only a relatively small amount of solid (packed in a column of 3.0 mm i.d.  $\times$  304.8 mm length) is required because of the system's high resolution, and gas flows through the column at 2.00 mL/min regulated by a digital mass flow controller. Constant vapor concentrations of organic contaminant and water in the flow line are achieved by bubbling the gas through organic liquid and water reservoirs submerged in a constant temperature water bath. Currently, we are studying sorption of TCE on several solid materials as a function of temperature and moisture content.

Data show that high concentrations of water vapor leads to rapid displacement of contaminant molecules sorbed/condensed in mesopores in a natural soil, a process that may be described as "chromatographic elution." By contrast, desorption of contaminants sequestered in micropores is significantly slower. We hypothesize pore throats restrict the exchange of background gas molecules with contaminant molecules in the micropores deeper inside. Experimental data indicate that water molecules have very small effect on the desorption rate of TCE sequestered in micropores in a natural soil, and the kinetics of TCE sorption. In an engineered microporous sorbent (silica gel) desorption is barely influenced by the presence of water molecules. These results suggest that both hydrophilic and hydrophobic micropores exist in these solids, and that sorption and desorption of hydrophobic species (TCE) only occurs in the hydrophobic micropores, which are not accessible to water molecules. That is, hydrophobic and hydrophilic species are sequestered into two separate micropore domains (hydrophobic micropores and hydrophilic micropores) independently, and there is no apparent competitive effect between them. This suggests that the property of micropores in geosorbents, rather than the total volume of the micropores, plays key role in controlling contaminant sequestration and desorption. Also, contaminant sequestered in hydrophobic micropores may not be in contact with water molecules, which prevents it from undergoing chemical and biological transformations (e.g., hydrolysis, biodegradation) during natural attenuation processes. We plan to further probe the hydrophobic-hydrophilic properties of micropores by studying the sorption and desorption of organic molecules with different hydrophobicity.

### **1-OSU-03: Development of the Push-Pull Test to Monitor Bioaugmentation with Dehalogenating Cultures**

Mark E. Dolan (PI) , Jennifer Field, and Jonathon Istok (Co-PIs), Oregon State University

*Goal:* The overall goal is to modify the single-well push-pull groundwater test as a means for obtaining quantitative information on in situ dechlorinating activity before and after bioaugmentation. The specific objectives include: 1) modifying TCFE and fumarate assays to determine TCE-transformation potential for use in monitoring bioaugmentation, 2) developing methods for monitoring the transport of dehalogenating cultures during push-pull tests, and 3) evaluating the ability of push-pull tests to monitor changes in TCE-transformation potential resulting from the injection of dehalogenating cultures.

*Rationale:* Technologies are needed to enhance the in situ remediation of groundwater contaminated by chlorinated aliphatic hydrocarbons (e.g., trichloroethene or TCE). Bioaugmentation may be a viable alternative for remediating TCE source zones. Currently it is difficult to assess if bioaugmentation is increasing in situ dechlorination activity. The single-well “push-pull” tests with the TCE surrogate trichlorofluoroethene or TCFE, can provide quantitative information on in situ biological activity and can be modified for use in determining the effectiveness of bioaugmentation.

*Approach:* Two cultures (Evanite and Pt. Mugu) that transform TCE to ethene will be characterized in collaboration with Dr. Semprini (Developing and Optimizing Biotransformation Kinetics for the Bio-remediation of Trichloroethylene at NAPL Source Zone Concentrations). The transport of the culture(s) will be determined during injection into anaerobic physical aquifer models (PAMs). Spatial distributions of dechlorinating activity and redox will be determined from a suite of assays conducted at sampling ports and at the injection/extraction well. Push-pull tests will be conducted at the injection/extraction well to assess changes in reductive dechlorination activity resulting from bioaugmentation.

*Status:* The background activity of sediment collected from a site with known indigenous reductive dechlorination activity has been characterized with respect to the kinetics of TCE, TCFE, fumarate, and succinate utilization and product formation. These four substrates were proposed for this project as substrates that could be used to assay for reductive dechlorination potential in situ. The microcosm study was used to determine the relationship between TCE and TCFE transformation rates and product speciation when fed fumarate and succinate prior to initiating the assays in PAMs. The microcosms were operated over a period of approximately 250 days. Succinate- and fumarate-fed microcosms produced very similar results for lag times, transformation rates and product speciation, with very similar results from triplicate microcosms at each condition. Lag time to the onset of TCE transformation in both fumarate- and succinate-fed microcosms was about two weeks. The corresponding lag times for TCFE transformation under the same conditions was about six weeks. TCE transformation rates, based on a first order model fit after the lag time, were from 3.3 times (fumarate-fed) to five times (succinate-fed) faster than microcosms without exogenous electron donor addition. TCFE transformation rates were about 2.4 times faster than control microcosms and about four to five times slower than TCE transformation rates. TCE transformation products were cis-DCE and trans-DCE in approximately a 2:1 ratio and TCFE transformation products were cis-DCFE and trans-DCFE in approximately 2:1 ratio as well. TCE was ultimately reduced to VC, but very little ethene was observed. TCFE was transformed into a mixture of DCFEs and CFEs, with no FE formation. CAH transformation rates were not affected by sulfate addition. From these tests it was determined that succinate was a potential electron donor for further experiments and that

TCFE transformation rates would have to be assessed in the sediments used in the PAM tests to determine the relationship to TCE rates.

A seed culture was obtained from Dr. Semprini's group from their Evanite culture reactor, was serially fed butanol and PCE for about two months, and has shown complete dehalogenation of PCE to ethene. This culture will be used in future tests related to this project. A series of microcosms have been prepared with the same sediments that were used to pack the PAM, and will be used to test the survivability of the bioaugmented culture under different geochemical conditions. The water phase in the microcosms consists of tap water or tap water amended with 5% media solution used in the culture reactor. Both lactate and butanol will be tested as fermentable substrates and bioaugmentation doses of 0.1, 1, and 10 mL of reactor culture will be tested. The microcosms have been recently inoculated and survivability should be assessed within about 30 days. The results will be used to determine the necessary water amendments and bioaugmentation dose for the PAM experiments.

A glass column of 5 cm diameter and 34 cm length has been packed with the same sediments used to pack the PAMs, and will be used to evaluate the transport characteristics of the bioaugmentation culture. A feed rate approximating the same linear average velocity to be used in the PAM will be used with an influent culture concentration approaching that found in the mother reactor (~25-40 mg/L protein). Effluent samples will be acquired and analyzed for *Dehalococcoides* sp. using group-specific PCR primers and compared to influent concentrations. The Evanite culture was tested using *Dehalococcoides* group-specific primers in PCR reactions and universal bacterial primers for T-RFLP analyses and was found to be highly enriched in *Dehalococcoides* sp. Serial dilutions of the Evanite culture were extracted and analyzed using *Dehalococcoides* group-specific PCR and dilutions down to  $10^{-4}$  were detectable by this process. Future work includes expanding this testing to limited real-time quantifiable PCR analyses to attain better enumeration of *Dehalococcoides* sp. within the effluent samples and for use in the PAM tests. A bromide tracer test is currently underway on the column to determine the flow characteristics of the system.

The PAMs have been packed with sediment from the Hanford, Washington, site and have been saturated with oxygen-free water to produce anoxic conditions for the start of the test. Lactate solution will be added to the PAM just prior to bioaugmentation in an effort to assure anaerobic conditions prior to bioaugmentation. Information in the literature on *Dehalococcoides* sp. involved in the critical step of VC transformation to ethane indicate an extreme sensitivity to oxygen, and every effort will be made to assure anaerobic conditions in the PAM before onset of bioaugmentation.

#### **1-OSU-04: Development and Evaluation of Field Sensors for Monitoring Bioaugmentation with Anaerobic Dehalogenating Cultures for In Situ Treatment of TCE**

James D. Ingle, Oregon State University, PI

*Goals:* The overall objective of this study is to refine and use redox sensors based on redox indicators as monitoring tools for assessing and optimizing redox conditions for treatment of PCE and TCE with dehalogenating cultures. Specific objectives are 1) to deploy, evaluate, and refine redox indicators for on-line monitoring of the redox conditions in two collaborative

situations involving a bioaugmentation approach, 2) to understand the nature of the redox conditions under which dechlorination microbial processes occur.

*Rationale:* Better on-line monitoring techniques for redox status are needed 1) for the initial assessment of laboratory samples or models and of subsurface conditions at a site, 2) for continued assessment of the progress of remediation, and 3) for control of injections of amendments (e.g., substrates, nutrients) during remediation. We have shown that redox sensors based on redox indicators exhibit promise for monitoring environmental redox levels. Research is needed 1) to understand the nature of the response of these indicators, 2) to improve the monitoring devices for practical use, and 3) to demonstrate that these devices can be employed for on-line monitoring of the status of anaerobic dehalogenating cultures in laboratory systems.

*Approach:* Redox indicators immobilized on transparent films have been shown to be able to differentiate between different microbial redox levels (Fe(III)-reducing, sulfate-reducing, methanogenic). These redox indicator flow sensors will be deployed in two primary situations for calibration and demonstration of their applicability: 1) continuous monitoring of redox conditions of cultures inside bioreactors or microcosm bottles as a tool for the optimizing conditions for effective dechlorination of PCE and TCE with enriched halorespiratory cultures, 2) on-line monitoring of the redox status of the material in a physical aquifer model (PAM) bioaugmented with the developed dehalogenating cultures. The design and characteristics of the redox sensor monitoring systems will be improved for low oxygen permeation and portability for easy operation in the field.

*Status:* We have refined the portable, immobilized redox monitoring system and used it to monitor sulfate-reducing and methanogenic conditions in a PAM containing a wastewater slurry and also dechlorinating cultures in bioreactors and modified microcosm bottles. The enriched dechlorinating culture (Lew Semprini lab) was loaded into our bioreactors and microcosm bottles to calibrate the response of the redox indicators to the dechlorination of PCE. The indicator data support the concept the dechlorinating process is increasingly more reducing as PCE is dechlorinated, with the most reducing step in the process being the dechlorination of vinyl chloride to ethene. Specifically, the reduction of Thionine (THI) indicates degradation of PCE and formation of TCE and cis-DCE; whereas, ~50% reduction of Cresyl Violet (CV) correlates to the formation of vinyl chloride and production of ethene is only observed when CV is nearly or fully reduced. We are now working more closely with Dr. Semprini and his students to address concerns about oxygen contamination during culture transfer steps and while monitoring with our redox, flow monitoring system. Refining techniques for transfer of highly oxygen-sensitive cultures is critical for eventual column and PAM studies.

We have developed a method to precipitate finely divided platinum particles into membranes with immobilized indicators through reduction of  $Pt^{2+}$  solutions.  $H_2$  levels as low as 0.01% by volume in the headspace reduce the indicator in the platinum embedded membranes. The indicator Phenosafranine (PSaf) is useful for monitoring dechlorinating cultures because, without Pt, PSaf is not reduced by reductants in dechlorinating cultures. Reduction of a PSaf membrane with embedded Pt indicates active fermentation and  $H_2$  production necessary for dechlorination. The rate of reduction of the indicator changes with varying  $H_2$  concentrations. Although the results are preliminary, this approach could be the basis of a convenient and inexpensive method to determine if  $H_2$  concentrations in cultures are sufficient for effective

dechlorination laboratory without the need to run expensive GC testing. Methods to lower the detection limit will be explored.

## **Outreach Project Reports**

### **Technical Outreach Services for Communities (TOSC) and Technical Assistance to Brownfields Communities (TAB) Programs**

**Kenneth J. Williamson, Director; Denise Lach, Co-Director, Oregon State University**

The TOSC and TAB programs involve a staff of faculty, consultants, and graduate research assistants including:

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### **Technical Outreach Services for Communities (TOSC)**

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

*Rationale:* TOSC provides interested community groups with technical information and assistance that can enable early and meaningful public participation in decisions that affect

health and welfare. The TOSC program provides a viable alternative strategy for communities that do not qualify for a Technical Assistance Grant (TAG) from the US Environmental Protection Agency.

*Approach:* The Western Region's outreach program is one of five nationally instituted community outreach programs. Centered at Oregon State University, the TOSC team is comprised of university faculty and students, as well as contracted environmental professionals with specialization in environmental engineering, risk communication, public health, information transfer, environmental justice, and community relations. The TOSC team provides communities with technical assistance related to understanding the effects of hazardous waste sites. Where appropriate, WR TOSC partners with staff of the Technical Outreach Services for Native American Communities (TOSNAC).

## **Status: Active TOSC Communities**

### **Region 10**

#### **OREGON**

**Organization:** OSP Community Group

**Site:** Oregon State Penitentiary

**City:** Salem

**TOSC Primary Contact:** Michael Fernandez

**Contaminants of Concern:** PCE and TCE

**Description:** Providing assistance to the Oregon State Penitentiary (OSP) community group regarding an interim removal action measure (IRAM), health concerns related to PCE and TCE exposures, and a permanent remedial action for cleanup of groundwater contamination. TOSC has also helped evaluate air quality concerns in local residential basements and possible exposures through ingestion of local produce, soil contact, and incidental ingestion of soil.

**Date Letter of Agreement Signed:** 8/31/1998

**Items in Letter of Agreement:** Evaluate and comment on IRAM and air stripping towers; Provide information on the long and short-term health effects of P/TCE exposure; review and comment on the Human Health Risk Assessment; evaluate air quality concerns in local residential basements; evaluate possible exposures through ingestion of local produce, soil contact, and incidental ingestion of soil.

**Organization:** Victims of TCE Exposure

**Site:** Mattel/Tyco/ViewMaster

**City:** Beaverton

**TOSC Primary Contact:** Michael Fernandez

**Contaminants of Concern:** TCE and its breakdown products

**Description:** Former employees and their family members are concerned about exposures to TCE in drinking water and the workplace and the health effects that may have resulted from these exposures; community members are working to have a health study conducted on exposures and associated health effects.

**Date Letter of Agreement Signed:** Not yet signed.

## WASHINGTON

**Organization:** Klickitat County

**Site:** Champion International Corporation mill site

**City:** Goldendale

**TOSC Primary Contact:** Michael Fernandez

**TOSNAC Participating**

**Contaminants of Concern:** Pentachlorophenol, petroleum products, metals

**Description:** TOSC reviewed and provided comments on documents related to the investigation and cleanup of an abandoned wood treatment facility; TOSC has also provided comments on a health consultation prepared by the Washington Department of Health.

**Date Letter of Agreement Signed:** 10/15/2000

**Items in Letter of Agreement:** Review the health consultation prepared by the Washington Department of Health; review work plans, site investigation and cleanup reports and other technical documents related to the Champion mill site to determine if the work complies with applicable state regulations and standard practices for site investigation and cleanup; attend meetings with community members as necessary and participate in public meetings as requested by the County to the extent possible.

## Region 9

## ARIZONA

**Organization:** Barrios Unidos

**City:** Phoenix

**EJ Community**

**TOSC Primary Contact:** Stephanie Sanford

**Contaminants of Concern:** Various air pollutants including VOCs, NO<sub>x</sub>, and particulate matter

**Description:** The community is concerned about the health of its residents particularly as it is affected by air quality, noise, traffic, contaminated groundwater, and other environmental impacts.

**Date Letter of Agreement Signed:** 10/30/02

**Items in Letter of Agreement:** Review consultant's environmental report, summarize the report, and produce educational materials for the community based on the report.

**Organization:** Downtown Southwest Neighborhood Association

**Site:** From 19<sup>th</sup> Ave. to 7<sup>th</sup> Ave., south of the railroad tracks to the northern banks of the Rio Salado (Salt River)

**City:** South Phoenix

**EJ Community**

**TOSC Primary Contact:** Stephanie Sanford

**Contaminants of Concern:** Various pollutants including VOCs, NO<sub>x</sub>, and particulate matter

**Description:** The community is concerned about the health of its residents particularly as it is affected by air quality, contaminated groundwater, and other environmental impacts.

**Date Letter of Agreement Signed:** 10/30/2002

**Items in Letter of Agreement:** Assist the community in obtaining a local air monitoring station; help the community track permits for local facilities' air emissions; review consultant's environmental report, summarize the report, and produce educational materials for the community based on the report.

## CALIFORNIA

**Organization:** Air Force Plant 42 ERAB

**Site:** Air Force Plant 42

**City:** Palmdale

**TOSC Primary Contact:** Michael Fernandez

**Contaminants of Concern:** TCE in groundwater

**Description:** TOSC is reviewing documents related to investigation and cleanup of soil and groundwater contamination at the facility.

**Date Letter of Agreement Signed:** 3/1/2002

**Items in Letter of Agreement:** Review remedial investigation and feasibility study and participate in RAB meetings.

**Organization:** Alameda Point Collaborative

**Site:** Alameda Naval Air Station

**City:** Alameda

**TOSC Primary Contact:** Jerry Orlando

**Contaminants of Concern:** PAHs, lead

**Description:** A former naval base has been converted to housing for transitioning homeless and other distressed persons. PAHs found in the soil have been removed. Towers painted with lead paint have been removed. TOSC assisted in a post-cleanup community meeting to address residents' concerns about exposures during the cleanup process.

**Date Letter of Agreement Signed:** no letter of agreement

**Items in Letter of Agreement:**

**Organization:** Chester Street Block Club Association

**City:** Oakland

**EJ Community**

**TOSC Primary Contact:** Michael Fernandez

**Contaminants of Concern:** Lead and vinyl chloride

**Description:** TOSC currently is participating in a series of mediation sessions with community and the California Department of Toxic Substances Control representatives. The mediation is related to the cleanup of contaminated properties and subsequent development as a neighborhood park. The neighborhood association has filed a Title VI environmental justice complaint against the State of California and the mediation sessions are an attempt to resolve the community's concerns.

**Date Letter of Agreement Signed:** 9/1/2001

**Items in Letter of Agreement:** Provide technical support for community during the alternative dispute resolution process; support includes reviewing investigation and cleanup documents for South Prescott Neighborhood Park and participating in mediation meetings.

**Organization:** Elem Tribe

**Site:** Sulphur Bank Mercury Mine  
**City:** Clearlake  
**TOSC Primary Contact:** Michael Fernandez  
**EJ Community; TOSNAC Participating**  
**TOSNAC Contact:** Brenda Brandon  
**Contaminants of Concern:** Mercury and other heavy metals  
**Description:** TOSC is providing assistance to the Elem regarding contamination at the Sulfur Bank Mercury Mine, on the Elem Tribal Colony, and in Clear Lake.  
**Items in Verbal Agreement:** Review remedial investigation and feasibility study for the Sulphur Bank Mercury Mine; provide other assistance as mutually agreed upon.

**Organization:** Fort Ord Environmental Justice Network  
**Site:** Fort Ord  
**City:** Marina  
**TOSC Primary Contact:** Michael Fernandez  
**EJ Community**  
**Contaminants of Concern:** Ordnance and explosives, landfill gases, carbon tetrachloride, TCE  
**Description:** TOSC is assisting the community in participating in the base cleanup and redevelopment process. TOSC will assist the community by providing document review and information on health effects.  
**Date Letter of Agreement Signed:** 4/1/2000  
**Items in Letter of Agreement:** Review and comment on technical documents; assistance in preparing for community meetings with the Army and regulatory agencies; and attending community group meetings and relevant public meetings when possible.

**Organization:** Involved Neighbors Seeking Information, Safety and Truth (INSIST)  
**Site:** Wyle Laboratories  
**City:** Norco  
**TOSC Primary Contact:** Jerry Orlando  
**Contaminants of concern:** TCE, metals, perchlorate  
**Description:** Community is concerned about the redevelopment of a defense contractor facility for housing and the potential contamination and exposure to hazardous substances manufactured or used at the facility.  
**Date Letter of Agreement Signed:** no LOA signed, presented to the community in July 2003  
**Items in Letter of Agreement:** Review and summarize technical documents; attend advisory group meetings and present information as mutually agreed upon.

**Organization:** San Martin Perchlorate Citizens Advisory Group  
**City:** San Martin  
**TOSC Primary Contact:** Jerry Orlando  
**Contaminants of Concern:** Perchlorate  
**Description:** Groundwater in the vicinity of the cities of San Martin and Morgan Hill has been contaminated with perchlorate which originated from a flare manufacturing facility. The contaminant plume affects hundreds of domestic water supply wells.  
**Date Letter of Agreement Signed:** July 2003  
**Items in Letter Agreement:** Review and summarize technical documents; attend advisory group meetings and present information as mutually agreed upon.

**Organization:** South Bay Cares

**City:** Palos Verdes

**TOSC Primary Contact:** Stephanie Sanford

**Contaminants of Concern:** Landfill byproducts.

**Description:** Community is concerned about potential health effects which may result from developing an old landfill as a golf course.

**Date Letter of Agreement Signed:** October 3, 2003

**Items in Letter of Agreement:** Review and comment on an environmental impact report for a proposed golf course project on the closed Palos Verdes Landfill.

**Organization:** Tustin RAB

**Site:** Marine Corps Air Facility

**City:** Tustin

**TOSC Primary Contact:** Ken Williamson

**EJ Community**

**Contaminants of Concern:** TCE and other VOCs in groundwater

**Description:** Providing assistance to established RAB dealing with remediation activities at a Marine Corps Air Station. TOSC assistance involves review and comment on RI/FS documents and ongoing educational programs for RAB members related to remediation plans and activities.

**Date Letter of Agreement Signed:** 8/21/1997

**Items in Letter of Agreement:** Regular attendance at Restoration Advisory Board meetings; review and comment on RI/FS and Draft and final ROD documents at OU-3; review and comment on Draft RI/FS at OU-1; ongoing educational programs for RAB members related to remediation plans and activities; TOSC presentation on viability of bioremediation for groundwater.

**Organization:** Valley Center Community Group

**City:** Valley Center

**TOSC Primary Contact:** Matt Hamman

**Contaminants of Concern:** Pesticides, petroleum products, MTBE

**Description:** Residents of this community are concerned about cancer incidence in the community and have asked TOSC to help them understand a cancer study performed by the University of California at Irvine.

**Date Letter of Agreement Signed:** 3/14/2003

**Items in Letter of Agreement:** Help the community understand an epidemiology report about childhood cancer; explain the results of MTBE sampling as well sample collection and analysis methodology; evaluate the regulatory status of the pesticide Chlorpyrifos; support the community in its request that the city test school grounds and water supply for pesticides and MTBE.

**Organization:** West College Neighborhood Association

**City:** Santa Rosa

**TOSC Primary Contact:** Michael Fernandez

**Contaminants of Concern:** PCE and its breakdown products

**Description:** The community is concerned about health effects from the contamination of groundwater with PCE, with health-related outreach activities, as well as with the cleanup of groundwater contamination.

**Date Letter of Agreement Signed:** 3/26/2001

**Items in Letter of Agreement:** Provide information related to water treatment options; review and comment on reports and other materials related to soil gas sampling, leaks from sewer systems, and groundwater sampling; provide information on health effects of exposure to PCE and medical outreach protocol; provide information on agencies' roles in cleaning up hazardous substances in the environment; provide information on cleanup technologies for PCE in soil and groundwater; provide other services as mutually agreed upon by TOSC and the West College Neighborhood Association.

**Organization:** Willits Citizens for Environmental Justice

**Site:** Abex-Remco Hydraulics

**City:** Willets

**TOSC Primary Contact:** Michael Fernandez

**EJ Community**

**Contaminants of Concern:** Hexavalent Chromium in soils and groundwater; TCE and other VOCs in groundwater

**Description:** TOSC has assisted this community during the investigation and remediation of the Abex- Remco facility. A TOSC member has served on the Site Team, which includes representatives from the community, the Regional Water Quality Control Board, and the California Department of Health Services. TOSC is providing assistance related to health impacts and cleanup of chromium and VOC contamination.

**Date Letter of Agreement Signed:** 4/1/2000

**Items in Letter of Agreement:** Review and comment on remedial investigation reports, sampling plans, health risk assessments; conduct public environmental education workshops.

## **Status: Inactive communities that may require future assistance**

### **Arizona Communities**

*South Phoenix, AZ*

*Union Hills (Phoenix, AZ)*

### **California Communities**

*Aerojet (Rancho Cordova)*

*Waste Disposal Inc. (Sante Fe Springs)*

## **Technical Assistance To Brownfields Communities (TAB)**

Goal: The TAB program provides assistance to communities attempting to address cleanup and redevelopment of properties whose reuse has been prevented by real or perceived

contamination. The TAB program makes use of the same faculty, consultant, and research assistant staff as those involved in the TOSC program. TAB attempts to improve involvement of all affected parties in cleanup and redevelopment process through education and training. TAB also attempts to accelerate the redevelopment process through the application of HSRC and other research and through improved community involvement.

## **Status: Active TAB Communities and Activities Follow**

### **Region 10**

#### **OREGON**

**Organization:** Clackamas County

**City:** Clackamas County, OR

**TAB Primary Contact:** Jerry Orlando

**Description:** TAB assisted in the RFP for consultant services and served on a committee to select a consultant.

**Organization:** Portland Development Commission (PDC)

**City:** Portland, OR

**TAB Primary Contact:** Jerry Orlando

**Description:** TAB has been asked to provide technical assistance to a group of neighborhood groups adjacent to a large brownfields redevelopment site on the Willamette River. TAB has also assisted PDC with the selection of an environmental consultant by serving on the selection committee.

**Organization:** Oregon Department of Environmental Quality (DEQ)

**TAB Primary Contact:** Michael Fernandez

**Description:** TAB helped coordinate Oregon participation in EPA's Brownfields 2003 conference. This annual conference takes place in Portland on October 27-29, 2003. Over 3500 representatives from local, state, and federal government, as well as from private sector consulting and finance participated are expected to participate in this year's conference. TAB also created and administered a community brownfields needs assessment survey to cities and counties of Oregon on behalf of DEQ.

**Organization:** Portland Showcase

**City:** Portland

**TAB Primary Contact:** Michael Fernandez

**Description:** TAB continues to assist this showcase community as a regulatory liaison and community involvement resource. We also continue to provide technical assistance as needed. This year we have invited the Showcase to participate in the Oregon Brownfields Conference planning process as a means of facilitating achievement of their community outreach goals.

**Date of Letter of Agreement:** 10/6/2000

**Items in Letter of Agreement:** Prepare "master" site cleanup fact sheet; evaluate current state/federal interagency workgroup for opportunities to expand and build improved partnerships; review existing Showcase Program web links and suggest improvements and additions; recommend 10-12 essential brownfields library documents; evaluate the existing

Regulatory Innovation Action Plan and suggest how to build upon DEQ reforms; evaluate implications of the Endangered Species Act.

## WASHINGTON

**Organization:** City of Spokane

**TAB Primary Contact:** Jerry Orlando

**Description:** TAB has agreed to provide technical and community outreach to this new EPA brownfields grantee. TAB created surveys to gauge community interest in brownfields site selection, assisted in the creation of an RFP for consultant services and served on a selection committee to choose a consultant.

## Region 9

## CALIFORNIA

**Organization:** City of East Palo Alto

**TAB Primary Contact:** Jerry Orlando

**Description:** TAB will assist the Agency with community outreach concerning redevelopment of several former nursery properties. TAB recently attended a presentation on the site assessment methodology the city is using to obtain data about possible pesticide contamination on these properties.

**Organization:** Richmond Redevelopment Agency, Richmond CA

**TAB Primary Contact:** Jerry Orlando

**Description:** TAB is assisting the Agency with community outreach concerning a large brownfields redevelopment project on the San Francisco Bay. TAB has written a Community Involvement Plan and been involved in a community meeting, giving technical assistance to community members. TAB will continue to assist the agency at future community meetings.

## NEVADA

**Organization:** Nevada Division of Environmental Protection (NDEP)

**TAB Primary Contact:** Michael Fernandez

**Description:** TAB explored opportunities to collaborate with NDEP brownfields coordinator Connie Lewis. TAB met with NDEP to discuss planning and presenting a rural brownfields conference. NDEP subsequently staged a very successful conference using both private consultant and TAB input. We have also met staff from Nye County, a recent EPA brownfields grant recipient, and discussed providing assistance with their brownfields project.

## Training and Technology Transfer

WRHSRC training focuses on educating graduate students. A total of 16 students have been funded through the center; two at the Masters level and 14 at the Ph.D. level. Through center funding, students are trained to do fundamental research and outreach activities in a broad range of disciplines. In 2003, two students (Lisa Gaines and Mike Behm) worked in the outreach area; all others worked on basic research.

**Table 7. Graduate Students Funded through the WRHSRC**

<u>Student</u>	<u>Field</u>	<u>Degree/ Institution/Graduation</u>	<u>Project</u>
Jian Luo	Environmental Engineering	Ph.D./Stanford/2005	1-SU-01
Ioannis Benekos	Environmental Engineering	Ph.D./Stanford/2005	1-SU-01
Seungho Yu	Environmental Engineering	Ph.D./ Oregon State University /2004	1-OSU-01
Andy Sabalowosky	Environmental Engineering	Ph.D./ Oregon State University /2006	1-OSU-01
David Doughty	Microbiology	M.S./Oregon State University /2004	1-OSU-02
Kim Lamothe	Molecular and Cellular Biology	Ph.D./ Oregon State University /2006	1-OSU-02
Bhargavi Maremanda	Environmental Engineering	M.S./Oregon State University /2004	1-OSU-02
Kristin Skinner	Molecular and Cellular Biology	Ph.D./ Oregon State University /2006	1-OSU-02
<u>Student</u>	<u>Field</u>	<u>Degree/ Institution/Graduation</u>	<u>Project</u>
Cecillia Razzetti	Environmental Engineering	Ph.D./ University of Bologna, Italy/2005	1-OSU-02
Naoko Munakata	Environmental Engineering	Ph.D./Stanford/2004	1-SU-02
Hefa Cheng	Environmental Engineering	Ph.D./Stanford/2006	1-SU-03
Jae-Hyuk Lee	Environmental Engineering	Ph.D./ Oregon State University /2005	1-OSU-03
Peter Ruiz-Haas	Chemistry	Ph.D./ Oregon State University /2005	1-OSU-04

Defne Cakin	Chemistry	Ph.D./ Oregon State University /2006	1-OSU-04
Lisa Gaines	Geosciences	Ph.D./ Oregon State University /2004	Outreach
Mike Behm	Public Health	Ph.D./ Oregon State University /2004	Outreach

Technology transfer is an important component of the WRHSRC. The goals are as follows:

- Promote teamwork and information exchange among researchers
  - Tools: listservs, webpages, seminars
- Promote information transfer with practitioners
  - Tools: webpages, electronic newsletter, video workshops, faculty presentations and publications
- Test new technologies
  - Tools: laboratory and pilot-scale testing, demonstrations, online project database
- Implement full-scale demonstration projects

*Rational:* In order for research advances to be effective, information must be effectively transferred among researchers and between researchers and practitioners.

*Status:* In 2003, tech transfer activities included further development of the WRHSRC website, creation of Research Briefs and WRHSRC News distributed by e-mail, and continuation of several technology demonstration projects.

The website <http://wrhsrc.oregonstate.edu/> provides an overview of the WRHSRC and links to publications and project information. Since its launch in January 2001 usage has increased to about 700 visitors per month. The website includes:

- ◇ A description of the HSRC program and WRHSRC goals and management.
- ◇ Links and contact information for center research and outreach staff.
- ◇ Descriptions of research focus areas and projects.
- ◇ A database of WRHSRC publications and previous projects, 1989-2002. This database has been made available in a searchable format (<http://wrhsrc.oregonstate.edu/publications/index.htm>)
- ◇ Descriptions of center outreach programs and links to the separate websites for the Western Region TOSC/TAB programs.
- ◇ A News and Events page with regular postings.

The web site features center publications and a searching capability, research briefs, demonstration projects for Technical Outreach Services for Communities, and a page that walks clients through the process of obtaining help from TOSC. Interested clients and individuals can subscribe to the new e-mail newsletter (launched in spring 2003) for WRHSRC and TOSC (started in fall 2002). Three e-mail Research Briefs were distributed on OSU research during 2003 as follows:

**Brief #1:** Field tools to measure redox potential in aquifers. (Profile of research by Dr. James Ingle, Oregon State University.)

**Brief #2:** Palladium catalysts as a tool to clean up halogenated volatile organic compounds in groundwater (Profile of research by Dr. Martin Reinhard, Stanford University.)

**Brief #3:** A field study on cometabolism – a process where microbes do not consume contaminants directly, but instead live on an alternate food source and fortuitously create conditions that trigger the degradation of the contaminants. (Profile of research by Drs. Semprini and Dolan of Oregon State University and Dr. Perry McCarty of Stanford University.)

The Research Briefs can be found on WRHSRC website at:  
<http://wrhsrc.oregonstate.edu/briefs/index.htm>

## **Western Regional Lead Training Center, OSU--Hazardous Waste Training**

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

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

*Approach:* The Western Regional Lead Training Center at OSU (WRLTC-OSU), originally established with U.S. EPA grant funding in 1993, is an accredited non-profit training provider of lead-based paint abatement workshops for U.S. EPA and the State of Oregon certification programs. Additional lead abatement training workshops are provided for U.S. Departments of Housing and Urban Development (HUD) and Energy (DOE).

*Status:* The Western Regional Lead Training Center–OSU (WRLTC-OSU) was established by an EPA-training grant in 1992 as an outgrowth of the WRHSRC-OSU. It is the only Oregon-accredited lead-based paint (LBP) training center and provides all of the federal LBP curricula. WRLTC-OSU is also accredited in Washington, Alaska, and Idaho, as well as the all of the Pacific Northwest Indian Tribes. In the past year, workshops have been presented in Washington (Seattle and Auburn), Alaska (Anchorage and Kenai), and Oregon (Portland, Salem, and Corvallis). In 2003, over 200 students attended 22 workshops and received 242 certificates. Accredited workshops included Lead Inspector, Lead Risk Assessor, Combined Lead Inspector & Risk Assessor Refresher, Lead Abatement Worker, Lead Abatement Supervisor, Combined Lead Abatement Worker and Supervisor Refresher, and Lead Project Designer. Custom workshops in 2003 were Elevated Blood Lead Case Management (Oregon Health Division) and Advanced Lead-Safe Work Practices (City of Corvallis Housing Department). In addition to these training workshops, the Oregon LBP-Program in the Oregon Health Division and EPA Region 10 have recently funded \$90,000 to the statewide lead outreach. This project will present 10 community outreach workshops in rural Oregon and develop new training materials for Oregon LBP Program use in their outreach activities. Since enrollment of the certification classes has diminished under poor economic times and reduced state/federal training funds, the WRLTC-OSU is exploring programs in geographically underserved areas and with different sectors of the workforce.

## Technology Demonstrations of In Situ CAH Treatment

Researchers of the WRHSRC have been involved in taking the results of their basic research and applying them in real world field demonstrations. These demonstrations are an extension of research begun in the original center and research that is continuing in the current center. A summary of these demonstrations is provided in Table 8, and represents our faculty's involvement in the technology transfer process. Through our involvement in these demonstrations we believe technology transfer will be accelerated. Also technical problems that are encountered in the field demonstrations provide feedback for the research program. Thus although these studies are funded by other federal agencies and private industry, they are truly part of the WRHSRC technology transfer program. A brief description of these field demonstration projects are provided below.

**Table 8. Tech Transfer Field Demonstrations by Center Researchers**

Demonstration	Investigators	Sponsor
In Situ Measurement of TCE Degradation Using a Single-Well, "Push-Pull" Test at the Homelite Site	Jack Istok Lewis Semprini Jennifer Field	Textron Corp., NIEHS Superfund
Field Testing of Palladium Catalyzed Hydrogenation for Chlorinated Hydrocarbon Removal: Evaluation of Catalyst Degrading Mechanism)	Martin Reinhard, Jeff Cunningham, Mark Goltz, Walt McNab, Carmen LeBron	US Navy, (NFSEC)
Development of Effective Aerobic Cometabolic Systems for the In-situ Transformation of Problematic Chlorinated Solvent Mixtures	Lewis Semprini Mark Dolan Perry McCarty	DoD SERDP Program
Demonstration	Investigators	Sponsor
Push-Pull Tests for Evaluating the In situ Aerobic Treatment of Chlorinated Mixtures in Groundwater (ESTCP Program of DoD)	Lewis Semprini Jack Istok	DoD ESTCP Program

### Push-Pull Tests to Demonstrate Enhanced Anaerobic Transformation of TCE

OSU Professors Jack Istok, Lewis Semprini, and Jennifer Field are performing a series of push-pull tests to evaluate the potential for enhanced anaerobic transformation of TCE at the Homelite Site in Greer, North Carolina. This work is being supported through a contract from the Textron Corporation with additional support through an NIEHS Superfund grant. The Homelite site is interesting, since both TCE and hexavalent chromium exist in several wells at the site. The researchers performed single well push-pull tests using methods developed through previous center research. Lactate and fumarate were added as substrates to different wells at the test site. Upon biostimulation, push-pull activity tests were performed to study fermentation and dehalogenation reactions. Trichlorofluoroethene (TCFE) was added as a surrogate compound for

TCE. Transformation products of TCFE were determined in samples obtained during the pull phase of the tests. The tests showed that despite repeated additions of the electron donors enhanced anaerobic dechlorination past cis-DCE could not be achieved.

At another industrial site the researchers are using push-pull tests to evaluate in situ treatment performance of a series of barrier bioreactors. In situ reactors were operated by biostimulating with different substrates including lactate and hydrogen, as well as a reactor with an iron barrier. Trichlorofluoroethene (TCFE) was added to these reactors and was transformed to fluoroethene at several locations monitored, indicating the potential for complete transformation to ethene. These tests are designed to obtain information on the system performance, and were funded through a NIEHS Superfund grant.

### **Field Testing of Palladium Catalyzed Hydrogenation for Chlorinated Hydrocarbon Removal: Evaluation of Catalyst Degrading Mechanism**

Stanford professor Martin Reinhard and OSU professor John Westall are leading a research team investigating the use of palladium (Pd) catalysts to remediate waters contaminated by chlorinated organics. In conjunction with the WRHSRC project, Dr. Reinhard is conducting a pilot-scale field study at Edwards Air Force Base (EAFB) in southeastern California in collaboration with Lawrence Livermore National Laboratory, the Naval Facilities Engineering Service Center, the Air Force Institute of Technology, and Edwards Air Force Base. The field site combines Pd catalysis with the dual horizontal-flow treatment well (HFTW) technology. For the Pd/HFTW system, two wells are installed in an aquifer and each is screened over two intervals, an upper interval and a lower interval. In each well, a Pd reactor is placed between the upper and lower screens, so that the contaminated water passes through the reactor as it travels between the screened sections in the well. One well pumps in an upflow mode, extracting water through the lower screen and injecting it through the upper screen. The other well pumps in a downflow mode, extracting water through the upper screen and injecting it through the lower screen. This setup results in two horizontal flow paths between the wells: one on the upper level, from the upflow well to the downflow well; and one on the lower level, from the downflow well to the upflow well. These flow paths create a zone of recirculation between the two wells, which provides the opportunity for multiple treatment passes, thereby enhancing contaminant removal. The combined Pd/HFTW system is scheduled to go on line in late 2002, with a throughput of 1-3 gpm (3.8-11.4 L/min) of water contaminated with 0.5-1.5 mg/L of trichloroethylene. The concurrent laboratory and field projects will facilitate more rapid transfer of information from the laboratory to the field, and from academia to potential end-users. In addition, the joint studies will verify applicability of laboratory results to the field scale. Finally, the field project will develop cost and performance data at the pilot scale. Thus far, the laboratory studies have provided reaction kinetics data for field reactor design and have indicated that catalyst activity may be successfully maintained in the field through periodic regeneration with sodium hypochlorite.

### **Bioaugmentation of a Butane Culture for the Aerobic Cometabolisms of CAH Mixtures**

Oregon State and Stanford University researchers are also exploring the bioaugmentation of microorganisms that have good potential for the aerobic cometabolism of troublesome chlorinated solvents. Professors Lewis Semprini, Mark Dolan and Perry McCarty are exploring bacteria that use n-alkanes such as butane and propane for energy and growth that cometabolize CAHs. This study is funded by Department of Defense Strategic Environmental Research and

Development (SERDP) Program. Pure cultures of microorganisms have been isolated that grown on butane that effectively transform 1,1-dichloroethene (1,1-DCE), 1,1-dichloroethane (1,1-DCA), and 1,1,1-trichloroethane (1,1,1-TCA). In situ bioaugmentation studies are currently being performed at the Stanford Field Demonstration Pilot Plant at Moffett Federal Air Field, California, to determine whether effective aerobic cometabolism might be achieved. The *Rhodococcus* culture, being studied in the 1-OSU-02 has been bioaugmented into a test leg and biostimulation through butane and oxygen addition is occurring. An indigenous experimental leg is also being biostimulated permitting a comparison of treatment achieved by the bioaugmented leg. The field tests have shown effective transformation of three contaminants was achieved in the bioaugmented test zone, compared to the indigenous leg, consistent with the results of laboratory tests. Molecular PCR methods have been successfully used to show the presence of the bioaugmented microorganism in the test zone.

### **Development of Push-Pull Single Well Tests to Evaluate the Aerobic Cometabolism of CAHs**

In a project supported by the Department of Defense Environmental Security Technology Certification Program (ESTCP), researchers at Oregon State University are developing protocols for using single well push-pull tests to evaluate the potential for aerobic cometabolism of CAHs. Professors Jack Istok and Lewis Semprini are developing the single well push-pull for stimulating indigenous microorganisms in situ through the addition of cometabolic substrates. Included in the protocol are methods for performing the tests, which include transport, biostimulation, activity, and inhibition tests. The ability of the stimulated population to cometabolically transform CAHs is being evaluated through a series of in situ activity tests. Tests over the past year were conducted at Ft. Lewis, Washington, using toluene as a cometabolic substrate. The tests demonstrated that toluene-utilizers that express an ortho-monooxygenase enzyme could be stimulated in situ. Transformation tests showed isobutene, a surrogate compound, could be transformed to isobutene oxide, which also indicated that microorganisms expressing an toluene mono-oxygenase were stimulated.

## **New Center Projects – 2004-2005**

In June a Request for Proposals (RFP) was issued for research projects for the third and fourth years of Center funding. Seven proposals were submitted. The Science Advisory Committee reviewed, discussed and ranked the proposals during the annual meeting in August. Based on the recommendations of the SAC panel, the following projects will be funded for the third and fourth years of the Center:

**2-OSU-05:** *Aerobic Cometabolism of Chlorinated Ethenes by Microorganisms that Grow on Organic Acids and Alcohols.* Peter Bottomley, PI; Daniel Arp,, Mark Dolan, Lewis Semprini, Co-PIs, Oregon State University

**2-OSU-06:** *Development and Evaluation of Field Sensors for Monitoring Anaerobic Dehalogenation After Bioaugmentation.* James Ingle, PI, Oregon State University

**2-OSU-07:** *Continuous-Flow Column Studies of Reductive Dehalogenation with Two Different Enriched Cultures: Kinetics, Inhibition, and Monitoring of Microbial Activity.* Lewis Semprini, PI, Oregon State University, Mark Dolan, Co-PI, Oregon State University, Alfred Spormann, Co-PI, Stanford University.

**2-SU-04:** *Novel Methods for Laboratory Measurement of Transverse Dispersion in Porous Media.* Peter K. Kitanidis, PI; Craig Criddle, Stanford Co-PI, Stanford University

**2-SU-05:** *The Role of Micropore Structure in Contaminant Sorption and Desorption.* Martin Reinhard, PI, Stanford University.

Two of the projects (2-OSU-05 and 2-OSU-07) deal with intrinsic and enhanced bioremediation of chlorinated solvents under aerobic and anaerobic conditions. One project is developing field methods for site characterization (2-OSU-06). The field redox sensors being developed in this project will also be used in project 2-OSU-07. The final two projects are dealing with important transport processes of dispersion and sorption: Project 2-SU-04 will investigate transport and dispersive mixing, while project 2-SU-05 will investigate mechanisms for slow sorption and desorption from aquifer materials.

## **2003 WRHSRC Publications**

Publications for 2003 listed below have resulted from work funded by the new WRHSRC. We continue to maintain the database for publications from both the original and current center.

During 2003 a total of 12 journal articles have appeared, accepted, or have been submitted for publication. Center researchers have also published in-bound conference proceedings, and have been active in conference participation, especially at the Seventh International Battelle In-Situ and On-Site Bioremediation Conference, which was held last June. This conference provided an excellent opportunity for students to present the results of their research and to transfer the technical information on the results of center research to practitioners and regulators working on the contaminants that are the focus of the WRHSRC.

### **Journal Articles (also includes those in press and submitted)**

- Cantrell, K. and J. D. Ingle, Jr. (2003). "The SLIM Spectrometer." *Anal. Chem.*, 75, 27-35.
- Cantrell, K. and J. D. Ingle, Jr. (2003). "Design and Evaluation of a Membrane Sampling Spectrometer Array for Real Time, In-Situ Depth Profiling of Sub-Surface Waters." *Aquatic Sciences – Research Across Boundaries*. Submitted.
- Doughty, D.M., D.J. Arp, and P.J. Bottomley. "Dichloroethylenes as Substrates and Inducers of Butane Monooxygenase in *Pseudomonas butanovora*." *Microbiology*. Submitted.
- Fienen, M.N., Luo, J. and Kitanidis, P.K. "Semi-Analytical, Homogeneous, Anisotropic Capture Zone Delineation." *Ground Water*. Submitted.
- Halsey, K.H., P.J. Bottomley and D.J. Arp. "TCE Degradation by Butane-Oxidizing Bacteria Causes a Spectrum of Toxic Effects." *Applied and Environmental Microbiology*. Submitted
- Luo, J. and Kitanidis, P.K. "Fluid Residence Times Within the Recirculation Zone Created by an Extraction-Injection Well Pair." *Journal of Hydrology*. Submitted.
- Martinez-Prado, M.A., K.M. Skinner, K.J. Williamson, and L.M. Ciuffetti 200X. "Kinetics of MTBE, TBF, And TBA Aerobic Cometabolism by an Alkane Grown Fungal Isolate, *Graphium*, sp." *Applied Environmental Microbiology*. (to be submitted. Nov. 2003)
- Pon, G. and Semprini, L. "The Use of Anaerobic Reductive Dechlorination of 1,1-Chlorofluoroethene to Track The Transformation of Vinyl Chloride. *Environmental Science and Technology* (to be submitted Dec. 2003).
- Pon, G., Hyman, M. R. and Semprini, L. Acetylene Inhibition of Trichloroethene and Vinyl Chloride Reductive Dechlorination. *Environmental Science and Technology*, 2003, Vol. 37(14): 3181-3188.
- Skinner, Kristin M., M.A. Martinez-Prado, K.J. Williamson, M.R. Hyman, and L.M. Ciuffetti. 200X. "Inhibition of MTBE Cometabolism In *Graphium Sp.* by Downstream Products and Various Environmental Conditions." *Applied Environmental Microbiology*. (to be submitted, Nov., 2003)
- Yeager, C.M., K. Arthur, P.J. Bottomley and D.J. Arp 2003. "Trichloroethylene Degradation by Toluene-Oxidizing Bacteria Grown on Non-Aromatic Substrates." *Biodegradation*, in press.
- Yu, S., M. E. Dolan, and L. Semprini. "Kinetics and Inhibition of Reductive Dechlorination of Chlorinated by Two Different Mixed Cultures." *Environmental Science and Technology*. (to be submitted, Dec, 2003)

## Theses

- Cantrell, Kevin (2002), *The Development and Characterization of Miniature Spectrometers for Measuring the Redox Status of Environmental Samples*. Ph.D. Oregon State University
- Prayoonpokarach, Sanchai (2003). *Development and Evaluation of Sampling Techniques, Instrumentation, and Pyridine Derivative Reagents for Fluorometric Determination of Chloroform and TCE in Water with a Portable Fluorometer*. Ph.D. Oregon State University

## Conference Abstracts

Cakin, D. and J. D. Ingle, Jr. (2003). "Development of a Liquid Core Waveguide Based Field Instrument For Analysis of Iron." Second Black Sea Basin Conference on Analytical Chemistry, Istanbul-TURKEY

Martinez-Prado, A., K.J. Williamson, L. M. Ciuffetti, and R. Guenther, "Modeling of MTBE Kinetics by Alkane Grown *Mycobacterium vaccae*," *The Seventh International Symposium on In Situ and On-Site Bioremediation*, June 2-5, 2003, Orlando, FL.

Munakata, N., J.A. Cunningham, R. Ruiz, C. Lebron, and M. Reinhard (2002). "Palladium Catalysis in Horizontal-Flow Treatment Wells: Field-Scale Design and Laboratory Study," *Remediation of Chlorinated and Recalcitrant Compounds: Advances in ex situ Treatment of Groundwater*, eds. A. Gavaskar and A. Chen, Batelle Press. Proceedings of the May 2002 Conference on the Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California.

Pon, G. and Semprini, L. "The Use of Anaerobic Reductive Dechlorination of 1,1-Chloro-fluoroethene to Track The Transformation of Vinyl Chloride." *In Situ and On-Site Bioremediation the Seventh International Symposium*, Orlando FL, June, 2-5, 2003

Yu, S and L. Semprini, "Kinetic Studies and Comparison for Reductive Dechlorination by a Binary Mixed Culture," *The Seventh International Symposium on In Situ and On-Site Bioremediation*, Orlando FL, June, 2-5, 2003

Yu, S. and L. Semprini, "TBOS as a Slow Release Anaerobic Substrate for Reductive Dechlorination of Chlorinated Aliphatic Hydrocabons." *In-Situ Contaminated Sediment Capping* (workshop), May 12-14, 21003, Cincinnati, OH.

Semprini, L, M. E. Dolan, M. Mathias, G. D. Hopkins, and P.L. McCarty, "Laboratory, Field, and Modeling Studies of Aerobic Cometabolism of CAHs by Butane-Utilizing Microorganisms," *The Seventh International Symposium on In Situ and On-Site Bioremediation*, Orlando FL, June, 2-5, 2003.