Water Resources Research Institute
Annual Technical Report
FY 2003

Introduction

The present management and development of the Nation's water resources will largely determine the quality of life for future generations. Decisions being made concerning the large number of competing water resources needs - municipal, industrial, and agriculture water supplies; wastewater disposal systems; flood and drought management; recreation areas for fishing, boating, and swimming; and fish/wildlife habitat - are poorly understood and provide insufficient opportunity for early and/or meaningful input by the public.

The Nation spends hundreds of millions of dollars every year on external and internal research. The data from this research ends up on shelves or on computer disks or otherwise is largely unavailable to society. The best strategy to adopt in order to successfully meet increasing demands for natural resource science without exploding budget growth, is to seek out external partners. Partnerships with universities are a natural path to address this situation. The Water Resources Research Institute program has demonstrated an effective partnership of state and federal government and higher education that uses knowledge about water science, engineering, and policy to meet the emerging challenges to protect, manage, and sustain the Nation's water resources as a vital asset for the future. It has demonstrated how the need to solve water problems can be met at the local level where problems tend to be solved more efficiently. The Institute program is essential to solving emerging and future water supply, management, and quality problems. The Nation needs to strengthen these links and create new ones to achieve its goals in providing the science needed for resource management.

The research results provided in this report will play a vital role in guiding water-management and protection strategies, research, and monitoring across our State and the Nation.

Research Program

A Molecular Approach to Determine the Orgin of Fecal Bacteria in Catoma Creek of the Alabama River Basin

Basic Information

Title:	A Molecular Approach to Determine the Orgin of Fecal Bacteria in Catoma Creek of the Alabama River Basin
Project Number:	2003AL7B
Start Date:	3/1/2003
End Date:	2/29/2004
Funding Source:	104B
Congressional District:	Third
Research Category:	Biological Sciences
Focus Category:	Non Point Pollution, Water Quality, Agriculture
Descriptors:	
Principal Investigators:	Yucheng Feng, Joey Nathan Shaw, C. Wesley Wood

Publication

Synopsis

Proposal Title: A Molecular Approach to Determine the Origin of Fecal Bacteria in Catoma Creek of the Alabama River Basin

Principal Investigators: Yucheng Feng, C. Wesley Wood, and Joey N. Shaw

Funding Period: March 2003 – February 2004 with a no-cost extension to May 2004

Statement of the Problem and Research Objectives

Fecal pollution impairs the quality of streams and rivers for recreational use and adversely affects fish and aquatic life. Fecal contamination can originate from both human and non-human sources including surface runoff from land application of animal wastes or farm animal feedlots, inadequate septic or sewer systems, improper waste disposal, and wildlife impact. Determining the sources of fecal contamination is necessary to develop effective pollution control strategies. Presence of fecal indicator bacteria is the second most common cause of surface water impairment in Alabama. Thirty percent of the 181 impaired water bodies in the state are attributed to fecal indicator bacteria according to Alabama's 2002 Section 303 (d) List. Catoma Creek in Montgomery County is a tributary of the Alabama River. Both agricultural and urban land uses exist in the watershed. A 23-mile segment of Catoma Creek has been included on the State 303(d) list due to impairment of fecal pollution.

The objectives of this research were to construct a library of rep-PCR DNA fingerprints from *Escherichia coli* strains isolated from a wide range of collection of human and animal feces, identify the sources of fecal contamination in the Catoma Creek watershed using the constructed library.

Research Methodology

To achieve the project objectives, first of all, experiments were conducted to isolate *E. coli* from the feces of eight types of warm-blooded animals (including humans) in the watershed, obtain a DNA fingerprint of each isolate using the rep-PCR DNA fingerprinting technique, and construct a host origin library of *E. coli* DNA fingerprints. Secondly, water samples were collected monthly at eight locations in the Catoma Creek watershed (Figure 1) from May of 2003 to April of 2004. Both chemical and microbiological analyses of the water samples were performed. Membrane filtration procedure was used to determine *E. coli* concentrations in the water samples using modified membrane-thermotolerant *Escherichia coli* agar (mTEC). The rep-PCR DNA fingerprints of *E. coli* isolates from the water samples were also obtained. Identification of the sources of fecal contamination will be achieved by matching the DNA fingerprints from the water isolates against fingerprints contained in the source library.

Principal Findings and Significance

Fecal samples were collected from (the number of fecal samples indicated in parentheses) cattle (20), chicken (20), horse (21), waterfowl (21), deer (28), wild turkey (15), dog (18), and human (15). A total of 484 *E. coil* isolates was obtained and characterized. Differences in the rep-PCR DNA fingerprints among different animals were observed. Construction of the rep-PCR DNA fingerprint library of known sources will soon be completed.

Monthly water sample collection was initiated in May of 2003 and continued through April of 2004 at 8 locations in the watershed, with 3 locations on the main stem of Catoma Creek and 5 on the tributaries. During the one-year sampling period, *E. coli* densities ranged from 18 to 12,650 CFU/100 ml, with 70% of the water samples exceeding the EPA criterion of 126 CFU/100 ml for full body contact recreation, and 41.6% above the criterion of 298 CFU/100 ml for moderate full body contact recreation. There was a high correlation between *E. coli* density and stream flow. Chemical analyses of the water samples showed that the concentration ranges for NH_4-N, NO_3-N, phosphorus, and potassium were 0.19 to 0.78 mg/l, 0.12 to 0.38 mg/l, 0.13 to 0.65 mg/l, and 0.16 to 4.74 mg/l, respectively. During the same period, 480 *E coli* isolates were obtained from the water samples. Figure 2 shows an example of the rep-PCR DNA fingerprint patterns of *E. coli* isolates from the watershed.

The presence of high *E. coli* densities in the Catoma Creek watershed limits the recreation use of the streams by the local communities. Relatively high concentrations of phosphorus suggest that eutrophication may occur in the watershed. Once the sources of fecal contamination in the Catoma Creek watershed are determined, corrective actions can be developed to target the contamination source(s). It will also assist water resource managers in designing TMDL implementation plans and lead to improved water quality.

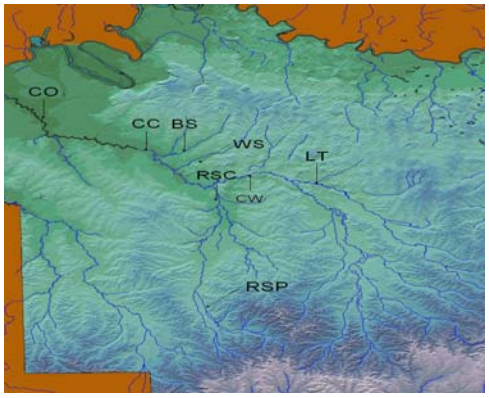

Figure 1. Water sampling sites in the Catoma Creek watershed.

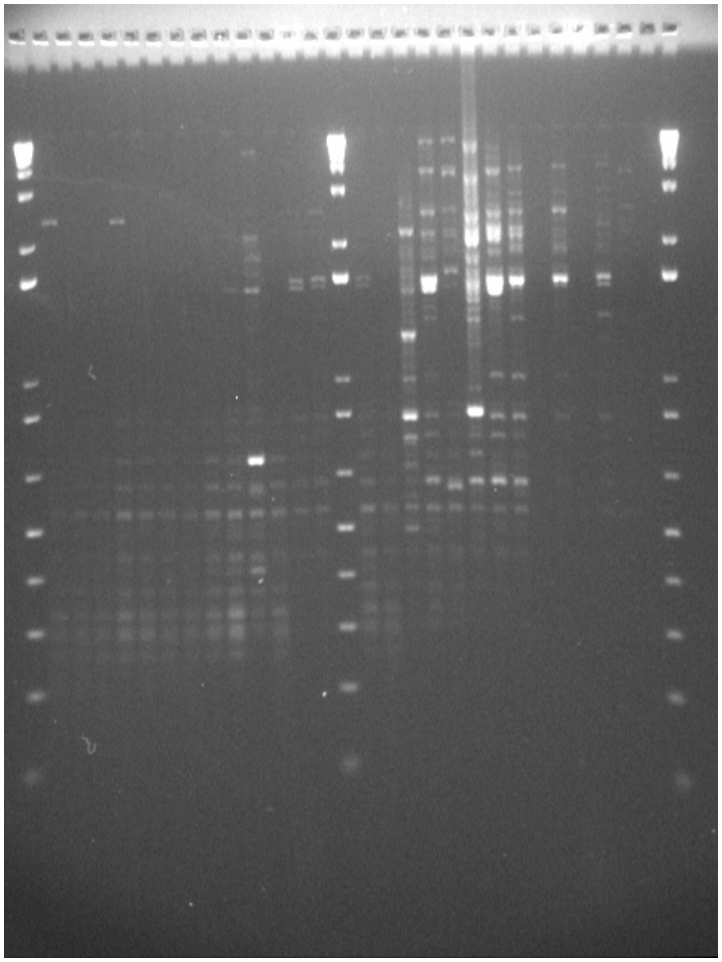

Figure 2. rep-PCR DNA fingerprint patterns of E. coli isolates obtained from water samples collected in May of 2003.

In-situ Destruction of PCbs, PCE and TCE in Alabama Soils and Groundwater Using a New Nanoscale Sorptive Catalyst

Basic Information

Title:	In-situ Destruction of PCbs, PCE and TCE in Alabama Soils and Groundwater Using a New Nanoscale Sorptive Catalyst
Project Number:	2003AL8B
Start Date:	3/1/2003
End Date:	2/29/2004
Funding Source:	104B
Congressional District:	Third
Research Category:	Engineering
Focus Category:	Groundwater, Management and Planning, None
Descriptors:	
Principal Investigators:	Dongye Zhao, Mark O. Barnett, Clifford R. Lange

Publication

1. Zhao, Dongye, and Feng He, 2004, Destruction of TCE and PCBs in Soils and Groundwater Using a New Class of Highly Reactive Nanoscale Bimetallic Particles, Manuscript submitted to Environmental Science and Technology.

SYNOPSIS

IN-SITU DESTRUCTION OF PCBS, PCE AND TCE IN ALABAMA SOILS AND GROUNDWATER USING A NEW CLASS OF NANOSCALE BIMETALLIC PARTICLES

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Date: June 8, 2004

A. PROBLEM STATEMENT AND OBJECTIVE OBJECTIVES

Polychlorinated biphenyls (PCBs), tetrachloroethylene (PCE), and trichloroethylene (TCE) are categorized as chlorinated hydrocarbons, which have been widely used in industries and caused serious groundwater and subsurface contamination in Alabama and hundreds of other sites in the U.S. All three chemicals are believed to be potent carcinogens.

For their non-flammability, stability, and electrical insulating properties, PCBs were used in hundreds of industrial applications (e.g., in electrical transformers and as plasticizers in paints and plastics). More than 1.5 billion pounds of PCBs were manufactured in the United States from its first industrial use in 1927 to the cessation of production in 1977. The U.S. EPA estimates that about half of the total domestically consumed PCBs (625,000 tons) were dumped into the environment (soil and groundwater) before the enactment of federal regulations in 1976. One of the most contaminated sites in the U.S. was discovered in Anniston, AL in the mid 1990's. From 1929 to 1971, large amounts of PCBs were produced at the Anniston Monsanto facility and hundred tons of PCB wastes were dumped into the local environment. In 1990 the Environmental Defense Fund Scorecard ranked Calhoun County, where Anniston is located, among the worst 20% of all counties in the US in terms of an average person's added cancer risk from hazardous waste. The discovery of PCBs in Anniston triggered a costly battle involving the local community, industry, state courts, state government, and US EPA, and has attracted national attention.

PCE and TCE are organic solvents widely used in dry cleaning and metal rinsing. In the past, large amounts of used PCE and TCE were simply dumped into the ground. As a result, high concentrations of PCE and TCE are commonly detected in areas adjacent to dry cleaners, automobile manufacturers or shops, asphalt processing plants, and military bases. The

nationally known PCE/TCE site in Alabama is the "Montgomery capital plume" site, which has been considered to be of the NPL (national priorities list) caliber. To avoid being added to the NPL (which would cost much more), the city of Montgomery has shut down two contaminated wells and initiated an $18.6 million clean up action.

Chlorinated hydrocarbons are highly persistent to natural degradation. Cleanup of soils and groundwater contaminated by chlorinated hydrocarbons has been a focus of the environmental remediation research. The primary obstacle is the lack of cost-effective remediation techniques. For instance, excavation of contaminated soil has been one of the common practices. However, the associated cost is between 100-700 dollars/yard^3. For the capital plume site, since the site is located in the heavily populated downtown area, engineered processes (e.g., excavation) are highly restricted. Therefore, there is an urgent need for developing new cost-effective in-situ techniques for the cleanup of Alabama soils/groundwater contaminated by chlorinated solvents.

This research aims to develop a new in-situ and cost-effective process for complete destruction of chlorinated hydrocarbons such as PCBs and PCE/TCE in soils and groundwater. The specific research objectives are to:

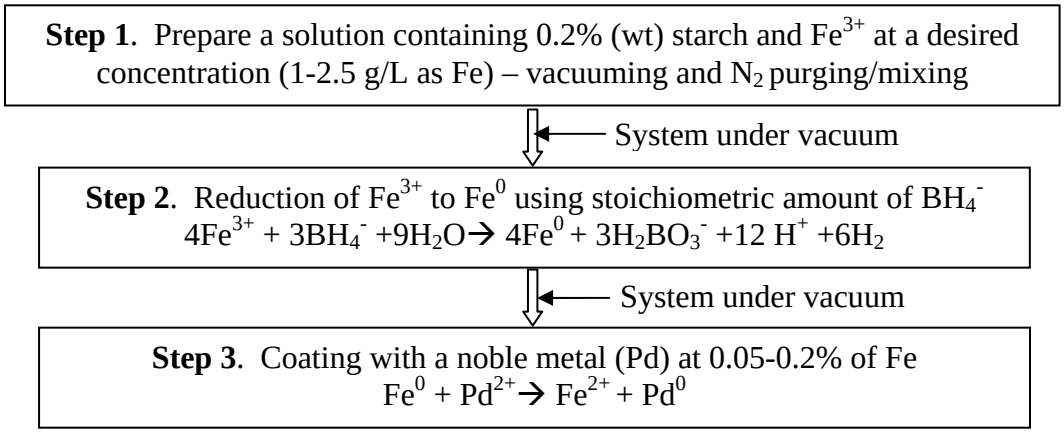
1). Develop a new class of highly reactive, nanoscale bimetallic catalysts that are effective for degradation of the chlorinated organic compounds in soils and groundwater.

2). Test the feasibility (reaction equilibrium, kinetics and dynamics) of the new material for in-situ destruction/mineralization of the chlorinated contaminants in selected Alabama soils and groundwater.

B. RESEARCH APPROACH

B1. Preparation of the nanoscale iron particles

The key to this research was the preparation of the reactive nano-materials. In this research, we developed a simple yet highly innovative procedure, which resulted in the production of a new class of truly nanoscale, highly reactive materials. The preparation method is briefed as follows (a U.S. Patent application on this approach is in processing):



Unlike conventional methods, we applied a low-cost and environmentally friendly carbohydrate (starch) in the preparation. The starch serves as a stabilizer that prevents subsequently formed nanoparticles from agglomeration, thereby maintaining their high

surface area and reactivity. Compared to dendrimers we attempted first, starch is much cheaper and much more effective.

In step 2, a stoichiometric amount of a reducing agent $NaBH_4$ was added to the solution containing Fe^{3+} and the stabilizer. Thereby, Fe^{3+} is reduced to Fe^0. To ensure efficient use of the reducing agent BH_4^-, the entire reactor system was operated under inert conditions though continuously vacuuming and/or N_2 purging.

In step 3, a small amount (0.05-0.1% of iron loaded) of a noble metal (Pd) is coated on the iron-loaded dendrimer by reducing Pd^{2+} to Pd^0. Pd serves as a catalyst to speed up the reaction.

B2. Experiments for TCE degradation

Batch experiments were conducted in 65 mL serum bottles, which were filled with 63 mL solution containing the nanoscale particles. The degradation was initiated by adding 2 mL of TCE stock solution, which resulted in an initial TCE concentration of 20 mg/L, to the solution with the nanoscale particles (no headspace). The bottles were then capped with Teflon Mininert valves and mixed on a rotary shaker (40 rpm) at 22 ± 1 ^oC in an incubator. At selected time intervals, 0.25 mL of the aqueous solution of TCE was withdrawn using a 250 µL gas-tight syringe into a 2 mL GC vial and extracted with 1 mL of hexane. The extract was then analyzed by a HP 6890 GC equipped with electron capture detector (ECD). Blank experiments were also carried out without the addition of the nanoparticles.

B3. Experiments for PCBs degradation

Sacrificial batch experiments were conducted in 2 mL GC vials with Teflon-lined caps. Reaction was initiated by injecting 25µL Aroclor 1254 (100 mg/L) 1 mL solution per vial containing 1 mg/L nanoscale Fe(0) (Pd-Fe). The initial concentration of PCBs was 2.5 ppm. The vials were then sealed and mixed on a rotary shaker (40 rpm) at 22±1 ^oC in an incubator. At predetermined times, the solution was transferred to a 10 mL vial and extracted with 1 mL hexane. The emptied GC vial was also washed using hexane twice using hexane (2 mL in wash 1 and 1 mL in wash 2) and during the first wash the vial was also sonicated for 10 minutes to ensure no PCBs were left in the vial. The rinsing hexane was then added into the 10 mL vial containing the solution. Upon mixing and sonication for 5 minutes, the vial was centrifuged for 5 minutes at 1500 rpm to separate the phase. PCBs in the hexane phase were then analyzed using an HP 6890 GC equipped with an HP5 capillary column (32 m long, 0.25 mm ID, Restek Co.) and ECD. Appropriate control tests were also carried out to ensure that the mass loss of PCBs was due to reaction.

C. PRINCIPAL FINDINGS AND SIGNIFICANCE

The most significant findings from this research are briefed as follows:

- For the first time, we developed a new generation of physically stable and chemically reactive nanoparticles with the aid of a low-cost stabilizer and by conducting the preparation process under vacuum. The particles can remain reactive for days without agglomeration.
- Based on the pseudo-first-order reaction rate, the degradation rate of TCE using the new nanoparticles is orders of magnitude faster compared to the best reported Fe-based nano-

materials to date. No toxic intermediate by-products such as VC, 1,1-DCE, cis-DCE and trans-DCE were detected.

- More than 80% of PCBs (C_0 = 2.5 ppm) in water solution was destroyed using the stabilized nano-materials within 100 hours, compared to only 24% with non-stabilized Pd-Fe nanoparticles.

The preparation procedure developed in this study resolved a key technical barrier in developing physically stable, reactive nanoparticles. The new materials developed in this study represent a substantial technical advancement in preparing nano-scale, reactive particles for reductive dechlorination. The innovative procedures we developed and the mechanisms behind are also highly valuable in the general realm of nano-technology.

The new nano-materials can be safely injected into contaminated subsurface and actively attack and destroy the contaminant plumes without disturbing the aquifer soil and without causing environmental side effects. Therefore, a cost-effective, environmentally benign, in-situ, active remediation technology can be readily conceived using the new materials.

Given the urgent technical need for remediation of soils and groundwater contaminated with PCBs, PCE and TCE, we foresee a great and immediate practical value of our research products. Because of the superior reactivity and low cost, the new materials and the proposed in-situ, active process will save millions of dollars of remediation costs.

Characterizing the Biodegradation Rates of Chlorinated Compounds Under Natural and Anthropogenic Electron Donor Conditions

Basic Information

Title:	Characterizing the Biodegradation Rates of Chlorinated Compounds Under Natural and Anthropogenic Electron Donor Conditions
Project Number:	2003AL9B
Start Date:	3/1/2003
End Date:	2/29/2004
Funding Source:	104B
Congressional District:	Third
Research Category:	Engineering
Focus Category:	Groundwater, None, None
Descriptors:	Chlorinated solvents, Bioremediation, Groundwater, Transport, Degradation
Principal Investigators:	Prabhakar T. Clement, Clifford R. Lange

Publication

1. Mendez-Sanchez, Naomi, T.P. Clement, and C.R. Lang, 2003, An Assessment of Microcosm Tests Used for Evaluating Chlorinated Solvent Bioremediation Model Parameters, in Proceedings of the MODFLOW and More: Understanding Through Modeling, Golden, Colorado, Vol-2, pages 814-818.
2. Quezada, C.R., C.M. Hansen, T.P. Clement, N.L. Jones, and K.K. Lee, 2003, ART3D An Analytical Model for Predicting 3-Dimensional Reactive Transport, in Proceedings of the MODFLOW and More: Understanding Through Modeling, Golden, Colorado, Vol-1, pages 275-279.
3. Quezada, C.R., T.P. Clement, and K.K. Lee, 2004, Generalized Solution to Multi-Dimensional, Multi-Species Transport Equations Coupled With a First-Order Reaction Network Involving Distinct Retardation Factors, Advances in Water Resources Journal, Vol-27, pages 507-520.
4. Clement, T.P., Y.C. Kim, T.R. Gautam, and K.K. Lee, 2004, Experimental and Numerical Investigation of NAPL Dissolution Process in a Laboratory Scale Aquifer Model, submitted for publication in Groundwater Monitoring and Remediation Journal.

CHARACTERIZING THE TRANSPORT AND BIODEGRADATION PATTERNS OF CHLORINATED COMPOUNDS UNDER VARIOUS ENVIRONMENTAL CONDITIONS

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A. PROBLEM STATEMENT AND OBJECTIVES

Due to their adverse effect to both human health and the environment, many researchers have studied the patterns of PCE and TCE degradation in laboratory-scale microcosm tests. Microcosms are small microbial habitats that simulate microbial degradation under various conditions observed in the natural environment. Currently, microcosm experiments are the best way to provide convincing evidence for demonstrating natural attenuation and predicting effects of bioremediation activities. Often this is accomplished by quantifying the disappearance of the target compound while tracking the evolution of various degradation byproducts within the controlled experimental system. While microcosms play a vital role in understanding the fate of chlorinated solvents in the subsurface environment, no standardized protocols for conducting these tests are used. Instead, investigators utilize their own techniques, making comparisons of studies problematic. Clearly, a consistent methodology for conducting microcosm studies is needed. A common procedure for conducting microcosm experiments involves the use of small serum bottles as microcosm reactors. This allows investigators to set up large numbers of replicates while using only a small amount of contaminated soil and thus generating small quantities of waste. However, the small sample size may exacerbate the effects of heterogeneities in the aquifer/soil material. To initiate a test, serum bottles are filled with a salt (buffer) medium, water, soil, substrate (electron donors), and target compound(s). Usually the salts medium is formulated to mimic conditions present at the site in question (i.e., pH, ionic strength, alkalinity, etc.) Different amounts and combinations of soil, substrate, and target compound(s) have been used which makes interpretation of the results difficult.

In addition to performing microcosm test, laboratory scale column experiments coupled with modeling can also provide a greater insight into understanding the overall fate and transport PCE and TCE species in realistic groundwater aquifers.

The overall objective of this work is to completed laboratory and modeling investigation of chlorinated solvent biodegradation patterns and various environmental conditions. Specific tasks completed as a part of this research project include development of a standardized protocol for conducting microcosm studies, standardizing the methods for performing PCE and TCE fate and transport experiments in soil columns, and to explore modeling methods for predicting the PCE/TCE degradation reactions that are coupled to biological degradation processes.

B. RESEARCH METHODOLOGY FOR LABORATORY WORK

For conducting the microcosm experiments, soil samples were obtained at three different locations from a Super Fund site. The site is located at the north of Baton Rouge, LA, approximately 1.5 km away from the Mississippi River. This waste site was opened in 1969 to accept different chemical wastes and its operations ended in 1980. Large quantities of dense non-aqueous phase liquids (DNAPLs) have been identified in this site; the DNAPL waste products originated from various chlorinated solvent manufacturing plants, and from other refineries. The soil samples were collected within one meter of the surface and were transferred into a glass container after removing roots, leaves, and dead vegetation. Analysis of the soil was performed as soon as it arrived to the laboratory. Afterwards, the soil was stored in a refrigerator.

In addition to this field soil samples, we also collected several soil samples near a creek in the downtown Montgomery area closer to the location where Capitol city plume was expected to present. However, these samples were found to lot less microbially active than the Louisiana superfund site plume. As stated before, the Louisiana site was heavily contaminated chlorinated solvent contaminants and the soil microbes are well exposed to the contaminants. Therefore, the overall activity of the superfund site soil was much higher than the Montgomery soil. Hence, in this study primarily used the Louisiana soil in all our test microcosms.

Microcosm Experiments

Small glass serum vials (160 mL) were used as microcosms and were filled with 40.0±0.2 g of the collected soil. A total of 9 bottles were prepared per soil. Table 1 presents the design matrix for the microcosms prepared using the soil obtained at the Super Fund site. Four microcosms from each soil were filled with 150 mL of a spring water-TCE solution (treatment A). A stock solution was prepared by adding 30 mL TCE (99.9+%, spectrophotometer grade, Aldrich Chemical Company, Inc.) in order to saturate the solution. Afterwards, dilutions were performed in order to obtain a final solution with an initial concentration of 30 ppm of TCE. The following salts were added to this solution (g/L): 0.053 KH_2PO_4, 0.1068 K_2HPO_4, 1.0 NH_4Cl, 2.0 Na_2SO_4, 2.0 KNO_3, and 0.2 $MgSO_4 \cdot 7H_2O$. Additionally, 2.0 g/L α – D (+) glucose was added as the electron donor in these experiments. The same solution was added to the rest of the bottles, which were used as controls in each soil (treatment B and C). TCE was not added to microcosm in treatment B. In treatment C, 200 mg/L of NaN_3 were added in order to observe the abiotic degradation of TCE in the system. The vials were closed with aluminum caps and PFTE lined rubber septa. After making sure the microcosms were securely sealed and air bubbles were not present, they were mixed by handshaking for one minute. The microcosms were kept in a shaker at 150 rpm in the dark at ambient temperature (21 °C) through the duration of the experiments.

Site	Treatment
I	A – TCE, nutrients, glucose
	B – nutrients, glucose
	C –TCE, nutrients, biocide, glucose
II	A – TCE, nutrients, glucose
	B – nutrients, glucose
	C –TCE, nutrients, biocide, glucose
III	A – TCE, nutrients, glucose
	B – nutrients, glucose
	C –TCE, nutrients, biocide, glucose

Table 1. Design matrix for the microcosms using the Super Fund site soil.

Soil Column Transport Experiments

A Kontes Chromaflex glass column (ID = 4.8cm, L = 30cm) was dry packed with Ottawa Sand Standard, mesh size 20-30. The column was packed by adding small amounts of sand at a time and tapping the sides of the column to ensure compaction. The dry and wet weight of the column was measured to calculate porosity. Once packed and weighed, the column was connected to a Masterflex Consol Drive pump and was flushed with deionized water for over 24 hours to ensure complete saturation and removal of air bubbles. After each experiment the column was emptied, cleaned and the sand was replaced. The weight of sand added to the column was weighed and the same weight was used for all experiments.

The inflow solution was prepared in a large 2.5L glass bottle. Stock solutions of PCE and TCE were initially prepared by adding 30mL of solvent to deionized water to create a saturated solution. Dilutions of this saturated solution were then made to achieve a target inflow concentration of approximately 60ppm. Uranine (fluoroscein sodium salt C20H10Na2O5 – Fisher Chemical) was used as a tracer. This solid salt was weighed and dissolved in deionized water to achieve a target inflow concentration of 25ppm for all column experiments. Sodium azide (NaN3) from Fisher Chemical was used as a biocide in some of the experiments. The solid was weighed and dissolved in deionized water to reach an initial inflow concentration of approximately 200ppm for all column experiments.

Column experiments were defined as either pulse or step. Pulse experiments involved pumping a known volume of spiked solution and then continuing the flow with deionized water. This type of experiment

allowed observation of the tail of the breakthrough curve. Step experiments involved continuously pumping a known volume of spiked solution and running the column until reaching the equilibrium concentration in the breakthrough curve. A flushing rate of approximately once per hour was desired. This was achieved by calculating the volume of water in the column using the porosity and adjusting the flow rate as required. This ideal pumping rate was manipulated slightly to achieve a flow rate that accommodated the sample size required (i.e. 4ml/min).

Analytical Procedures

The concentration of the chlorinated ethenes was measured at times days 0, 3, 7, 14, every two weeks for two months, and every four weeks after the third month. A 10 mL gas tight syringe was used to extract 6 mL of water solution from the microcosms. This sample was filter using a 0.22 μm nylon syringe filter (Osmonics Laboratory Products). One milliliter of the sample obtained was placed in a 10 mL test tube to which hexane was added in a sample to solvent ratio of 40:60 to make the extractions. The test tube was shaken by hand for 30 seconds. Afterwards, part of the organic phase was placed in a 2 mL auto sampler amber glass vial and analyzed by gas chromatography.

An Agilent 6890 gas chromatograph was used to quantify the concentrations of the target compounds and degradation byproducts. The method used a split injection port (split ratio 3:1) using a helium carrier gas at a temperature of 250^{o}C (482^{o}F) and an inlet pressure of 34.13 kPa (4.95 psi). The capillary column used was an HP-1 methyl siloxane 30 m by 0.32 mm by 1.8 μm. The carrier velocity was 20 cm/sec (flow rate of 2 cc/min). A micro electron capture detector (ECD) was used with a temperature of 340^{o}C and an argon methane (5%) makeup flow of 30 mL/min. The oven was ramped from 40^{o}C to 170^{o}C at a rate of 10^{o}C/min. and then ramped to a final temperature of 300^{o}C at 40^{o}C/min

Standards were prepared by dissolving PCE, TCE, or DCE in hexane in order to make a 250 ppm standard solution. The solutions were used to make sequential dilutions (150 – 0.05 ppm) of the standard; again hexane was used as the solvent. The remaining 5 mL of sample was used to measure the oxidation-reduction potential (ORP) and pH immediately after filtering the sample. An ATI Orion expandable ion analyzer (EA 940) was used to measure both the ORP and pH. Tukey's honestly significant difference test (α = 0.05) was performed in order to determine statistical differences between the soils and treatments used in the experiments.

C. RESEARCH FINDINGS AND SIGNIFICANCE

The laboratory work completed as a part of this project is the first step in completing a set of experiments for the standardization of microcosm tests. Results obtained are satisfactory as ORP decrease to levels optimal for the reductive dechlorination of chlorinated compounds. TCE levels decreased by approximately 10 ppm after one week of experiments. Biodegradation byproducts concentration had increased from zero to 1.6 ppm for 1,1-DCE. Also, other unidentified compounds have been observed in the microcosms, and their quantification is currently being pursued. Future experiments for the standardization of microcosms experiments will focus on the variation of the soil to water ratio, as well as the use of microcosms with headspace.

Column tests on TCE and PCE carried out in this study found that there was minimal retardation or adsorption onto sand at a flow rate of 4mL/min. Full recovery of both TCE and PCE was obtained in the final experiments. It was also found that due to the relative insolubility of PCE, concentration levels of PCE after complete breakthrough were always lower than TCE concentrations. The protocol developed during this study needs to be followed to ensure accurate results. A glass column should be used with fittings that are non-reactive with chlorinated solvents (e.g. PTFE), and all tubing should be made from viton. Solutions and samples should be kept covered from light at all times to reduce photo degradation. The inflow solution should also be very slowly stirred to keep the solution homogeneous. This technique can now be used to observe these same characteristics with mediums other than sand, and the results from these further experiments will complement the microcosm study currently underway.

The modeling work supported by this project allowed us to develop a novel modeling method for predicting the fate and transport of PCE and TCE species in bioreactive groundwater aquifers. In addition, the funding also allowed us to team-up with an overseas research partner to study a PCE-DNAPL dissolution experiment using a numerical reactive transport model. The modeling results were submitted for journal publications.

Information Transfer Program

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	2	0	0	0	2
Masters	2	0	0	0	2
Ph.D.	6	0	0	0	6
Post-Doc.	0	0	0	0	0
Total	10	0	0	0	10

Notable Awards and Achievements

A U.S. Patent application is in process for the "Preparation and Application of a New Class of Nanoscale Bimetallic Particles for Destruction of TCE and PCBs in Water" developed as a result of research funded through the USGS Section 104 Base Grant program.

Publications from Prior Projects

None