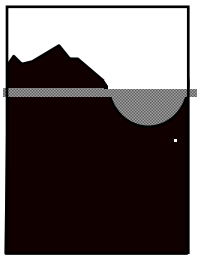

WESTERN REGION
HAZARDOUS SUBSTANCE RESEARCH CENTER

2002 ANNUAL REPORT

Oregon State University
Stanford University

December 2002

Sponsored by the U. S. Environmental Protection Agency

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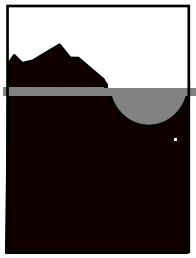

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WESTERN REGION HAZARDOUS SUBSTANCE RESEARCH CENTER
2002 ANNUAL REPORT

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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 22 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 committees.

The center budgets for the 2001 fiscal year and since the center's inception are listed by category of support in Table 4. During the first year of operation, core funding totaled $1,140,000. 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. Eleven graduate students have been supported during the first year of the center, with nine 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

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

Table 2. Science Advisory Committee

Member	Affiliation	Expertise
Dr. Richelle M. Allen-King (Vice-Chair)	Department of Geology, Washington State University	Geochemistry; Hydrogeology
Dr. Harold Ball	U.S. EPA Region 9	Environmental Engineering
Dr. Roseanne Ford	Chemical Engineering Department, University of Virginia	Microbial Processes; Chemical Engineering
Dr. Joe Hughes (Chair)	Department of Civil and Environmental Engineering, Rice University	Bioremediation; Environmental Engineering
Dr. Andrea Leeson	SERDP/ESTCP Program Office, DoD	Bioremediation; Environmental Engineering
Dr. Kirk O'Reilly	Chevron Research and Technology Company	Biochemistry; Microbial Processes
Dr. Gregory D. Sayles	USEPA Cincinnati	Microbial Processes; Bioremediation
Dr. Jim Spain	Air Force Research Laboratory	Microbiology

Table 3. Outreach Advisory Committee

Member	Affiliation	Expertise
Mr. Tim Brincefield	U.S. EPA, Region 10	Superfund cleanup and brownfields
Mr. Brooks Koenig	Oregon Department of Environmental Quality	Policy/Law of environmental regulations
Ms. Debbie Schechter	U.S. EPA, Region 9	Community involvement
Mr. Lenny Siegel	Center for Public Environmental Oversight	Policy/Guidance for cleanup and reuse
Ms. Kathleen Veit	U.S. EPA, Region 10	Community involvement
Ms. Susan Warner	North Coast Regional Water Quality Board (California)	Regulations

Table 4. Center Funding

Funding Sources	FY 2001*	Funds to Date
EPA: Centers Program	$900,000	$900,000
EPA: Brownfields	$150,000	150,000
Oregon State University	90,000	90,000
TOTAL	$1,140,000	$1,140,000

*Oct. 1, 2001- Sept. 30, 2002

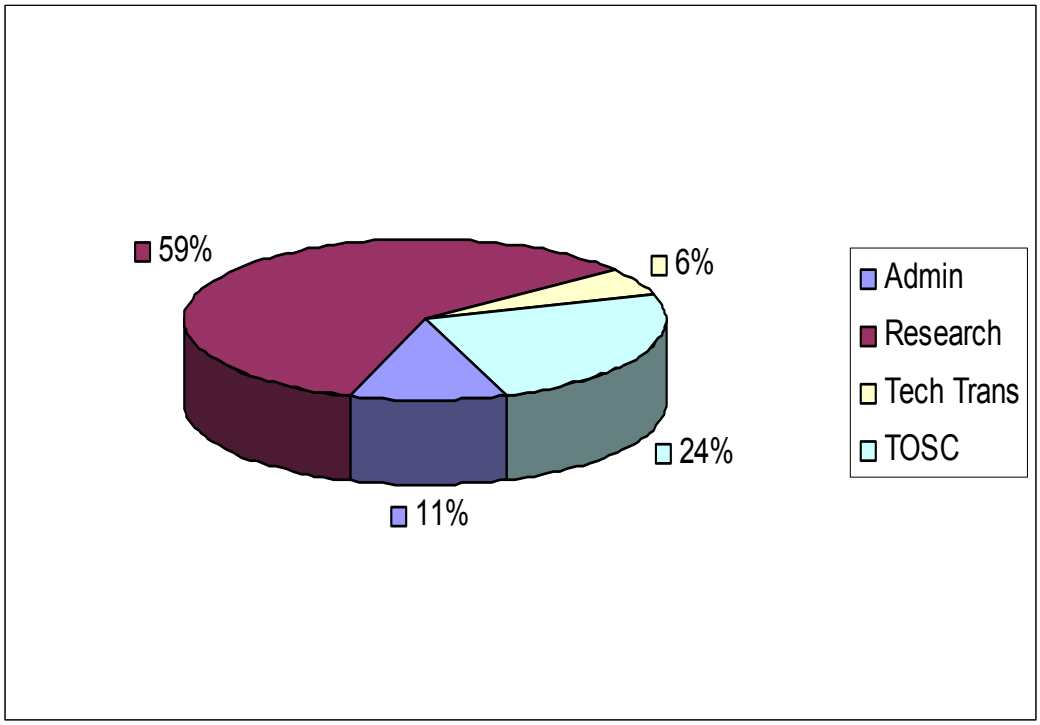
Table 5. Student Support

Student Support	Number*	Funds to Date†
M.S.	2	$70,000
Ph.D.	9	515,000
Post Doctoral	-0-	-0-
TOTAL	11	$585,000

* 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 been initiated 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

Project	Title	PI Co-PIs	Year 1 Budget
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
1-OSU-01	Developing and Optimizing Biotransformation Kinetics for the Bio-remediation of Trichloroethylene at NAPL Source Zone Concentrations	Lewis Semprini, PI; Mark E. Dolan, Co-PI	$70, 224
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
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
1-SU-03	Effects of Sorbent Microporosity on Multicomponent Fate and Transport in Contaminated Groundwater Aquifers	Martin Reinhard, PI	$56,026
1-OSU-03	Development of the Push-Pull Test to Monitor Bioaugmentation with Dehalogenating Cultures	Jennifer A. Field, PI; Jonathan D. Istok, Co-PI	$45,627
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

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. The research is evaluating specific methods of chemical delivery and mixing and comparing them on the same basis in terms of effectiveness and cost. A set of tools and guidelines is being produced for designing effective in situ delivery and mixing systems. The researchers are planning to field test developed methodologies at their own sites and/or collaborate with other researchers who design field-scale in situ remediation projects.

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 μM) 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. During the current year the researchers have demonstrated that more effective transformation of high PCE concentrations can be achieved by a mixed culture consisting of the two cultures compared to either of the cultures separately.

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. During the past year they have examined the impact of cometabolism of different CAHs on mono-oxygenase activity, and assessed the effect of cometabolism on cell viability and recovery from cometabolism. The researchers are also studying the potential for bioaugmenation of these cultures for in situ remedation and are studying the bioaugmentation processes in laboratory column studies.

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. Laboratory reactors have been constructed and used to remove trichloroethylene (TCE, a model substrate) from water sources of varying quality, e.g., deionized water or groundwater using dispersed catalysts and model catalysts. 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. Such information will be coupled with mathematical modeling to assess the risk associated with organic contaminants sequestered in micropores of natural soils.

In project 6 (1-OSU-03), being conducted by Jennifer Field and Jonathan Istok at OSU, the push-pull test to monitor the bioaugmentation with dehalogenating cultures is being developing. 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) 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. The investigators are currently evaluating the survivability of the cultures in groundwater/sediment microcosms and their basic transport behavior in columns.

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. This work is being performed in collaboration with Projects 2 and 6. Portable flow systems have been developed for monitoring redox status of solutions in bioreactors and microcosm bottles and physical aquifer models (PAMs).

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 Table 5. Two M.S. students and nine Ph.D. students have received center funds through graduate research assistantships. Two of the students have been funded through the center outreach program and nine 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. Over the past year a new WRHSRC web site has been developed and maintained at OSU. Since its launch in January 2002, usage has increased to 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, 1989-2001; 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 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 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). The WRLTC-OSU has presented 29 accreditation or certification workshops (1 to 5 days in duration) from Dec. 1, 2001 to September 30, 2002.

TOSC and TAB Programs

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 communites in Alaska (1), Oregon (2), Washington (2), Arizona (1), and California (10) (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, Arizona, and Nevada. The TAB program as helps coordinate an annual Brownfields conference in partnership with Oregon Department of Environmental Quality and Oregon Economic and Community Development Department. The fourth annual conference took place in Portland this year.

Center Annual Research Meeting

In August 2002, center researchers, graduate students, outreach specialists, and Science Advisory and Outreach Advisory Committee members met for the first annual meeting of the new WRHSRC. The meeting was an excellent introduction to the center's goals: to improve technologies for cleanup of chlorinated solvents in groundwater and to provide assistance to western communities affected by hazardous substance contamination. In the morning researchers from Oregon State University (OSU) and Stanford gave presentations highlighting the center's seven main 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.

Research Project Reports

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

Strategies for Cost-Effective In Situ Mixing of Contaminants and Additives in Bioremediation
Peter K. Kitanidis, Stanford University, PI; Craig S. 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: In the absence of effective mixing and chemical delivery schemes, technologies that could potentially remove contaminants from geologic formations and groundwater will not be translated to practice. 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, we study principles of mixing and the performance of mixing schemes, and we evaluate a broad range of existing and new full-scale mixing and chemical delivery schemes through comprehensive mathematical, technical, and economic analysis. We are guided by case studies.

Status: We 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. 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. They will be implemented in the next few months. We have developed mathematical models of flow, transport and biogeochemistry and are comparing predictions with the results of experiments and field tests.

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 μM) 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; and (4) provide kinetic information and cultures in support of these 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 cis-DCE, and vinyl chloride to ethylene. By mixing both cultures, we hope to achieve rapid transformation of PCE and TCE to ethylene. Batch kinetic studies are being used to determine optimum electron donors for the transformation, and we will use molecular methods to track the two microbial communities. We are also determining electron transfer efficiencies for halorespiration as well as hydrogen thresholds. We will also evaluate the effect of varying environmental conditions on reductive dechlorination kinetics. These conditions include the apparent oxidation/reduction potential, pH, electron donor type and concentration, and hydrogen partial pressure.

Status: Kinetic studies are being performed to characterize the three different mixed cultures: Point Mugu culture (PM), the Evanite culture (EV), and a binary mixed culture (BM) containing PM and EV cultures. The PM culture showed reductive dechlorination of TCE up to a concentration of 3.4 mM, but dechlorinated PCE at very slow rate. The PM culture rapidly dechlorinates TCE and *c*-DCE to VC, but slowly transforms VC to ETH. The EV enrichment is capable of reductively dechlorinating PCE at its solubility limit (0.9 mM) and completely dechlorinates PCE to ETH, but slowly transforms *c*-DCE to VC. The $k_{max}X$ of PM culture for PCE, TCE *c*-DCE, and VC at 20°C were found to be 1.4, 102, 1280, and 40 μM/day with K_S values of 1.3, 5.1, 8.3, and 604 μM, respectively. These kinetic values for PCE and VC explain why PCE and VC were reductively dechlorinated at very slow rates by PM culture. The $k_{max}X$ values of EV culture for PCE, TCE, *c*-DCE, and VC were 104, 95, 65, and 205 μM/day with K_S values of 2.8, 1.8, 4.2, and 51 μM, respectively. Theses results reflect why the EV culture slowly transforms *c*-DCE to VC. Kinetic studies are currently being performed on PCE, TCE, *c*-DCE, and VC transformation by the binary mixed culture. Work is also in progress to better characterize these cultures using molecular techniques and to quantify the dehalogenators that are present the in order to determine the k_{max} values and to estimate growth yield. Tests are also planned to access the long term stability of the binary enrichment in maintaining the observed transformation rates. Model simulations with these kinetic values will be compared with the results from batch reactor studies containing PCE NAPL.

*Publication*s: Yu, S., and L. Semprini (2002). "Comparison of trichloroethylene reductive dehalogenation by microbial communities stimulated on silicon-based organic compounds as slow-release anaerobic substrates." Water Research **36**(20): 4985-4996

Yu. S. and L. Semprini, "Dechlorination of PCE DNAPL with TBOS Using a Binary Mixed Culture," The Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 20-23, 2002, Monterey, California (In press).

Aerobic Cometabolism of Chlorinated Aliphatic Hydrocarbon Compounds with Butane-Grown Microorganisms

Daniel J. Arp, Oregon State University; Peter Bottomley, Lynda Ciuffetti, Stephen Giovannoni, Lewis Semprini, Ken Williamson, Mark Dolan, Oregon State University, Co-PIs

Goal. The project aims to evaluate 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; (3) evaluating the performance of cultures in laboratory column studies; and (4) applying improved cometabolic transformation models to the results of laboratory studies.

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.

Approach. The investigators bring a range of microbiological and environmental expertise to the project. We have examined the CAH degrading properties of several individual strains of butane-oxidizing bacteria and fungi that are known to possess distinctly different butane monooxygenases. We have examined the impact of cometabolism of different CAHs on monooxygenase activity, and assessed the effect of cometabolism on cell viability and recovery from cometabolism. In one part of this project we are focused upon the cometabolic properties of the lesser chlorinated solvents such as the dichloroethenes (DCEs) because they are often persistent products of reductive dechlorination at field sites. By using molecular approaches with a reporter strain of *P. butanovora* we are carrying out an examination of the ability of DCEs to induce BMO genes in *P. butanovora*, and the ability of various sources of electron donors to drive the cometabolism of the DCE induced BMO activity. In another part of this project we are evaluating the potential for bioaugmentation of butane-utilizing cultures that are effective in transforming mixtures of 1,1,1-trichloroethane (1,1,1-TCA), 1,1-dichloroethane (1,1-DCA), and 1,1-dichloroethene. Pure cultures have been isolated that effectively transform mixtures of these compounds and also perform well under the nutrient conditions of groundwater, and in the presence of indigenous microorganisms. Molecular tools have been developed to track the these cultures upon their addition in subsurface remediation. A third part of this project is to evaluate the potential of *Graphium sp.,* a filamentous fungi, to cometabolically 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.

Status. Decline of TCE metabolism in *P. butanovora* is primarily influenced by TCE mediated loss of BMO activity rather than due to loss of cell viability caused by general cellular toxicity. Distinct differences were observed, however, between the cometabolism of cis and trans 1,2

DCE, and 1,1 DCE by *P. butanovora*. In particular, 1,1 DCE was shown to rapidly inactivate reductant supply to cometabolism in an acetylene-sensitive manner implying that extremely toxic metabolites are produced during the oxidation of this compound. cis 1,2 DCE is a better substrate for the BMO of *P. butanovora* than is 1, 2 trans DCE, and yet BMO gene expression is induced more effectively by 1,2 trans DCE than by 1,2 cis DCE. It is well known that high concentrations of butane interfere with co-oxidation of most CAHs. We have shown that lactate is an effective electron donor for driving cometabolism of CAHs. Lactate drives cometabolism more effectively than butyrate which tends to inhibit the process as concentration is raised. Further work is in progress to characterize the role of CAHs in induction of butane oxidizing activity and the efficacy of alternate electron donors for driving cometabolism. We believe these observations might have important implications for the role of hydrocarbon oxidizing bacteria along the periphery of anaerobic plumes where a combination of fermentative products and less chlorinated products of PCE or TCE degradation are available for further biodegradation.

Two pures have been isolated for the biaugmentation studies, a Rhodococcus culture and a culture that is currently being identified using 16S-RNA methods. Kinetic studies have shown that both microorganisms effectively transform 1,1-DCE, 1,1-DCA, and 1,1,1-TCA. A mixture of these two cultures has been bioaugmented to the pilot scale test zone at Moffett Air Field, as a DoD SERDP funded project. In the laboratory part of this program, kinetic parameters are being determined for each of the individual cultures. In the center project continuous flow column studies are being performed with these two cultures biaoaugmented into Moffett Field core material. The continuous column study will permit a comparison with results from the field, and will also allow a broad range of conditions to be evaluated, such as the concentration range that can be effectively treated. The distribution of the bioaugmented microorganisms in the column(s) will also be determined through destructive testing. Model simulations of the column studies and field tests will also be performed and compared.

Propane grown filter-attached *Graphium* sp. cultures are being used in short term laboratory studies to determine the extent and rate of cometabolism of TCE, carbon tetrachloride (CT), chloroform (CF), an naphthalene. We are also characterizing the oxygenase responsible for the initial transformation of the target compound. We have cloned a full length genomic copy of an alkane inducible cytochrome P-450 from *Graphium* sp. This clone will be transformed into *Saccharomycetes cerevisae* AH109 and expressed under the control of a constitutive promoter. Heterologous expression in a yeast will allow us to more quantitatively describe CAH and PAH degradation because yeast cells are more amenable to laboratory manipulations. Furthermore, if *S. cerevisae* does not possess the other endogenous enzymes required for mineralization of the substrate, we will have the opportunity to identify intermediates in the catabolic pathway. These experiments will conclusively determine the function of the cytochrome P-450 in the cometabolic transformation of CAHs, PAHs, and trichloromethanes.

Publications Kim, Y., D. J. Arp, and L. Semprini (2002) "A combined method for determining inhibition type, kinetic parameters, and inhibition coefficients for aerobic cometabolism of 1,1,1-trichloroethane by a butane-grown mixed culture." *Biotechnology and Bioengineering* 77: 564-576.

Kim, Y. D. J. Arp, and L. Semprini (2002). "Kinetic and inhibition studies for the aerobic cometabolism of 1,1,1-Trichloroethane, 1,1-Dichloroethylene, and 1,1-Dichloroethane by a butane-grown mixed culture." *Biotechnology and Bioengineering*.80:498-508.

Martinez-Prado, A., K. Skinner, L.M. Ciuffetti and K.J. Williamson (2002, in press)." MTBE Kinetics By Alkane Grown Mycobacterium vaccae JOB5 and Graphium sp." Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Battelle Press, Columbus, Ohio.

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 understanding changes in the catalyst surface during treatment and correlating these to changes in catalytic activity. Laboratory reactors will be constructed and used to remove trichloroethylene (TCE, a model substrate) from water sources of varying quality, e.g., deionized water or groundwater. Samples will be removed from the reactor periodically over the course of treatment for spectroscopic characterization. The experiments will use dispersed catalysts, which are typically used in field applications, and model catalysts, which are more amenable to spectroscopic analyses and therefore may yield more insight into surface phenomena. The research will be undertaken in collaboration with a field study at Edwards Air Force Base (EAFB) near Lancaster, California.

Status: The model catalyst has been developed and tested for catalytic activity. The reactor for the model catalyst has been designed and constructed, but has not yet been tested in flow-through mode. The reactor system for the dispersed catalyst has been constructed, tested, and modified, based on results (see details below).

The reactor system with the dispersed Pd catalyst successfully removed TCE from EAFB groundwater. Observed deactivation was consistent with sulfide poisoning and was attributed to the growth of sulfate-reducing bacteria. In response, the reactor system was modified so that feed water for the reactor is no longer stored under hydrogen, i.e., conditions are now less favorable for the growth of sulfate-reducing bacteria. During the experiment, sodium hypochlorite was able to fully regenerate a deactivated catalyst; it is expected to maintain catalyst activity in the field as well, through periodic regeneration. Future work will complete testing of the laboratory catalyst systems and will compare the data with kinetic results from the field study. In addition, the model and field catalysts will be analyzed with x-ray photoelectron spectroscopy, to identify chemical changes on the catalyst surface. Finally, a comparison will be made of the effectiveness of regeneration using sodium hypochlorite, hydrogen peroxide, and ammonium chloride. This study commenced 1 January 2002 and is authorized for a two-year period terminating 31 December 2003.

Publications: Munakata, N., J.A. Cunningham, R. Ruiz, C. Lebron, and M. Reinhard. (2002, In Press) "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 Third International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California.

Effects of Sorbent Microporosity on Multicomponent Fate and Transport in Contaminated Groundwater Aquifers
Martin Reinhard, Stanford University, PI

Goal: This project aims to: (1) evaluate techniques for characterizing microporosity (pore size distribution and micropore volume) of aquifer sediments and other natural sorbents; (2) determine how measurements of effective micropore volume and size distribution depend on environmental variables and contaminant properties; (3) quantify the interactions among multiple contaminants during uptake in micropores; and (4) predict the time scale for multicomponent release from natural sorbents when micropore sorption is the dominant sequestration mechanism.

Rationale: Microporosity exists to some level in most natural soils. It has been demonstrated that the micropores of natural soils can sequester significant amounts of organic contaminants, and that a very long time (months to years) may be required for these contaminants to be completely released again. Contaminant properties (e.g., molecular size, structure, and polarity) and environmental variables (such as relative humidity and temperature) may have major impacts on the equilibrium and/or kinetics of the micropore sequestration. Understanding the contribution of micropore sequestration to the overall sorption capacity of natural soils, and the impacts of environmental variables on this process, is crucial for assessing the risk associated with contaminated groundwater aquifers, and for designing risk-based remediation technologies.

Approach: This project investigates the importance of one of the most fundamental processes of organic sequestration on porous sorbents—micropore sorption. The "physical" microporosity

of natural sorbents will first be characterized with traditional vacuum gravimetric/piezometric techniques. Then the "effective" uptake of different organic contaminants on these sorbents under various environmental conditions will be measured. The difference between the ideal micropore sequestration capacity and the experimental value will provide insight into the contribution of micropore sequestration relative to surface adsorption, capillary condensation, partitioning into organic matter, etc., with respect to the overall sorption capacity of natural sorbents. While this project focuses on the least understood micropore sequestration process, sorption contribution from each potential sink on a sorbent will be analyzed and compared, which makes this study different from most observational studies. The impacts of the environmental variables affecting micropore sequestration will also be quantified. With this knowledge, the competitive sorption/desorption of multiple contaminants on the natural soils will be studied to elucidate the interactions among molecules with different properties during micropore sequestration. The kinetics of contaminant uptake and release from micropores will also be measured and compared with other sorption/desorption pathways. Such information will be coupled with mathematical modeling to assess the risk associated with organic contaminants sequestered in micropores of natural soils.

Status: The sorption of several vapors on engineered solids and natural soils will be studied; engineered solids will be used for calibrating and comparing microporosity characterization techniques, while natural soils will be the focus of this study. Engineered solids with micropores that are predominately hydrophobic (carbon black), hydrophilic (silica gel), and with variable degree of hydrophobicity (zeolites) are selected. Natural soils with various degrees of microporosity and organic matter content are also selected.

A setup for measuring the sorption of organic vapors under different environmental conditions was designed and installed. Traditional vacuum piezometric and gravimetric methods can only be used to study the sorption of a single sorbate. Our experimental setup measures the accumulation of sorbates at different relative pressures by combining gravimetric and gas chromatographic (with solvent extraction) measurements. The gas phase relative humidity can be independently varied, and extremely low concentrations (pg level) of chlorinated compounds can be detected by electron capture detector (ECD). Furthermore, the "real" sorbate adsorption capacity and kinetics under various environmental conditions can be obtained instead of those in vacuum. As the micropore sorption process is very slow under real world conditions, it will take very long time to reach sorption equilibration with this setup. The major disadvantage is that all the contaminant sequestered in micropores may not be completely recovered by solvent extraction, and we will investigate the remedial techniques.

Development of the Push-Pull Test to Monitor Bioaugmentation with Dehalogenating Cultures

Jennifer A. Field, Oregon State University, PI; Jonathan D. Istok, Oregon State University Co-PI

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 in 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. 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: Currently the background activity of sediment collected from a site with known indigenous reductive dechlorination activity is being characterized with respect to the kinetics of TCFE, fumarate, and succinate utilization and product formation. These three substrates are proposed for this project as substrates that can be used to assay for reductive dechlorination potential in situ. These microcosm studies are being used to determine the relationship between TCFE, fumarate, and succinate prior to initiating these assays in PAMs. The PAMs that are in place and under saturated conditions will be driven anaerobic with the introduction of oxygen free water. Dissolved oxygen concentrations will be measured and compared to in situ redox measurements made in collaboration with Dr. Ingle's project. Once anaerobic conditions are established in the PAMs and verified using these two techniques, the background reductive dechlorination activity will be determined by modifying the TCFE and succinate as necessary for use as assays in the PAMs.

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 TCE and PCE with dehalogenating cultures. Specific objectives are 1) to deploy, evaluate, and refine redox sensors 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 field site, 2) 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 differentiate between different microbial redox levels (e.g., Fe(III)-reducing, sulfate-reducing, methanogenic). Flow sensors based on redox indicators will be 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, 2) on-line monitoring of the redox status of the material in a physical aquifer model (PAM) bioaugmented with the developed dehalogenating cultures. Throughout these studies, the design and characteristics of the redox sensor monitoring systems will be improved.

Status: We have developed a portable flow system for monitoring redox status of solutions in bioreactors and microcosm bottles and physical aquifer models (PAMs)). It is based on a specially constructed peristaltic pump and housing and improved flow cells for immobilized redox indicators. For the pump housing, the gas permeable pump tubing is enclosed and protected by purging with an inert gas or by contact with a deoxygenating solution (e.g., ascorbic acid). This pump can be powered by a small 12-V battery in field applications. Microcosms are easily adapted to the flow system by inserting PEEK or stainless steel tubing through the container wall. The flow system is directly applicable for monitoring redox levels of anaerobic material inside PAMs with minimal oxygen contamination. With this flow system, we have achieved O_2 permeation rates as low as 2.4 μL/h.

We have continued to improve the design and fabrication of inexpensive spectrophotometric flow cells suitable for containing redox indicators immobilized on thin transparent films. Critical points in the design of these flow cells include ease of replacing membranes, providing a pathway for trapped bubbles to escape, and rigid construction, which minimizes O_2 permeability through the cell walls.

Preliminary work has begun on platinum/redox membrane electrodes constructed with the film of the immobilized indicator press-fit to the surface of a modified platinum electrode. These devices are conceptually simpler than optically based detection systems and could be the basis of simple in-situ redox probes.

Publications. K. Cantrell and J. D. Ingle, J. (2002, In Press)). "The SLIM Spectrometer." *Anal. Chem.*

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

ALASKA
Organization: Tanana Tribe
Site: Tanana Village, central Alaska
TOSC Primary Contact: Michael Fernandez
EJ Community, **TOSNAC Participating**
Contaminants of Concern: Chlorinated solvents and petroleum products
Description: TOSC has been asked to consider providing technical services to the Tanana; we are talking with several individuals familiar with the community in order to determine if TOSC can help and have spoken with a tribal employee to ascertain what services may be appropriate.
Date Letter of Agreement Signed: Letter not yet written.

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 though 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 though ingestion of local produce, soil contact, and incidental ingestion of soil.

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.

Organization: Quincy Concern
Site: CENEX Facility
City: Quincy
TOSC Primary Contact: Michael Fernandez
Contaminants of Concern: Dichloropropopane
Description: TOSC has reviewed and will provide comments on a recent health consultation prepared by the Washington Department of Health.
Date Letter of Agreement Signed: 12/1/1999
Items in Letter of Agreement: Review site investigation reports on the CENEX facility; attend meetings with community members as necessary.

Region 9

ARIZONA
Organization: Downtown Southwest Neighborhood Association
Site: From 19th Ave. to 7th 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_x, 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: Letter not yet written.

CALIFORNIA
Organization: Aerojet Community Advisory Group
Site: GenCorp Aerojet
City: Rancho Cordova, California
TOSC Primary Contact: Michael Fernandez
Contaminants of Concern: Perchlorate and VOCs
Description: TOSC reviewed and commented on a site assessment report for land proposed for removal ("carve-out") from the Superfund site. The lands were proposed for carve-out due to the lack of evidence suggesting that waste handling or disposal activities ever took place in these areas.
Date Letter of Agreement Signed: No letter agreement was prepared.
Items in Letter of Agreement: Although there is no letter agreement, TOSC verbally agreed to review the site assessment report and previous reports on which the assessment was based, as well as to participate in CAG meetings as appropriate.

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: 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 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: Reviewing remedial investigation and feasibility study for the Sulphur Bank Mercury Mine.

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: Protect Our Neighborhood Committee
Site: Waste Disposal Inc.
City: Santa Fe Springs
TOSC Primary Contact: Stephanie Sanford
Contaminants of Concern: Metals, VOCs, PAHs, PCBs, and pesticides in soils, methane, benzene, vinyl chloride, TCE and other VOCs in soil gas, VOCs in groundwater
Description: The community is concerned about the adequacy of cleanup plans for the EPA Superfund site and about the potential relationship between community illness and exposures to site-related contaminants. PONC requested that TOSC review the Record of Decision and sampling data from groundwater, soil, and air studies. PONC has also asked TOSC to provide an updated list of contaminants affecting the area and provide assistance in determining the health related concerns of area residents.
Date Letter of Agreement Signed: 5/29/1998
Items in Letter of Agreement: Review the Record of Decision; determine health related concerns of residents living adjacent to the site; provide an updated list of contaminants affecting groundwater, soil, and air both at the site and in the adjacent community; review and comment on investigation and feasibility studies.

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: Letter not yet written.

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: 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: Other communities with which TOSC was involved in 2001:

Organization: Del Amo Action Committee
Site: Montrose
City: Del Amo, California
TOSC Primary Contact: Kenneth Williamson
Contaminants of Concern: DDT
Description: TOSC reviewed a soil removal action along Kenwood Avenue, in the neighborhood next to the Montrose Chemical DDT plant. The removal action followed the discovery of high concentrations of DDT in a drainage channel originating near the Montrose facility. Perry McCarty, former Director of the Western Region Hazardous Substance Research Center, and Yurom Cohen from UCLA, worked with the WRHSRC TOSC program to conduct the review. TOSC and HSRC personnel attended a community meeting to provide comments on the report.

Status: Inactive communities that may require future assistance:

Arizona Communities
ME West Castings (Tempe)
South Phoenix
Union Hills (Phoenix)

California Communities
Alameda Point (formerly Alameda Naval Air Station) (Alameda)
Bay Area Drum (San Francisco)
Naval Air Station North Island (Coronado)
Mare Island Naval Shipyard (Vallejo)

Hawaii Communities
Makua Military Reservation (Oahu)

Washington Communities
Brewster

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
TAB Primary Contact: Michael Fernandez
Description: The county was recently selected as a brownfields grant recipient. TAB has agreed to assist the county in its community outreach and education program. TAB anticipates preparing and presenting workshops on site assessment and cleanup for community members and selected property owners.

Organization: Oregon Brownfields Conference
TAB Primary Contact: Michael Fernandez
Description: TAB helps coordinate this annual conference in partnership with Oregon Department of Environmental Quality and Oregon Economic and Community Development Department. The fourth annual conference took place in Portland on September 5-6, 2002. Over 200 representatives from local, state, and federal government, as well as from private sector consulting and finance, participated in this year's conference.

Organization: Oregon DEQ Brownfields Program
TAB Primary Contact: Michael Fernandez
Description: TAB acts as a resource to the ODEQ brownfields program and participates in their monthly meetings. TAB has begun to prepare and administer a survey of community brownfields needs this year at ODEQ's request.

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. We will be scheduling a meeting to discuss specific needs in October.

Region 9

ARIZONA
Organization: Arizona Department of Environmental Quality
TAB Primary Contact: Michael Fernandez
Description: Working with the Arizona Department of Environmental Quality, we anticipate assisting four small communities in need of technical assistance related to site assessments performed on properties within their jurisdictions.

NEVADA
Organization: Nevada Division of Environmental Protection (NDEP)
TAB Primary Contact: Michael Fernandez
Description: TAB is exploring opportunities to collaborate with NDEP brownfields coordinator Connie Lewis. We have scheduled a meeting to discuss helping NDEP plan and present a rural brownfields conference. 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 Program

Kenneth Williamson, Director, and Maria Wright, Technology Transfer Coordinator, Oregon State University

Goals:

- 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 2002, tech transfer activities included development of a new WRHSRC website, continuation of several technology demonstration projects, and training through the OSU Lead Program.

The website 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, 1989-2000. This database will soon be available in a searchable format.
- ◊ 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.

In 2002, center researchers also continued with several field demonstration projects. The projects allow new technologies to be tested and demonstrated in a field setting. Projects involve many different center researchers and receive support from several funding sources outside of the WRHSRC's main grant.

Publications. Goltz, M.N. and K.J. Williamson, "Transfer and Commercialisation of Contaminated Groundwater Remediation Technologies," *International Journal of Technology Transfer and Commercialisation*, **1**(4):329-346 (2002).

Hazardous Waste Training

Peter O. Nelson, Ann Kimerling, and Kenneth Williamson, Oregon State University

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

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

Approach: The 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 WRLTC-OSU has presented 29 accreditation or certification workshops (1 to 5 days in duration) from Dec. 1, 2001 to Sept. 30, 2002. In those classes, 297 students received training certificates and enabled them to receive Oregon or EPA work certificates. The WRLTC-OSU has been actively involved in the Oregon Department of Human Services Lead Program regulatory review. Fall of 2002 activities focus on the Oregon lead program implementation through the public housing sector and weatherization programs.

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 7, 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 this field demonstrations tend to feedback into 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 7. 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.
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
Enhanced Natural Attenuation in Commingled Plumes	Martin Reinhard, Jeff Cunningham, Carmen Lebron,	(US Navy, NFSEC)
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 are performing single well push-pull tests using methods developed through previous center research. Lactate and fumarate are being added as substrates to different wells at the test site. Upon biostimulation, push-pull activity tests are being performed to study fermentation and dehalogenation reactions. Trichlorofluroethene (TCFE) is being added as a surrogate compound for TCE. Transformation products of TCFE are being

determined in samples obtained during the pull phase of the tests. The tests are also determining whether the reduction of Cr^{+6} to Cr^{+3} is occurring upon stimulation of anaerobic conditions at the site. This work is providing evidence for enhanced anaerobic treatment at the site. Based on the results of this work a full scale in situ treatment process will be designed.

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 have been operated by biostimulating with different substates including lactate and hydrogen, as well as a reactor with an iron barrier. Trichlorofluroethene (TCFE) has been added to these reactors and its transformation is being monitored. These tests are designed to obtain information on the system performance, and are funded through a NIEHS Superfund grant.
TCE Treatment Using palladium (Pd) catalysts

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-dichlorothene (1,1-DCE), 1,1-dichloroethane (1,1-DCA), and 1,1,1-trichloroethane (1,1,1-TCA). These cultures have been demonstrated to perform well in transforming a mixture of all three CAHs when bioaugmented into groundwater microcosms. Molecular PCR methods developed to track the bioaugmented microorgansisms, have shown these microorganisms are a significant fraction of the community present in the microcosms after 100 days of operation. 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. A dual culture, containing two pure cultures, has been in 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. Results of model simulations of the field experiments using kinetic parameters derived from laboratory and microcosm studies indicate that effective treatment of a mixture of all three CAHs should be achieved in the bioaugmented treatment 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. Thus far tests have been conducted at the McClellan Air Field in Sacramento, California, where propane and methane have been evaluated as cometabolic substrates. Different methods of biostimulation are being tested including the addition of gases substrates, such as propane and methane either as dissolved components of the injected groundwater or by sparging these gases directly into the saturated zone. Different surrogate compounds, such as ethylene and propylene, are being tested that can be cometabolized, like the CAHs, and products of their transformation, including ethylene oxide and propylene oxide, can be tracked. These tests will conclude, with tests conducted at Ft. Lewis, Washington, using toluene as a cometabolic substrate.

2002 WRHSRC Publications

Publications for 2001 and 2002 listed below have resulted mainly from work funded by the original WRHSRC. Since the center was initiated this year, research has not yet resulted in articles appearing in peer reviewed journals. We will continue to maintain the database for publications from both the original and current center.

During 2001 and 2002 a total of 21 journal articles have appeared or been accepted for publication. Center researchers have also published in-bound conference proceedings and book

chapters, and have been active in conference participation, especially the Battelle International Conference on the Remediation of Chlorinated and Recalcitrant Compounds. 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.

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