UNITED STATES • ENVIRONMENTAL PROTECTION AGENCY

TECHNOLOGY NEWS AND TRENDS

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

Issue 31 **July 2007**

This issue of Technology News and Trends (TNT) *looks back to find lessons learned from site characterization and remediation projects described in earlier issues of the newsletter. These site-specific updates encompass expanded field operations, the results of longer-term monitoring, techniques for system integration, and recent research on technical focus areas of the U.S. EPA's Office of Superfund Remediation and Technology Innovation.*

Contents

ART System Performance Enhanced by Effective Site Assessment

The U.S. EPA's Region 7 office has used analytical data from small-diameter tree cores over the past eight years to identify shallow areas of soil and ground water with volatile organic compounds (VOCs) at the Riverfront Superfund site, located along the Missouri River in New Haven, MO. As an initial site assessment technique, tree-core analysis continues to significantly reduce the extent of analytical sampling (and associated costs) needed to identify contaminant source areas at the Riverfront site and to facilitate cleanup design and implementation. Success of this simple and inexpensitve tool was demonstrated in 2004 at the site's operable unit 1 (OU1), where a tetrachloroethene (PCE) plume and source area in soil were discovered through tree coring and subsequently confirmed by traditional soil and ground-water sample analysis [November 2005 *TNT*].

In early 2005, results from the OU1 tree-coring analysis were used with portable gas-chromatograph (GC) analysis of soil borings to guide placement of an advanced remediation technology (ART) well for treating a vadose-zone hotspot adjacent to the river. An ART well provides the opportunity for treatment-system optimization by operating as a combined soil vapor extraction (SVE)/in-well aeration well using a single, continuous screen. System optimization also was achieved by down-sizing the 5-horsepower (hp) compressor to a 3-hp unit, while retaining the 3-hp blower and 0.5-hp well pump originally anticipated for the ART system. This 2-hp reduction in the total energy demand resulted in a 25% reduction in energy costs for system operation. Monitoring over the past two years showed a rapid decrease in hotspot PCE concentrations, suggesting that the well-defined contaminant characterization effectively optimized treatment-well placement and, in turn, will minimize treatment duration and cost.

The ART system consists of a single 6-in. diameter, 30-ft.-deep well with a 25-gpm recirculation pump at the leading edge of the contaminant plume. A small building 70 feet away houses a 10 ft^3/min air sparging unit and a 100 ft^3/min vacuum blower. A trench between the well and equipment shed contains the compressed air and vacuum return lines and the well pump's power cable. The system removes contaminated vapor from both contaminated soil and stripped

[continued on page 2]

CLU-IN Resources

The U.S. EPA Science Policy Council formed a cross-Agency workgroup in 2004 to examine potential environmental applications and implications of nanotechnology. The workgroup's findings were published earlier this year in the *EPA Nanotechnology White Paper* (EPA 100/B-07/001), now available on CLU-IN (http://www.clu-in.org/download/remed/nanotechnology_white_paper.pdf).

[continued from page 1]

ground water at a rate 100 ft^3/min. Water-table mounding and associated negative gradients promote subsurface recirculation of ground water through the soil formation and the treatment well casing.

As an ongoing partner in large-scale remediation of the site, the U.S. Geological Survey (USGS) installed nine monitoring wells prior to system startup. An existing residential well at OU1 is used to monitor the northwest edge of the plume. Analytical results of ground-water and vapor sampling in March 2007 indicate that the ART system has removed more than 1,000 lbs. of subsurface contaminants, primarily PCE (Figure 1). Ground water near the treatment well, which treats a portion of the total source area, shows a 98% reduction in PCE concentrations and a 97% decrease in concentrations of PCE breakdown products such as *cis*-dicholoroethene. A monitoring well approximately 100 feet downgradient of the treatment well (2-3 years travel-time distant) demonstrated a 63% decrease in PCE concentrations.

Performance evaluation includes monitoring the system's tolerance to changes in ground-water and surface-water levels and the effectiveness of the selected screened intervals of the wells (12-44 below ground surface [bgs]). Air sparge turbulence in the treatment well casing prevents direct measurement of water levels in the treatment well. In addition, ground-water levels below 27 feet stop the ART well pump from operating, preventing collection of samples directly from the treatment well. Consequently, samples are collected from a deep piezometer. No signs of well screen clogging have been observed, and results suggest that treatment rates are relatively unaffected by changes in water table elevation. The ART pump portion of the remedy can operate with ground-water levels at least as low as 26.8 ft bgs, although with some reduction in capacity.

Comparison of results from multiple sampling events suggests that SVE-induced off-gassing and ground-water fluctuations likely caused the upward and downward variability in VOC concentrations displayed in some deep ground-water samples. Also, seasonal variations in the river's elevation and oxygen levels caused variations in analytical results from downgradient monitoring wells. One drum of activated carbon was used to treat system vapor until analytical sampling confirmed that emissions were below Missouri air standards.

Installation costs for the ART well, associated aboveground equipment, and monitoring wells totaled approximately $140,000. Project capital costs are estimated to be one-tenth of that for capping and sheet-pile containment of the source area, the least expensive alternative remedy.

Semi-annual sampling of the well network and treatment vapor, as well as annual sampling of selected locations of the river, will continue over the next three years. The remedy's five-year review in 2009 will include detailed analysis of the impact of water levels on the ART system's performance and on monitoring well results. Ground-water analyses indicate that 60-95 % of the PCE plume naturally degrades prior to entry into the Missouri River; travel time for OU1 ground water migrating to the river is estimated to be 12-17 years.

A time-critical removal involving in-situ chemical oxidation recently was initiated to treat contaminated soil and shallow ground water at Riverfront's OU4, a residential area where tree-coring analysis unexpectedly identified PCE-contaminated soil. Initial injections of sodium permanganate were completed in May, and a second round is scheduled to occur by early fall. More information on tree coring as a site characterization and remediation planning tool is available in EPA's new *User's Guide: Tree Coring to Examine Subsurface Volatile Organic Compounds*, available on CLU-IN (www.cluin.org).

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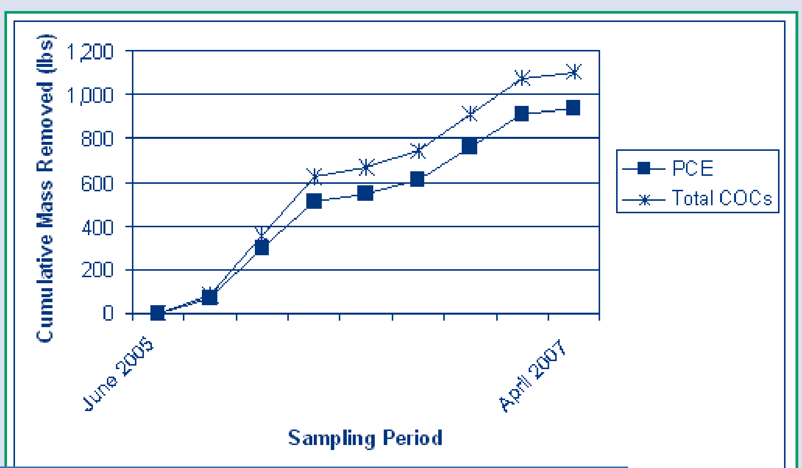

Figure 1. *To date, the Riverfront OU1 ART system has removed approximately 83% of the source-area VOCs.*

EPA Compares Three Soil-Gas Sampling Systems for Vapor Intrusion Investigations

EPA's National Risk Management Research Laboratory (NRMRL) recently completed a soil-gas sampling study in a VOC-contaminated residential area at the Raymark Superfund site in Stratford, CT. The study evaluated equivalence of three common sampling methods: traditional dedicated vapor probes, a truck-mounted direct-push Geoprobe® post-run-tubing (PRT) system, and the hand-held rotary-hammer AMS gas vapor probe (GVP) kit. The Raymark site earlier served as a study location for various techniques to assess VOC vapor intrusion into buildings, such as a combined sub-slab sampling and indoor air sampling approach (November 2005 *TNT*).

NRMRL's recent study focused on expanded use of quantitative data from direct-push/hammer systems for assessing potential exposure through vapor intrusion. Soil-gas samples traditionally are used for delineating ground-water and vadose-zone contamination rather than for evaluating cleanup actions or establishing cleanup goals.

Dedicated probes are considered the most reliable method for soil-gas sampling due to associated use of a bentonite layer for isolating a sand-packed screened interval. Recent increased use of direct-push/hammer soil-gas sampling techniques during vapor intrusion investigations is attributed to a greater convenience (ability to sample the same day as probing) and lower cost when compared to dedicated probe installations. Direct-push/hammer techniques also allow collection of soil-gas samples close to a building, minimizing concern about interpolation and extrapolation of soil-gas concentrations beneath the building. The PRT system can be used to collect soil gas samples to depths up to 20 m bgs, while the hand-held rotary hammer GVP kit is suitable for soil gas sampling up to 4 m bgs.

NRMRL's study was conducted at five Raymark locations with sand or sand/gravel of high gas permeability (1.0E-06 cm^2). EPA Region 1 provided onsite GC analysis with VOC detection limits of 2-5 ppbv for each sample. As with all soil gas sample collection systems, non-analytical quality assurance/quality control factors included sampling methods, flow rates, applied vacuum, purge volume, total extraction volume, equilibration time, leakage, and gas permeability. Purging and sampling of vapor probes were conducted at a flow rate of 0.5 L/min.

The study included tests for evaluating factors potentially affecting sampling results. To evaluate the impact of pre-sample internal volume exchanges, 10 soil gas samples were collected after various internal volume exchanges (starting with zero) at one PRT and one dedicated vapor probe sampling location. Using the PRT system, up to 9 L of air and 74 internal volume exchanges were extracted with little impact on vapor concentration. Using the dedicated vapor probe, up to 103 L (103 internal volume exchanges) were extracted with little impact on vapor concentration. The internal volume of the GVP system was significantly lower than the PRT and dedicated probe systems.

To evaluate the potential for air extraction at one location to impact sample results at a nearby location and depth, three samples were taken non-sequentially using each sampling system. For example, at one location samples were collected by the PRT system, followed by the GVP system, and lastly by the dedicated probe. The sequence then was changed to sampling first with the GVP system, next with the dedicated vapor probe, and finally with the PRT system. This order was followed until three samples were obtained from each system at each depth. Comparison of first and third VOC concentrations at locations and depths where three samples were collected indicated that sample collection at one location did not impact sample results at another location.

Another potentially complicating factor in method comparison was spatial variability. PRT and GVP sampling locations were positioned relatively close (usually within 1 m) to dedicated vapor

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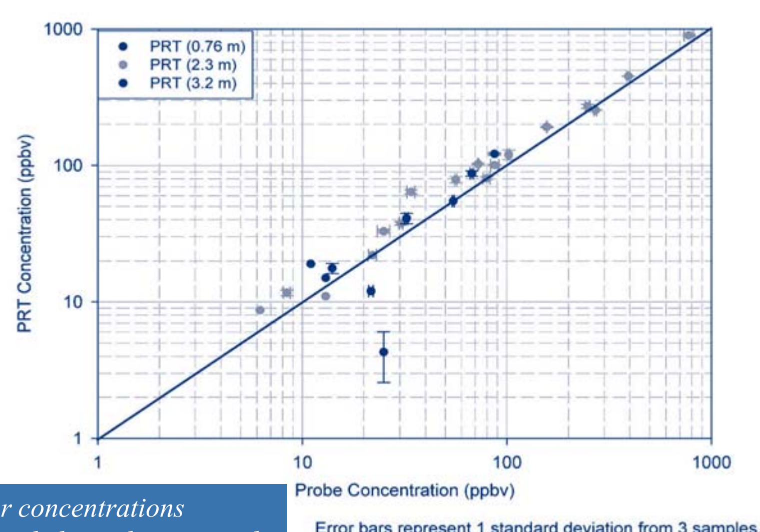

Figure 2. *Vapor concentrations measured by the dedicated vapor probe and PRT systems at three depths show relatively minor variations.*

[continued from page 3]

probes to minimize the effect of spatial variability on soil-gas concentration. To assess the presence and extent of spatial variability at this scale, the PRT system was used to collect samples at three depths across five locations separated by 1.5 ft. in a cross pattern. Variation in VOC concentration with location at each depth was present but relatively minor.

Sampling systems were compared using data from all locations and at depths of approximately 3, 8, and 11 ft. bgs for the dedicated probes, PRT, and GVP, respectively. Comparison of VOC concentrations obtained by each of the three systems indicated that the methods provided similar results (Figure 2). At one location, however, carbon dioxide, oxygen, and vapor concentrations were noticeably different, indicating potential leakage in the GVP system. Use of the PRT system generally resulted in observation of slightly higher VOC concentrations compared to the GVP sampling system and dedicated vapor probes.

This testing was conducted in highly permeable soils where the potential for leakage from direct-push/hammer soil-gas sampling systems would be expected to be low compared to less permeable soils such as silt and clay. As a result, these findings may not apply to other soil textures without additional investigations. Findings also may not apply to other direct-push/hammer soil-gas sampling techniques since only one direct-push and one rotary-hammer method was compared to dedicated vapor probes. The full study report (EPA/600/R-06/111) is available online at http://www.epa.gov/ada. Region 1 also plans to test methods for mitigating vapor intrusion at Raymark.

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Activated Carbon Applied to Sediment Potentially Reduces PCB Bioavailability

Alcoa, Inc., the U.S. EPA, Stanford University, and the University of Maryland-Baltimore County (UMBC) are conducting a joint in-situ pilot study to evaluate use of activated carbon (AC) for reducing bioavailability of polychlorinated biphenyls (PCBs) in river sediment. The study is taking place along the Grasse River in Massena, NY, 3.5 miles southeast of the Alcoa Massena West Plant. Past aluminum-manufacturing discharges from the facility resulted in PCB contamination of sediment and accumulation in the food chain, including fish. Recent laboratory studies on sediments from the Grasse River and other surface waters confirmed that AC incorporated into surface sediment effectively reduces PCB bioaccumulation in benthic organisms, which in turn is expected to reduce PCB concentrations in fish over time.

A non-time critical removal action involving dredging was conducted in 1995. In 2001, an extensive pilot-scale sediment cap was installed [September 2002 *TNT*]. As a result of partial ice-scouring of the cap and native sediment and a need for additional data [May 2005 *TNT*], a remedial options pilot study was initiated in 2005 to evaluate: dredging followed by sediment capping in the river's main channel and near-shore areas; thin-layer capping of near-shore areas with no prior dredging; and armored capping of the main channel with no prior dredging. In addition, source controls such as land-based remediation and wastewater treatment system upgrades at the Alcoa facility now are reducing PCB levels in both surface sediment and fish.

AC treatment involved adding black carbon to the upper, biologically active layer of sediment (typically the top 3-6 in.) where PCBs adsorb onto the surface of the carbon particles. To determine baseline conditions prior to treatment, surveys of sediment, aquatic vegetation, and benthic communities were performed. In-situ and ex-situ PCB bioaccumulation tests on caged worms also were conducted to support future post-treatment assessment of AC effectiveness.

A 0.5-acre portion of the river was selected for the AC study area based on its surface sediment PCB concentrations (4-13 ppm) and relatively extensive width and shallow depth (620 and 15 ft, respectively). Selection of this area allowed continued passage for recreational users, supplied contiguous fine-grained sediment deposits with minimal rock/boulder hindrances, and provided a relatively uniform river bottom to simplify AC placement and mixing. A temporary silt curtain was installed around the study area to minimize release of suspended sediment and AC into the surrounding river channel.

In addition to assessing reductions in PCB bioavailability, the pilot study is evaluating methods for in-situ delivery of AC to river sediment and determining the extent of PCB and sediment release to river water during applications. Delivery/mixing equipment includes a specially designed roto-tiller with and without rotating tines (Figure 3) and a tine sled, both enhanced with nozzles to inject AC directly into the upper sediment.

AC placement and mixing was conducted over six weeks last September through October. Applications occurred in four areas: (1) a 50- by 100-ft. initial area where all three application techniques were implemented; (2) a 75- by 100-ft. area where a roto-tiller with rotating tines was deployed for placement and mixing; (3) a 50- by 60-ft. area for placement/mixing by the tine sled; and (4) a 50- by 50-ft. area for deploying a roto-tiller without rotating tines (without mixing). Treatment areas were separated by buffer zones in which no AC was applied. In total, the study used a mass of 18,000 lbs of AC.

Based on the results of UMBC's site-specific treatability studies, a derivative of bituminous coal (Calgon Carbsorb 50 x 200) with a 75- to 300-µm particle size was selected as the AC. When Carbsorb product was not readily available, additional AC

[continued from page 4]

derived from coconut shells (of identical particle size and similar chemistry as Carbsorb) was used to complete applications in the tine sled and unmixed tiller treatment areas.

Water-quality monitoring during applications indicated no measurable changes in water-column PCB concentrations downstream of the study area. Downstream turbidity was slightly higher than upstream but no negative impacts on water quality were identified. Sediment cores collected immediately after the applications were analyzed for AC content at an offsite laboratory. UMBC is monitoring the treatment system's overall effectiveness and refining analytical methods for distinguishing the site's natural organic matter from black carbon to measure achievements in AC dosage.

Stanford University developed PCB mass transfer and biodynamic models for evaluating the treatment system's long-term effects on sediment. The models describe PCB uptake by benthic organisms based on feeding processes and PCB assimilation efficiencies from water/sediment ingestion. Analyses of species in the laboratory showed a 93% reduction of PCB concentrations when sediment was amended with 2.5% AC (dry weight), confirming that AC mixing into the surface sediment effectively reduces PCB bioaccumulation in benthic organisms.

Physicochemical and biological assessments over the next two years will evaluate effectiveness of AC technology in reducing PCB bioavailability in Grasse River sediment. Pending the results, a third-year assessment or large-scale AC application may be implemented. UMBC and Stanford University are evaluating this technology further in a similar pilot study to remediate PCBs at a tidal mudflat of San Francisco Bay.

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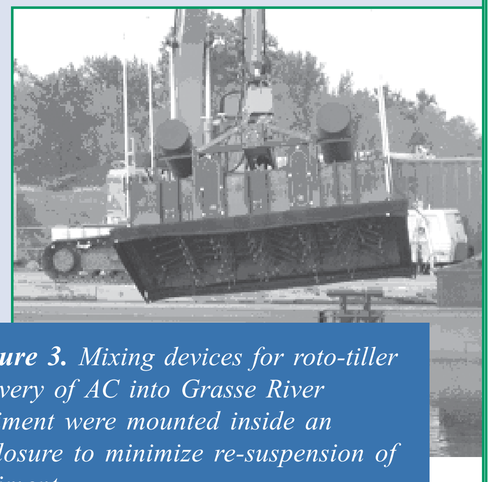

Figure 3. *Mixing devices for roto-tiller delivery of AC into Grasse River sediment were mounted inside an enclosure to minimize re-suspension of sediment.*

Research Examines Phytostabilization at Mining Sites in Arid and Semi-Arid Environments

Technologies such as phytoremediation continue to show success in immobilizing metal contaminants and reducing acid rock drainage at mining sites [March 2006 *TNT*]. Superfund Basic Research Program (SBRP) researchers at the University of Arizona recently conducted field and greenhouse studies to evaluate phytostabilization at two semi-arid sites in Arizona. This type of phytoremediation aims to revegetate barren sites by replanting native plants capable of sequestering metals in the root zone without metal uptake in shoot tissues. Studies focused on identifying simple, low-cost revegetation strategies with minimal site preparation, compost application, or vegetation maintenance.

One study involved an 18-month field trial at the 100-acre Boston Mill mine tailings site adjacent to the San Pedro River. Testing evaluated growth of the salt- and drought-tolerant fourwing saltbush (*Atriplex canescens*) under the site's neutral pH conditions, with and without compost amendment. Study results showed more than 80% of the 40 *Atriplex* transplants survived regardless of compost treatment. With the exception of lead, uptake did not exceed regulatory guidelines for metals (aluminum, arsenic, cadmium, copper, iron, mercury, manganese, and zinc). A two-year study initiated earlier this year on 1.5 nearby acres uses a native seed mixture including quailbush as another potentially effective *Atriplex* species (*lentiformis*) for phytostabilization.

Quailbush also was tested under greenhouse conditions using low- and medium-pH samples— more typical of mining sites— collected from lead/zinc tailings of the Klondyke mine, a state-designated Superfund site in Arizona's upper Aravaipa Valley. Lead concentrations at this site exceed 20,000 mg/kg, and no vegetation remains. Due to wind and water erosion of tailings, downstream fish in Aravaipa Creek exhibit elevated levels of lead and cadmium. The greenhouse tests evaluated germination, growth, and metal uptake of plants in tailings amended with 0 - 25% compost (by weight). Results showed that a tailings amendment of 15% compost was required for normal plant growth. Bacterial analysis of tailings after plant growth indicated a 4- to 6-fold decrease in the autotrophic microbial populations associated with the site's acidic and stressed soil/plant conditions. Plant shoot tissue analysis showed little accumulation of metals.

Results from both sites demonstrate significant potential for native *Atriplex* species to stabilize mine tailings in arid and semi-arid environments. Current SBRP tests evaluate effectiveness of other native species as well as plant-growth promoting bacteria with potential to minimize the compost amounts needed for plant establishment. For details on these and other SBRP studies, contact Monica Ramirez, University of Arizona (ramirez@pharmacy.arizona.edu).

Editor's Note: EPA recommends site evaluation and restoration of soil when necessary for optimal planting success. EPA is a proponent of using amendments such as biosolids to restore soil and stabilize metal contaminants along with planting.

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Multi-Process Phytoremediation System Field Tested on POPs

Researchers continue to explore innovative strategies for addressing environmental contamination caused by persistent organic pollutants (POPs) [January 2007 *TNT*]. Recent studies by the University of Waterloo demonstrate POP degradation through a multi-process phyto-remediation system (MPPS) based on accelerated remediation kinetics from multiple physical and biological processes. Greenhouse and pilot tests indicate that the process removes polycyclic aromatic hydrocarbons, total petroleum hydrocarbons (TPHs), and chlorinated hydrocarbons (CHCs) from soils while stabilizing metals.

The process employs *land farming* for aeration, physical volatilization, and photochemical degradation; *microbial inoculation* to begin the contaminant degradation process; and *rapid growth of plants with plant-growth promoting rhizobacteria (PGPR)* to help partition POPs and metals out of the soil. Testing indicates that the PGPR reduces stress-induced ethene production by microbial populations and promotes microbial synthesis of auxin, a significant promoter of root growth.

MPPS field tests show successful results: a 60-70% reduction of TPH was achieved over a two-year treatment period in soil containing 15% TPH (primarily heavy fractions) at a site in Sarnia, Ontario; and a 30% reduction of CHC in soil was achieved over only three months at a DDT-contaminated site near Simcoe, Ontario. Work on this technology is supported by a collaborative research and development grant from the Natural Sciences and Engineering Research Council of Canada. For details, contact Bruce Greenberg, University of Waterloo (greenber@uwaterloo.ca).

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