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Ground Water Currents

Developments in Innovative Ground Water Treatment

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About this Issue

This issue highlights field testing of innovative technologies for the cleanup and characterization of ground water contaminated with DNAPL. The field tests range from a large side-by-side demonstration of technnologies at Cape Canaveral, FL, to a smaller pilot study in Ogallala, NE. In addition, the use of acoustic crosswell tomography to produce permeability images of the subsurface, which can aid in locating DNAPL, is highlighted in this issue.

Interagency Demonstrations on DNAPL Conducted at Cape Canaveral

by Laymon Gray, Florida State University

The Interagency Dense Non Aqueous Phase Liquid (DNAPL) Consortium (IDC), a strategic alliance of several government agencies, was initiated in 1997. The IDC was formalized in 1999 through the signing of a memorandum of agreement between the participating agencies with the mission of demonstrating innovative DNAPL remediation and monitoring systems. Members of this Consortium include the U.S. Department of Energy (DOE)/Office of Science and Technology, U.S. EPA/National Risk Management Research Laboratory, National Aeronautics and Space Administration (NASA), U.S. Navy (NAVFAC), and U.S. Air Force/45th Space Wing. As part of this effort, the IDC is evaluating and comparing the cost and performance of three innovative DNAPL remediation technologies at a former Cape Canaveral, FL, launch site.

DNAPLs are a common cause of soil and ground-water contamination at DOE, NASA, and U.S. Department of Defense sites. At the Cape Canaveral site, the primary contaminant of concern is trichloroethylene (TCE), a solvent historically used for flushing rocket engines and the cleaning or degreasing of metal parts, electronics, and heavy machinery. An early snapshot of two of the technologies demonstrated thus far indicates that favorable alternatives exist for DNAPL remediation.

In side-by-side plots, this project demonstrates three innovative DNAPL remediation technologies: chemical oxidation using potassium permanganate (conducted by IT Corporation), Six Phase Heating™ (conducted by Current Environmental Solutions), and co-air steam injection (conducted by Integrated Water Resources, Inc.). Testing in a side-by-side setting allows the Consortium to evaluate the cost and performance of each technology under essentially identical site conditions. Each test cell used in this evaluation is approximately 50 by 75 feet in size, with a total depth extending to the underlying aquitard at 45 feet. Data gathered during the demonstrations will be used to expedite regulatory acceptance and use of the technologies at other federal and private sites.

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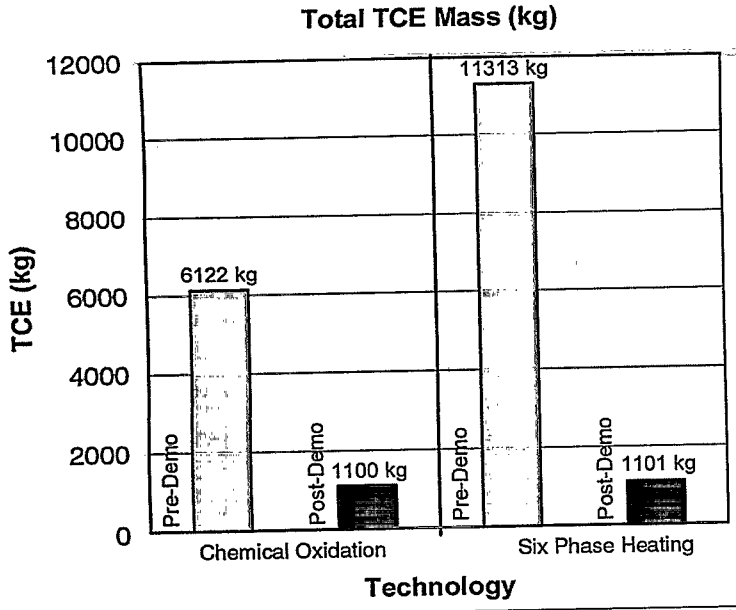
In Situ Chemical Oxidation with Potassium Permanganate

This in situ treatment technology uses potassium permanganate ($KMnO_4$) to destroy DNAPL through an oxidative reaction. The $KMnO_4$ reacts with the carbon-carbon double bonds found in chloroethenes to produce primarily carbon dioxide, chloride ions, and manganese dioxide as byproducts.

The oxidant was delivered using an array of injection wells with a lance approach, thereby allowing precise delivery to target depths within the treatment area. In September 1999, the first of three injection phases was initiated and the third (final) phase was completed in March 2000. Based on cores collected before and after implementation of this technology, an overall 82 percent reduction of TCE was achieved, with an 84 percent reduction of residual DNAPL saturation. Preliminary results are shown in Figure 1.

During operation of the system, high injection pressures were encountered. It was determined that the high pressure sand filter used to remove suspended solids from the permanganate solution was clogging, which resulted in the need for frequent backwashing of the filter system. To overcome this problem, the filter was replaced with a large settling tank that allowed for uninterrupted delivery of the oxidant to the subsurface. In addition, modifications were made to the permanganate storage system. The original design used an automated hopper system. This system proved to be ineffective, however, due to high moisture conditions at the site, which resulted in frequent maintenance and system shutdowns. The hopper system was replaced with portable bins that solved the humidity-related issues and resulted in a more efficient operation.

Figure 1. Pre- and Post-Demonstration Mass Estimates



In Situ Thermal Remediation with Six Phase Heating™

Six Phase Heating™ (SPH) uses an in situ electrical resistance heating technique with the potential to remove DNAPL by heating the subsurface sufficiently to vaporize the DNAPL. This technology can be applied to contamination in both the vadose and saturated zones. SPH typically heats the subsurface by using a hexagonal array of electrodes that are driven into the ground to the depth of the aquitard. The steam and chlorinated volatile organic compound vapors rise to the vadose zone, where they are recovered through vertical and/or horizontal vapor extraction wells. These vapors then are condensed, and the effluent air stream is discharged after polishing with activated carbon.

The SPH technology demonstration began in August 1999 and continued intermittently through July 2000. Based on cores collected before and after implementation, a 92 percent reduction of TCE was achieved, with a 96 percent reduction of residual DNAPL saturation. Preliminary results are shown in Figure 1.

It was discovered during operations that the system's monitoring wells were becoming pressurized, thus creating a significant health and safety concern for on-site personnel. To overcome this problem, the well heads were retrofitted with pressure gauges and off-gas pressure relief valves that were piped to the soil vapor extraction system. This modification allowed for the wells to be safely depressurized and ground-water samples to be safely collected without turning off the system.

Based on the heating profile observed

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anaerobes in utilizing the substrate, additional samples were collected and transferred to the Idaho National Engineering and Environmental Laboratory for analysis of volatile acid constituents.

Pilot observations found that initial concentrations of PCE flowing into the treatment cell may have been too low to allow for the detection of daughter products, once sulfate reducing and mild methanogenic conditions had developed and the microbes had become more efficient in lactate fermentation. After nine months of operation, a more concentrated slug of PCE had moved into the treatment cell area. Analytical results for samples collected as the slug moved through the cell indicated that PCE concentrations had decreased from 180 µg/l in the upgradient monitoring well to non-detect levels in the downgradient monitoring wells. During this time, both trichloroethylene (TCE) and *cis*-1,2-dichloroethylene (DCE) were detected within the treatment cell, with TCE decreasing and DCE increasing in the downgradient direction. Analytical results for the last round of samples collected from a monitoring well located 35 feet downgradient of the injection system indicated that both PCE and TCE concentrations had dropped to non-detect levels, and that the concentration of *cis*-1,2-DCE had decreased to 14 µg/l. Non-detection of vinyl chloride within the treatment cell area may indicate that degradation of the daughter products was incomplete, or that further degradation of *cis*-1,2-DCE occurred downgradient of the test cell area.

The "geochemically challenged" ground-water conditions, coupled with the relatively high average linear ground-water velocity, initially suggested that achieving the appropriate reducing environment to support lactate fermentation and PCE biodegradation would be difficult at this site, at best. Data suggested that the indigenous microbial population of nitrate and sulfate reducers was small, and that acclimation to the lactate during the first several months of operation was slow. Adjustments in the amount and frequency of lactate injection were required to overcome carbon limitations and eliminate the relatively high concentrations of inorganic electron acceptors. In general, it was found that approximately three months were required for nitrate-reducing conditions to develop.

The increased frequency and amount of lactate injection appeared to have a pronounced effect four months into the study, when sulfate-reducing conditions began to develop. At six months into the study, methane and volatile acids were clearly detected, and the microbial community was found to be capable of degrading PCE and TCE. Although vinyl chloride was not detected, it is possible that bioaugmentation or a return to aerobic conditions may be required to complete the degradation process. While initial geochemical conditions suggested that this technology may not be feasible at the Ogallala site, the results of this pilot study suggest otherwise. For more information, contact Vicki Murt (U.S. Corps of Engineers) at 816-983-3889 or e-mail vicki.l.murt@usace.army.mil.

Imaging Permeability Structure through Acoustic Crosswell Tomography

by Tokuo Yamamoto, Ph.D., Hua Sun, and Junichi Sakakibara, University of Miami/Geoacoustics Laboratory and Paul E. Mattausch, Collier County, Florida/Water Department

Researchers at the University of Miami's Geoacoustics Laboratory have developed new techniques for using high-resolution images to track ground-water movement in shallow and deep sediments. By analytically inverting acoustic wave velocity and attenuation fields that have been measured through acoustic tomography, the permeability, porosity, and shear strength of a site may be obtained. Earlier studies have found that other crosswell methods are capable of producing porosity, but not permeability, images. Acoustical images developed with these new techniques have shown high correlation with data obtained through conventional, and more resource-intensive, pumping methods.

In partnership with Kawasaki Steel Corporation of Tokyo, Japan, this technology has been used to characterize aquifers subjected to contamination from nearby sources and by salt water intrusion. Acoustic tomography can be used to produce permeability images of a wide range of geologic materials, including near-surface sediments, andesite, limestone, tuff, and shallow water sea-bottom, and complex contaminant scenarios such as dense non aqueous phase liquids.

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Acoustic wave velocity and attenuation fields typically are measured by covering the area of interest between two wells with acoustic wave fields. These fields are measured by locating a pieso-electric source in one well and an array of hydrophone receivers in another, and then moving the source and receivers repeatedly in a vertical fashion. The sources are activated to generate a continuous pseudo-random binary sequence (PRBS) to ensure a maximum signal-to-noise ratio. Using various tomography systems capable of imaging target areas at different ranges and depths of up to 12,000 feet, numerous acoustic images at frequencies of 200 to 30,000 Hz can be taken.

At a deep limestone aquifer site in Collier County, FL, permeability images were produced to provide the South Florida Water Management District with a better understanding of contaminant dispersion in the area. The permeability model developed with PRBS data taken from field measurements was found to correlate highly with the results of pumping tests conducted at the site. Overall, the error between acoustically imaged permeability and pump tests is estimated to be within 50 percent, and the errors for porosity to be within 10 percent.

Use of this technique at the Collier County site provided a single, continuous measure at a cost of approximately $100,000. In contrast, researchers estimate that total permeability estimates obtained through use of traditional pumping tests would have required testing at several locations, and cost as much as $200,000 per pumping point. Additionally, it is estimated that conventional pumping tests would have required approximately one month to obtain 100-foot deep permeability estimates, while a 1,800-foot tomographic image could be obtained in a single day in the field.

In addition to providing analytical results within as little as 48 hours, this technology avoids the testing problems and potential data inaccuracies involved when using sandy samples to measure porosity and permeability in the laboratory. Two- and three-dimensional images interpreted in this way have provided more accurate modeling of contaminant dispersion at other sites in complex geophysical settings, including military and air transportation facilities located in coastal areas of the U.S. and Japan. The approach used in this (patented) technology has been approved by Kawasaki Steel Corporation for widespread use by cleanup contractors at contaminated ground-water sites in the U.S. For more information, contact Dr. Tokuo Yamamoto (University of Miami) at 305-361-4637 or e-mail tyamamoto@rsmas.miami.edu.

Clarification

The passive barrier described in the article "Iron Reactive Barrier Used as Rocky Flats Site" in the April 2001 issue of *Ground Water Currents* was designed and installed by the U.S. Army Corps of Engineers, Omaha District.

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supported anaerobes capable of successfully dechlorinating the PCE. EPA currently is evaluating the pilot study to determine whether full-scale application of this technology will be implemented.

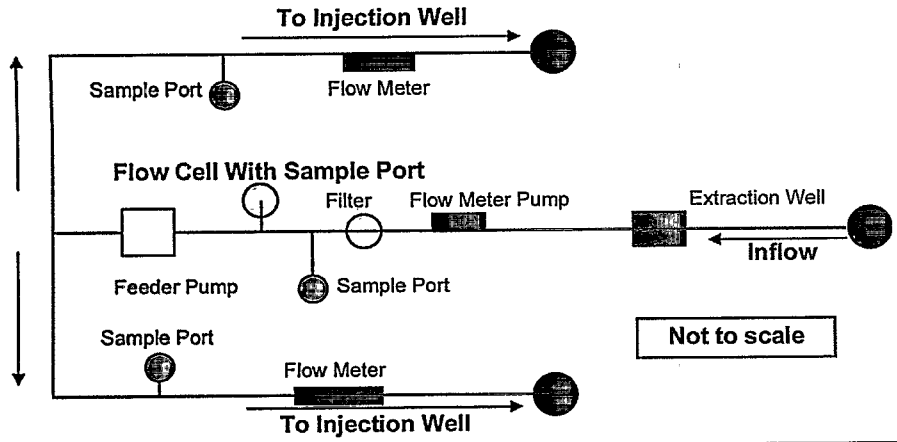
The Ogallala Ground Water Contamination Site was placed on the NPL in 1994 after five municipal drinking water wells were found to be affected by contaminants from multiple sources, including PCE from a nearby dry cleaning operation. During earlier site investigations, the area's shallow, unconfined alluvial aquifer was found to contain PCE concentrations ranging from 0.78 µg/l to 1,400 µg/l. The aquifer in the pilot study area consists of fine- to medium-grained sand overlying channel deposits of coarse sands, gravels, and cobbles to a depth of 26 feet below ground surface. The Ogallala Aquifer lies beneath this shallow alluvial aquifer. Depth to ground water is typically 11 feet, with seasonal fluctuations of up to 2 feet. The horizontal gradient is approximately 0.002 feet/foot and ground water flows at an average linear velocity of 3-3.5 feet/day.

The 12- by 35-foot in situ treatment cell was located 800 feet downgradient of the dry cleaning facility. The semi-passive extraction/injection system consisted of one extraction well, two injection wells, and six sets of nested monitoring micro-wells. The extraction/injection wells were aligned perpendicular to ground-water flow, with the extraction well centered between the two injection wells (Figure 2). During operation of the system, extracted ground water was pumped at a rate of 10-12 gallons/minute through a closed-loop system to minimize aeration of the water. The filtered ground water was amended in-line with a solution containing 60 percent food-grade sodium lactate to supply indigenous microorganisms with a fermentable organic food source, and then injected back into the aquifer. The ground water was recirculated for 7-8 hours after the lactate addition until equilibration had been achieved. Extracted ground water was monitored for conductivity as an indicator of the amount of lactate saturation and degree of equilibration during the recirculation process.

After the system was shut down, the substrate solution was transported away from the injection system under natural ground-water gradient conditions. This type of system promoted passive dispersive mixing that enhanced substrate delivery to the microbes in a continuous supply as it flowed downgradient with the contaminated water. It was found that pulsed injection of the lactate did not result in biofouling of the injection well screen interval. Initially, 40 kg of lactate was injected every four weeks, but these rates were increased to 75 kg and then 100 kg every three weeks to sustain the developing anaerobic microbial population as reducing conditions continued to develop.

Several monitoring strategies were employed throughout the pilot project. Field chemistry measurements were collected using various portable instruments to measure pH, conductivity, dissolved oxygen, and oxidation-reduction potential. During initial stages, the results of weekly sampling and analysis for potassium bromide, a geochemical tracer, and total organic carbon were used to adjust the frequency and amount of injected lactate. Analyses for nitrate and sulfate were performed periodically to monitor the development of nitrate and sulfate reducing conditions. (By the fourth month, a discernible odor of hydrogen sulfide was noted in most of the wells throughout the cell, indicating that sulfate reduction was occurring). Methane, ethene, and ethane analyses also were performed periodically to determine if methanogenic conditions were present within the treatment cell, and whether complete degradation of the daughter products was occurring. To monitor the efficiency of the

Figure 2. Schematic Diagram of Injection System



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during system operation, it was determined that the original electrode design was ineffective. As a result, the electrodes were redesigned and the predicted heating profiles were achieved. It was found that the electrode design for this technology is critical, and will vary depending on site-specific conditions. Continued research and development should enhance the performance of this system and its application at others sites, and potentially reduce electricity costs for SPH.

In Situ Thermal Remediation with Steam and Co-Air Injection

An alternative thermal treatment technology uses steam injection and extraction to remove DNAPL from the subsurface. DNAPLs such as TCE with a boiling point below that of water are removed by a combination of volatilization, steam stripping, and oxidation. Introduction of heat to the subsurface produces a wide variety of physical and chemical effects that are beneficial for the breakdown or removal of DNAPL contaminants in both saturated and unsaturated subsurface materials, including:

- Increased mobility, volatility, and diffusion rates
- Distillation, and
- Hydrous pyrolysis and oxidation.

The steam stripping system uses boilers to generate steam that is pumped into injection wells within the treatment zone. The resulting steam front volatilizes and mobilizes the contaminants as it moves toward a network of vertical and/or horizontal vapor extraction wells.

The thermal treatment system in this demonstration was designed to include the co-injection of air. This injected air combines with steam to create a broader thermal front containing a larger volume of air saturated with contaminant, therefore inhibiting condensation of the contaminant and reformation of NAPL. An extended thermal front is produced, creating a larger volume within which the contaminants can be held in vapor phase. The air/steam mixture reduces injection temperatures in the subsurface, and the co-injected air simultaneously increases the carrying capacity of contaminant in vapor. The optimal ratio of air to steam is based on the expected concentration of contaminant and its known vapor pressure. Implementation of this technology is scheduled to begin in June 2001.

Following completion of this thermal treatment technology demonstration, final cost and performance evaluations will be completed for all three technologies. In addition to evaluating the contaminant removal efficiencies, the IDC is evaluating the effects of these technologies on indigenous microbial communities and the long-term impacts of application.

Several innovative sensors for site characterization also have been deployed at the Cape Canaveral site, using DOE's Site Characterization and Analysis Penetrometer System (SCAPS). These sensors are used for lithologic mapping, in situ vadose zone and saturated zone sampling, in situ hydraulic conductivity measurements, and the determination of subsurface DNAPL locations. Detailed reports concerning each aspect of the project can be found at the IDC's Web site, www.getf.org/dnaplguest. For more information, contact Laymon Gray (Florida State University, Institute for International Cooperative Environmental Research) at 850-644-5524 or e-mail lgray@ispa.fsu.edu.

Enhanced Reductive Dechlorination Pilot Study Completed

by Vicki Murt, U.S. Corps of Engineers (formerly with Nebraska Department of Environmental Quality)

The Nebraska Department of Environmental Quality recently completed a pilot study on the potential for achieving reductive dechlorination of perchloroethylene (PCE) under "geochemically challenged" conditions of the Ogallala Ground Water Contamination (Superfund) Site in Ogallala, NE. Treatment of PCE-contaminated ground water in the pilot study consisted of substrate injection into the plume downgradient of a dry cleaning facility over a period of one year. This project required significant changes to the geochemical environment of the in situ treatment cell in order to promote sufficient microbial growth under anaerobic conditions. Initial geochemical conditions indicated that the shallow alluvial aquifer was highly oxygenated; dissolved oxygen was measured at 3.9 mg/l, and elevated levels of nitrate (11 mg/l) and sulfate (135 mg/l) also were present. In addition, limited funding (approximately $135,000) required completion of the project without the benefit of a full-scale microbial analysis. Despite these challenges, the final pilot study results indicated the achievement of appropriate reducing conditions that

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