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Ground Water Currents

Developments in Innovative Ground Water Treatment

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About this Issue

This issue highlights multi-agency efforts to accelerate the development and implementation of innovative DNAPL remediation technologies, research into increasing the effectiveness of permeable reactive barriers, and development and implementation of innovative site characterization and remediation technologies.

Federal Roundtable Proposes National Action Plan for DNAPL Source Reduction

by Jim Cummings, U.S. EPA Technology Innovation Office

The Federal Remediation Technologies Roundtable has developed a national action plan for accelerating the development and implementation of innovative technologies for remediating Dense Non-Aqueous Phase Liquids (DNAPLs) in ground water. DNAPLs are present at 60-70 percent of Superfund National Priorities List (NPL) sites. Due to their complexity, including the numerous variables influencing their fate and transport in the subsurface, the ultimate path taken by DNAPLs can be difficult to characterize and predict. As a consequence, DNAPLs can be a significant limiting factor in site remediation.

The Roundtable is an interagency group that undertakes cooperative efforts to promote greater application of innovative technologies for site cleanup. Its members include the U.S. EPA, the U.S. Departments of Defense (DoD), Energy (DOE) and Interior (DOI), the U.S. Geological Survey (USGS) and the National Aeronautics and Space Administration (NASA).

The Plan

The focus of the new initiative is on sites contaminated with free DNAPL product at which current technologies (particularly pump and treat systems) take too long to meet national needs. The ultimate goal of the action plan is to develop a national model for technology development programs that reduces the development cycle from about 10 years to 3 to 5 years. The plan calls for a coordinated effort to determine what the nation needs to solve the current DNAPL source term problem and keep the focus on solving that problem. The Roundtable has identified three technology classes as having potential to greatly augment, if not replace, pump and treat systems, the most common DNAPL remediation methods. These are on *in situ* thermal, surfactant flushing, and chemical oxidation. Initial work under the action plan will focus on these processes.

To accelerate the development and implementation of innovative DNAPL remediation technologies, the plan proposes collaborative efforts among federal agencies, private sector vendors, and responsible parties in research and development, technology demonstrations, and full-scale technology deployment. In addition, an expert panel will provide technical input and review of activities and results.

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Research and Development

The objective of the research and development portion of the action plan is to identify and address critical issues hampering commercialization of innovative DNAPL remediation technologies. DOE and the University of California Berkeley are coordinating collection of input from federal agencies, private sector researchers, and technology vendors about areas of potentially beneficial research, relevant ongoing research activities, and future plans. In addition, agencies with research support programs are being asked to include areas of potentially beneficial research in their individual solicitations. These areas include: characterization and performance assessment; process factors and monitoring; scale of effective testing/application; and a number of issues specific to the three initial-focus technologies.

Outreach

The action plan includes implementation of a variety of activities to encourage collaboration and disseminate information. These include:

- Preparing and maintaining an up-to-date, Internet-based description of ongoing research and development, proposed demonstration projects, and full-scale deployments;
- Developing an ongoing program to actively solicit private sector partners;
- Scheduling seminars and workshops to facilitate information exchange and audio/video conferences to discuss results of demonstrations; and
- Preparing and distributing hard-copy and Internet-based versions of lessons learned from each demonstration and application.

For more information about the National Action Plan for DNAPL Source Reduction, contact Jim Cummings of EPA (703-603-7197) or Skip Chamberlain of DOE (301-903-7248).

Role of Microbes in Remediation with Fe^0 Reactive Barriers

G.F. Parkin, P.J. Alvarez, M.M. Scherer, and J.L. Schnoor, University of Iowa

Experiments conducted at the University of Iowa have shown microbes can play an important role in enhancing the treatment of ground water using permeable reactive barriers (PRBs). Increasingly, PRBs made of zero-valent iron (Fe^0) are being used to treat ground water contaminated with reducible pollutants such as chlorinated solvents, nitrate, chromium, uranium, munitions wastes, and pesticides. These same pollutants also can be degraded by a variety of anaerobic bacteria. Using anaerobic bacteria together with Fe^0 PRBs can increase the *rate* and *extent* of transformation of some common contaminants. In addition, the combination can produce more environmentally benign end products and perhaps remove Fe oxides and hydrogen (H_2) gas bubbles that can reduce the reactivity of the PRB.

Reductive treatment with Fe^0 is driven by the oxidation of Fe^0, which releases electrons:

$$Fe^0 \rightarrow Fe^{2+} + 2e^-$$

These electrons can then be used to transform reducible pollutants. For example, both carbon tetrachloride (CCl_4) and chromate (CrO_4^-) can be reduced by Fe^0:

$$CCl_4 + H^+ + 2e^- \rightarrow CHCl_3 + Cl^-$$

$$CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$$

The electrons can also be used to reduce water-derived protons to make hydrogen gas ($H_{2(g)}$), the overall reaction being written as:

$$Fe^0 + H_2O \rightarrow Fe^{2+} + 2OH^- + H_{2(g)}$$

Hydrogen gas is an excellent energy source for a wide variety of anaerobic bacteria. Removal of $H_{2(g)}$ by these microbes increases the rate of Fe^0 corrosion and thus the production of more $H_{2(g)}$. This stimulates microbial reduction of target pollutants and the further degradation of some dead-end products that accumulate during abiotic reduction by Fe^0. Microbes can also remove the $H_{2(g)}$ layer from the Fe^0 surface enhancing the reactivity of Fe^0. Microbial consumption of H_2 gas bubbles can also enhance barrier permeability and potentially enhance the treatment efficiency of a barrier through reductive dissolution of Fe^{3+} oxides. Such biogeochemical interactions may enhance the performance of bioaugmented Fe^0 barriers under most commonly encountered hydraulic regimes and redox conditions.

Over the past five years, the University of Iowa team has investigated a variety of pollutants and experimental conditions. The team has demonstrated that bioaugmenting Fe^0 with a methanogenic

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enrichment increased the rate and extent of chloroform (CF) and carbon tetrachloride (CT) transformation. Column studies with CF, CT, PCE, and 1,1,1-TCA have shown that the process is sustainable and that the choice of microbial seed plays an important role.

A variety of batch and column experiments with nitrate as a secondary contaminant have shown that bioaugmentation with mixed cultures and pure cultures of denitrifying bacteria results in production of nitrogen gases. Abiotic reduction of nitrate yields primarily ammonia, which is an undesirable end product. These studies and others have demonstrated the importance of Fe^0 source and surface area, microbial seed, and pH.

Experiments with mixtures of contaminants have shown that bioaugmentation of PRBs with bacteria offers promise when more than one contaminant is present. More complete dechlorination occurred when the Fe^0 was bioaugmented. Batch experiments with mixtures of CT, Cr^{6+}, and nitrate showed that bioaugmentation reduced competition by these pollutants for active sites on the Fe^0 surface.

Bioaugmenting Fe^0 in microcosms and in flow-through columns showed enhanced rate and extent of removal of RDX (hexahydro -1,3,5-trinitro-1,3,5-triazone). In abiotic Fe^0 reactors, undesirable heterocyclic breakdown products were found. In bioaugmented Fe^0 reactors, these products were not detected.

The University of Iowa team has begun to assess whether microbes colonize the Fe^0 surface in field PRBs. Scanning electron microscopy of samples from a PRB treating a chlorinated solvent plume shows microbial colonization of the surface. Fluorescent *in situ* hybridization of samples from a PRB treating a uranium plume showed the presence of more microbes within the barrier than either upgradient or downgradient from the PRB. The role of these microbes has yet to be ascertained.

In summary, research at the University of Iowa has demonstrated the potential advantages of bioaugmenting Fe^0 barriers for the removal of a wide variety of redox-sensitive contaminants. Results also indicate that performance of these barriers might be enhanced by the participation of indigenous microbes. The effects of these biogeochemical interactions on the long-term performance of PRB systems remains to be determined.

For additional information about the University of Iowa studies on bioaugmentation of Fe^0 PRB systems, contact Gene Parkin, Ph.D, P.E. at (319) 335-5655. References used to prepare this article are listed on the CLU-IN website at www.clu-in.org/pub1.htm.

Well-Head Monitoring Technology Verification

by Eric Koglin, U.S. EPA National Exposure Research Laboratory, and Dan Powell, U.S. EPA Technology Innovation Office

Five well-head monitoring technologies for measuring volatile organic compounds (VOCs) in water have been tested over the past four years under the U.S. EPA's Site Characterization and Monitoring Technologies (SCMT) Pilot. The SCMT Pilot is one of 12 Environmental Technology Verification (ETV) programs designed to verify the performance of commercial-ready environmental technologies.

For these tests, EPA partnered with the U.S. Department of Energy's (DOE's) Sandia National Laboratories to demonstrate the well-head monitoring technologies at DOE's Savannah River Site (SRS) near Aiken, SC, and McClellan Air Force Base near Sacramento, CA.

Three technologies based on gas chromatography were tested:

- Electronic Sensor Technology's surface acoustic wave detector (EST Model 4100),
- Sentex Systems, Inc.'s microargon ionization and electron capture detector (Sentograph Plus II), and
- Perkin-Elmer Photovac's dual capture photoionization and electron capture detector (Voyager).

The demonstration included one technology based on gas chromatography/mass spectrometry:

- Inficon, Inc.'s gas quadrupole mass spectrometer (HAPSITE).

In addition, a single technology based on photoacoustic infrared monitoring was tested:

- Innova AirTech Instruments' pressure wave (sound) detector (Innova Type 1312 Multi-Gas Monitor).

For each technology, performance indicators such as correlation coefficients, false positives, false negatives, and sample throughput were evaluated. This information is tabulated below.

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Complete verification reports for these technologies are available through the ETV Web site at www.epa.gov/etv.

Under the SCMT Pilot, a total of 29 innovative technologies have been tested and verified. For more information, contact Eric Koglin (EPA/National Exposure Research Laboratory) at 702-798-2432 or e-mail koglin.eric@epa.gov, or Dan Powell (EPA/Technology Innovation Office) at 703-603-7196 or e-mail powell.dan@epa.gov; or visit the Internet at www.epa.gov/etv.

Highlights of Well-Head Monitoring Technology Demonstration

Technology	Correlation Coefficient at SRS (greater than or equal to 100 *u*g/L)	False Positives for 16 Blank Samples/ Number of Calibrated Compounds	False Negatives/PE Samples at SRS (10 *u*g/L)	Sample Throughput (number of samples/hour)
EST Model 4100	0.969	0/31	6/10	2-3
Sentograph Plus II	0.907	0/19	1/8	2
Voyager	0.830	6/24	4/10	1-3
HAPSITE	0.996	8/38	5/11	2.5
Innova Type 1312	0.984	3/5	1/2	1-2

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