



TECHNOLOGY

NEWS AND TRENDS

A newsletter about soil, sediment, and ground-water characterization and remediation technologies

Issue 21

November 2005

Zero-Valent Iron PRB Application Expands to Arsenic Removal

The U.S. EPA Office of Research and Development's National Risk Management Research Laboratory (NRMRL) and Region 8 have begun evaluating the performance of a pilot-scale permeable reactive barrier (PRB) to treat arsenic-contaminated ground water at the East Helena Superfund site near Helena, MT. High ground-water flow rates coupled with high arsenic concentrations required the barrier design to involve wider dimensions in the path of ground-water flow than most PRBs currently in operation. Barrier construction also was challenged by the presence of some boulders in the subsurface, requiring use of large excavation equipment. Preliminary results indicate that arsenic concentrations as high as 20 mg/L in ground water entering the PRB are reduced to concentrations below 10 µg/L within the barrier. Concentration reductions downgradient of the PRB are anticipated after construction impacts on the treatment system subside and the ambient ground-water flow system is re-established.

Primarily due to smelting activities over the past century, arsenic in ground water at the East Helena site exists in the redox states of arsenite (As^{3+}) and arsenate (As^{5+}). The target arsenic plume is approximately 450 feet wide and extends 2,100 feet downgradient from the primary source of subsurface contamination. The site is underlain by alluvial deposits of cobble mixed with varying proportions of fine-to coarse-grained sand to a depth of 48 feet below ground surface (bgs). The water table is 30 feet bgs. Only ground water within the the alluvial deposits and not the underlying volcanic tuff was found to be contaminated. Ground-water flow varies from about 0.5 to 3.0 ft/day according to the hydraulic properties of the aquifer materials and the prevailing hydraulic gradient.

NRMRL conducted batch and column studies on simulated ground water in 2003 to assess the effectiveness of zero-valent iron (ZVI) for arsenic remediation, determine arsenic removal mechanisms, and evaluate potential use of a ZVI barrier in long-term remediation of arsenic-contaminated ground water. Prior to these studies, ZVI was used more commonly to treat metals and halogenated organic solvents. Study results showed that arsenic removal is a two-step reaction with an initially rapid removal of arsenite (10-fold within 50 hours) followed by a slow removal process that involves formation of smaller amounts of As^{5+} . Additionally, analysis of surface precipitates indicated that As^{3+} uptake by carbonate green rust and other iron-corrosion products may play a major role in the treatment process. The overall removal capacity of ZVI was estimated at 7.5 mg arsenic/g iron.

Installation of the PRB was completed over five days earlier this spring. Heavy excavation equipment was used to construct a 6-foot-wide and 46-foot-deep trench running 30 feet in length perpendicular to the plume (Figure 1). During excavation, biopolymer slurry was used to stabilize the walls of the trench. Approximately 175 tons of ZVI filings were added to the trench through the biopolymer slurry using tremie equipment to achieve an (upper) depth of 25 feet bgs, 5 feet higher than the average ground-water level. The remainder of the trench was filled with coarse bedding sand.

A network of fully screened, short-screen, and multi-level wells, including 25 within the trench itself, will be used to monitor performance of the PRB. In addition, an in-situ flow sensor was installed to collect information on ground-

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CLU-IN Resources

The State Coalition for Remediation of Drycleaners has compiled detailed technical profiles on remediation projects underway or completed at more than 100 sites throughout the U.S. The profiles are available online, along with related information on federal policies, state drycleaner programs, and technical reports, through CLU-IN's "Initiatives and Partnerships" at <http://www.cluin.org> or directly from the coalition at <http://drycleancoalition.org>.

Figure 1. Construction of the extensive PRB trench at the East Helena site required use of a 50-foot-high excavator equipped with a long-reach arm and a 3-foot-wide bucket.

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water flow direction and velocity within the PRB. The first round of monitoring occurred in June 2005, 30 days after treatment began. Results showed arsenic concentrations below 10 µg/L in ground water within the barrier. Analysis of ground water within the PRB showed expected trends in pH, oxidation-reduction potential, and ferrous iron concentrations typical for ZVI systems.

Data analysis is underway for the second round of monitoring, which was conducted last month. Evaluation of the pilot-scale PRB will continue for two years to determine its long-term success in reducing arsenic concentrations to levels near the maximum contaminant level (MCL) of 10 µg/L. If successful, the PRB could be extended an



additional 450 feet in length to capture 100% of the arsenic plume. The pilot project shows that the full-scale system likely should employ variable PRB thicknesses to effectively deal with variable arsenic concentrations across the plume width. Region 8 estimates a construction cost of \$325,000 for the existing pilot-scale system.

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EPA Evaluates Approaches for Assessment of Vapor Intrusion

The U.S. EPA Office of Solid Waste and Emergency Response developed guidelines in 2002 for screening the migration of volatile organic compounds (VOCs) from the subsurface into buildings, otherwise known as “vapor intrusion” (VI). The guidance applies to sites where halogenated organic compounds constitute the primary risk to human health. To supplement the guidance recommendations, EPA currently is evaluating empirical methods that provide increased reliability in VI data quality at a reasonable cost and which address bias caused by non-environmental anthropogenic conditions.

To assess VI empirically, EPA’s Office of Research and Development (ORD) recommends concurrent use of sub-slab sampling and indoor air sampling. This combined approach helps to differentiate VOCs potentially originating from environmental sources from those originating from non-environmental sources such as

gasoline, paint, or solvents stored inside buildings. Sub-slab air sampling allows for sample collection directly beneath living spaces, thereby eliminating uncertainty posed by the analysis of data collected from distant monitoring locations. Sub-slab sampling also helps to determine whether, and to what extent, petroleum hydrocarbon biodegradation may be occurring onsite.

In the absence of standardized methods for collecting or interpreting sub-slab air samples, ORD and Region 1 used the sub-slab approach to assess VI at 15 homes and one commercial business near the Raymark Industries Superfund site in Stratford, CT. Elevated VOC concentrations in basement air were determined to be caused by VI if: (1) a VOC was detected in ground-water or soil-gas measurements taken in the building’s vicinity; and (2) the results of statistical testing on empirical sub-slab and indoor-air data indicated VI was the cause of VOC presence. Basement and sub-

slab air samples were collected at each of the study locations through use of evacuated canisters in accordance with EPA Method TO-15, *Determination of VOCs in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry*. Additional sub-slab air samples were collected using one-liter Tedlar bags.

Statistical testing required the use of an “indicator” VOC known to be associated only with subsurface contamination. In this case, 1,1-dichloroethene (DCE) and 1,1-dichloroethane (DCA) were considered indicator VOCs due to the presence of their degradation daughter product, 1,1,1-trichloroethane (TCA). *Cis*-1,2-DCE also was considered an indicator due to its presence as a daughter product of trichloroethene (TCE) and its unlikely association with commercial products. Statistical testing involved

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comparing each basement/sub-slab concentration ratio of an indicator VOC with that of a VOC of concern. Statistical testing found that detection of 1,1-DCE, 1,1-DCA, and *cis*-1,2-DCE in indoor air consistently was caused by VI, but the presence of TCA occasionally generated false positives and negatives.

The use of radon as an indicator compound was evaluated by statistically comparing basement or sub-slab concentration ratios for radon against indicator VOCs at six of the Raymark locations. Comparisons exhibited statistical similarities at half of the locations but varied at a level of significance less than 0.1 at the remaining locations. Based on these findings, indicator VOCs were relied upon when basement/sub-slab concentration ratios for both types of indicators were available, and radon ratios were used only in the absence of indicator VOCs. Indoor air radon sampling was conducted in accordance with EPA's *Home Buyer's and Seller's Guide to Radon* [EPA-402-R-003].

A significant objective of the Raymark study was to document the installation and sampling of 3-5 vapor probes in each of the 16 basements. Generally, one sub-slab vapor probe was positioned in the center of each building while two or more probes were placed within 1-2 meters of the basement walls (Figure 2). Among other benefits, this arrangement helped to ensure detection of vacuum

throughout the entire sub-slab for implementation of corrective measures (sub-slab depressurization). In addition, spatial variability of sub-slab concentrations of VOCs and radon was noted across each building's footprint.

In assessing efficacy of the sub-slab protocol, ORD considered factors such as rate-limited mass transport during air extraction, the radius of perturbation during probe installation, and the impact of indoor air infiltration into a sample container during air extraction. Using three methods to evaluate the impact of indoor air infiltration, for example, the extraction volume was found to have little effect on sampling results.

Based on the Raymark study results and other recent findings, ORD is developing specific recommendations for sub-slab sample collection, data interpretation, and probe installation, including:

- ▶ Design of a multi-use sub-slab vapor probe that "floats" in a slab, which allows for air samples to be collected from sub-slab material that is in direct contact with a slab or from an air pocket directly beneath a slab;
- ▶ Use of a rotary hammer drill to create concrete slab holes for probe installation; and

- ▶ Sealing of a probe's annular space through use of quick-drying, lime-based cement that allows for installation of three probes within two hours.

A detailed summary of the study will be available from ORD and Region 1 in early 2006. EPA's earlier guidance, *OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance)* [EPA530-D-02-004] is available online at <http://www.epa.gov/epaoswer/hazwaste/ca/eis/vapor.htm>.

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Figure 2. Only a small hole in the concrete slab was needed to install a multi-use vapor probe in each basement of the Raymark study.

Tree-Core Analysis Brings Savings to Site Assessments

The U.S. Geological Survey (USGS) collaborated with University of Missouri-Rolla researchers during the past several years in using tree-core samples to quickly assess VOC presence in shallow soil and ground water (20-25 bgs) at the Riverfront Superfund site in New Haven, MO. Unlike previous applications of tree-core sampling, little subsurface data previously existed at this site- and tree-core sampling was the primary tool for initial site assessment. Conventional soil and ground-water sample analysis later confirmed the results of tree-

core analysis, which suggested the presence of subsurface VOC contamination in a 600-by-200-foot area at operable unit 1 (OUI) known as the "Front Street site" in downtown New Haven. The site is one of five potential tetrachloroethene (PCE) source areas in New Haven under investigation by the U.S. EPA.

The 1-acre Front Street site is located in alluvial deposits approximately 400 feet south of the Missouri River, a regional ground-water discharge zone. In the late 1980s and early 1990s, steadily increasing concentrations of

PCE were measured in water from two 800-foot-deep municipal drinking water wells serving the New Haven community. One of the wells, Well 2, was taken out of service in 1993 after PCE concentrations reached 140 mg/L, substantially above the 5 mg/L MCL. Water from a new well installed the following year about 1.5 miles farther south and upgradient from the contaminated wells showed no signs of PCE contamination. During an expanded site investigation in 1995, the Front Street

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site was presumed to be the source of PCE contamination because of its location only 600 feet north of Well 2. Bedrock monitoring wells installed throughout the city as part of a remedial investigation in 2000, however, showed relatively low (less than 20 mg/L) PCE concentrations between the Front Street site and the contaminated public supply wells.

During the USGS site assessment, core samples generally were collected from trees with diameters of three inches or more. If multiple species were present, preference was given to rapid-growing species with deep root systems such as mulberry, poplar, and cottonwood. Samples were collected at a height of approximately three feet above ground surface using a 0.169- by 6-inch-long increment borer. The samples were placed immediately into standard 40-mL VOC vials and allowed to equilibrate overnight at room temperature. Headspace in the vials was analyzed the following day for VOC content using a portable gas chromatograph. Over a course of five years, core samples were collected from more than 70 trees and from apples of trees located on or adjacent to the Front Street site.

Onsite tree-core samples contained PCE and TCE concentrations reaching 3,850 mg-h/kg (micrograms in headspace per kilogram of wet core) and 249 mg-h/kg, respectively. In addition, offsite tree-core analyses detected subsurface PCE contamination on downgradient residential properties between the site and the river. Conventional sample analysis later confirmed the presence of PCE

at the site with concentrations as large as 6,200,000 mg/kg in soil and 11,000 mg/L in ground water. Tree-core analysis indicated no detectable PCE or TCE contamination at a nearby former dry cleaning facility under investigation as a potential contaminant source, and these findings were confirmed by later soil sampling.

PCE generally was detected in cores from trees growing in soil containing PCE concentrations of 60 to 5,700 mg/kg or overlying ground water containing PCE concentrations ranging from 5 to 11,000 mg/L. The lateral extent of PCE contamination suggested by tree-core analysis closely agreed with the results obtained by conventional soil sampling techniques. A correlation coefficient (r^2) of 0.88 was found between PCE concentration in trees and PCE in subsurface soil at depths of 4 feet (Figure 3) and similar correlations were found for soil up to 12 feet deep. The correlation between PCE concentrations in trees and ground water was much lower (0.17). Researchers attribute the low correlation to a lack of direct contact between tree roots and ground water or to non-equilibrium between tree roots and PCE concentrations in soil and soil vapor. These results show that the presence of contaminants in a tree core likely indicates onsite contamination but that the absence of tree-core contaminants does not preclude the need for further evaluation.

Several variables were found to affect the distribution of VOCs in trees. The loss of PCE from tree trunks by diffusion usually resulted in an exponential decrease in contaminant concentrations with increasing tree height. In addition, diffusional loss in small trees (0.5-inch-

diameter cuttings planted in contaminated soil) occurred at a rate 10-fold higher than in trees with a diameter of 6.5 inches. Up to five-fold variations in PCE concentrations around individual tree trunks were attributed to spatial differences in contaminant concentrations in the soil, the natural twisting of tree trunks, and possible diffusion of PCE vapors from the unsaturated zone into tree roots. Comparison of PCE concentrations in core and sap samples confirmed laboratory sorption studies indicating that more than 95% of the PCE and TCE mass resided in wood rather than the transpiration stream.

Ongoing investigations indicated that samples from bedrock monitoring wells located between the contaminated public supply wells and an area farther south (at what would become another operable unit, OU4) contained unexpectedly high concentrations of PCE reaching 350 mg/L at a depth of 465 feet bgs. Reconnaissance sampling of trees across OU4 during 2004-2005 identified a new and substantial PCE source area upgradient from the contaminated public supply wells.

Results from OUI indicate that tree-core sampling can be used to detect subsurface PCE contamination in soil at levels of several hundred mg/kg or less. Experimental data from hydroponic field tests, in which trees were grown in nutrient solution rather than soil, suggest that this approach may be able to identify PCE in ground water at concentrations as low as 8 mg/L. Additional experiments on trees growing adjacent to contaminated creeks at the Riverfront Superfund site found that the method could identify PCE in ground water at similarly low concentrations of 30 mg/L, as long as the tree roots are in direct contact with the

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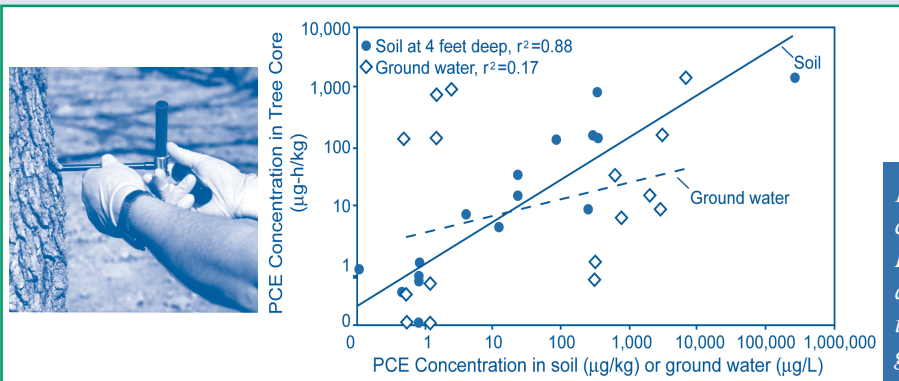


Figure 3. Correlation analysis of data collected from individual trees at the Front Street site indicates that tree cores accurately predicted PCE concentrations in the soil but only loosely predicted ground-water concentrations.

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contaminated ground water and the unsaturated zone is virtually non-existent. Otherwise, as the depth to ground water increases, this sensitivity will decrease with diffusional loss in the unstaturated zone.

Overall, data collected from the site demonstrate that tree-core sampling is an effective, quick, and inexpensive method for determining relative high and low concentrations of chlorinated solvents and for optimizing both soil and ground-water sample locations. The project also showed that tree-core sampling serves as a valuable tool for soil screening in residential settings, which typically involve sensitivities regarding

private property access and difficult sampling areas.

The initial tree-coring reconnaissance at the Front Street site, which employed 26 trees, required the resources of two field staff for one day at a cost of less than \$2,500. In contrast, the estimated cost for the collection and analysis of soil samples from an equivalent number of soil borings at the site is \$25,000 and requires two field staff for four days and a direct-push drill rig for several days.

EPA Region 7's use of this novel technique for site assessment, in addition to innovative strategies for remediation and property re-use, merited the Agency's 2003 "ROD of the Year Award." The complete scientific investigations

report [USGS SIR 2004-5049] on this application is available online from the USGS at <http://pubs.er.usgs.gov/pubs/>. Detailed methods for using tree-core analysis in site assessment are under development by the U.S. Department of Agriculture, which pioneered this approach. The methods will be incorporated into an upcoming U.S. EPA user's guide.

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Cleanup Closure Reached through In-Situ Bioremediation of Ground Water at Drycleaner Site

The Florida Department of Environmental Protection (FDEP) is working with the State Coalition for Remediation of Dry Cleaners and private industry to exchange drycleaner-specific information that will help expedite assessment and cleanup at drycleaner facilities. As part of the Florida Drycleaning Cleanup Program, the FDEP recently oversaw assessment and remediation at King of Cleaners, an operating facility in Orlando, FL.

The site's ground water contained low concentrations of PCE, TCE, and *cis*-1,2-DCE, as is common at many drycleaning sites. Monitored natural attenuation was selected as a remediation strategy in 1998. After five years of monitoring, however, one well continued to exhibit concentrations exceeding MCLs. In-situ bioremediation consequently was used to increase reductive dechlorination of chlorinated organics through the introduction of potassium lactate as a carbon donor in the aquifer.

During initial site assessments, PCE and TCE were detected in monitoring wells at concentrations of 220 µg/L and 43 µg/L, respectively. *Cis*-1,2-DCE also was detected but at concentrations below the 70 µg/L MCL. In addition, direct-push sampling indicated a low concentration (7.8 µg/L) of vinyl chloride

in ground water. PCE was detected in soil at concentrations averaging 170 µg/kg, but testing indicated that concentrations did not exceed the state's leachability criteria. The water table is located 6-10 feet bgs within a 46-ft layer of silty, fine- to medium-grained sand. The ground-water flow rate ranges from approximately 1 to 24 ft/day within a gradient of 0.01 ft/ft.

Bioremediation of the 150- by 100-ft ground-water plume began in October 2003. Two 2-inch-diameter wells screened at depths of 33-43 feet were installed for the injection process, which was monitored using three existing wells. Approximately 2,000 gallons of native water were extracted from a monitoring well to help establish a gradient between the injection wells and the downgradient monitoring well, and mixed with 10 gallons of 60% potassium lactate to enhance reductive dechlorination. The solution was injected into each of the injection wells at a rate of 1.5 gpm. The event concluded with injection of 100-200 gallons of potable water to remove residual lactate and prevent biofouling.

Two months of performance monitoring showed no major changes in VOC concentrations, which remained above target

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Studies Show That ...



An estimated 20,000 drycleaners are contaminated across the country. Based on an average cleanup cost of \$250,000 per site, \$5 billion is needed to address these sites.

Source: Drycleaner Site Assessment & Remediation: A Technology Snapshot (March 2004)

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Solid Waste and
Emergency Response
(5102G)

EPA 542-N-05-006
November 2005
Issue No. 21

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levels. Therefore, a second injection was conducted in February 2004, again employing 2,000 gallons of water and a 1.5-gpm injection rate but a larger volume of 60% potassium lactate solution (50 gallons).

Approximately one month later, a significant decrease in contaminant concentrations was achieved. PCE and TCE concentrations had decreased to non-detect and 4 µg/L, respectively. As a degradation product, *cis*-1,2-DCE concentrations had increased 80% but were not above the 70 µg/L MCL. Data

collected during the earlier natural attenuation monitoring period had indicated that conversion of *cis*-1,2-DCE to vinyl chloride was unlikely, and in fact, no vinyl chloride was detected in any of the monitoring wells during post-remediation monitoring. Gradual but continued decreases in VOC concentrations resulted in a February 2005 determination that no further remedial action was required.

The FDEP estimates a total cleanup cost of \$168,400 for the King of Cleaners site, including \$81,000 for assessment, \$3,400 for design of the limited remedial action plan, \$34,400 for the

injection well installations and two injection events, \$4,200 for site restoration, and \$45,400 for six years of ground-water monitoring. Additional technical profiles describing cleanup at other drycleaning sites are available from the coalition at www.drycleancoalition.org.

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Recent Workshop Increases Understanding of Environmental Impacts from Nanotechnologies

The U.S. EPA's Office of Solid Waste and Emergency Response and Office of Research and Development partnered with the Federal Remediation Technologies Roundtable (FRTR) and the U.S. Department of Commerce in sponsoring a *Workshop on Nanotechnology for Site Remediation* on October 20-21, 2005, in Washington, D.C. Presentation and breakout session topics addressed:

- ▶ Findings of recent studies using nanomaterials for contaminant destruction or sequestration,
- ▶ Results of field tests using nanoscale ZVI for reduction of VOC contamination in ground water,
- ▶ Use of dendrimers, functionalized nano-porous ceramic particles, and zeolites for contaminant reduction, and
- ▶ Research needs, research barriers, and incentives involved in using new nanotechnologies while minimizing environmental pollutants.

The workshop presentations and summary proceedings will be available online from the FRTR at <http://www.frtr.gov/hotnew.htm>.