



TECHNOLOGY



NEWS AND TRENDS

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Complexing Sugar Removes DNAPL from Aquifer

The U.S. Department of Defense recently completed a field demonstration using cyclodextrin, a corn starch-based sugar, to enhance in-situ removal of dense non-aqueous phase liquid (DNAPL) at the Naval Amphibious Base Little Creek (NABLC) in Virginia Beach, VA. The primary objective of the demonstration was to determine whether trichloroethene (TCE) could be separated from the cyclodextrin solution above ground, and if the solution could be reconcentrated to reduce treatment costs. (The cyclodextrin molecule forms a weak complex with contaminants such as TCE, thereby increasing contaminant solubility and removal efficiency.) Cyclodextrin solution was injected directly into a TCE-contaminated aquifer. Air stripping of the extracted cyclodextrin solution produced an effluent containing TCE concentrations 99% lower than initial concentrations and below the maximum contaminant level (5 µg/L).

An underground neutralization tank and soil containing DNAPL (primarily TCE) had been removed near a former plating facility at NABLC in 1995. Follow-up site investigations revealed residual DNAPL below the excavation limit, in a trough approximately 7 m below ground surface. The area comprises a shallow, sandy, unconfined aquifer underlain by a layer of low-permeability marine clay. The hydraulic gradient is shallow, with an average ground-water flow velocity close to 0.3 m/day.

Pre-treatment sampling indicated an average aqueous TCE concentration of 15 mg/L. Based on the screen length, nature of the source zone area, and porosity of the sandy aquifer, the treatment zone was estimated to contain approximately 9,000 liters of water. Based on

preliminary partition tracer test data, 0.5-1% of this volume consisted of DNAPL.

Eight 4-in wells were installed at NABLC in or within 5 m of the source zone to depths of 7.5-8 m. Each well reached the uppermost portion of the clay layer and was screened across the bottom 1.5 m of the aquifer. This relatively short screened interval permitted a focused delivery of cyclodextrin solution to the lowest, most contaminated part of the aquifer. The treatment system flushed one pore volume (PV) of solution (approximately 9,000 liters) per day.

A "line drive" flushing system was initiated in July 2002 to inject one PV of a 20% cyclodextrin solution (1,800 kg) into two to four wells. After passing through the source zone, the solution was extracted from one to three downgradient wells, treated, and reinjected. The distance between injection and extraction wells ranged from 3 to 6 m. The initial (combined) flow rate was 6.25 L/min, but the rate decreased sharply over the first eight days of operation. This reduction resulted from the mixing of injected aerated water with anaerobic subsurface water, which caused iron fouling and ultimate well clogging. The reduced flow rate did not allow for sufficient hydraulic control of the flow field, thereby decreasing cyclodextrin recovery efficiency and contributing to dilution of the flushing solution.

The treatment scheme was modified to employ a multiple-well "push-pull" system. This method involved cyclodextrin injection into three wells within the DNAPL source

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This Issue Highlights...

...pilot tests that inject various additives to remediate contaminated ground water through in situ-chemical oxidation, co-oxidation, and bioremediation.

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zone. After all cyclodextrin solution was injected, it was extracted through the same wells, treated through air stripping, and stored in commercial holding tanks. The recovered solution, which contained an average of 11% cyclodextrin, was used in the next push-pull cycle by adding 40% cyclodextrin stock solution to obtain the appropriate volume of 20% flushing solution. Sampling data collected from a well during the initial push-pull test (Figure 1) represent similar results achieved during subsequent tests involving varied pumping rates and well constellations over longer durations. From July through August, approximately 5 kg of TCE were removed during three push-pull tests.

Preliminary results indicate that approximately 50% of the estimated DNAPL volume in the subsurface was removed during the demonstration. On a per-flushing volume basis, cyclodextrin enhanced removal of DNAPL 9-12 times more effectively than a (theoretical) conventional pump and treat system. Direct field comparison demonstrated that the push-pull system outperformed the line drive system by flushing 48% less cyclodextrin to remove 127% more TCE mass.

Project researchers estimate that the use of cyclodextrin adds \$2,000 - \$4,000 per kilogram of TCE removed through pump and treat technology. Under the Environmental Security Technology Certification Program, which sponsored this demonstration, a detailed cost and performance assessment is being developed to compare this technology with other innovative technologies for remediating contaminated ground water and soil.

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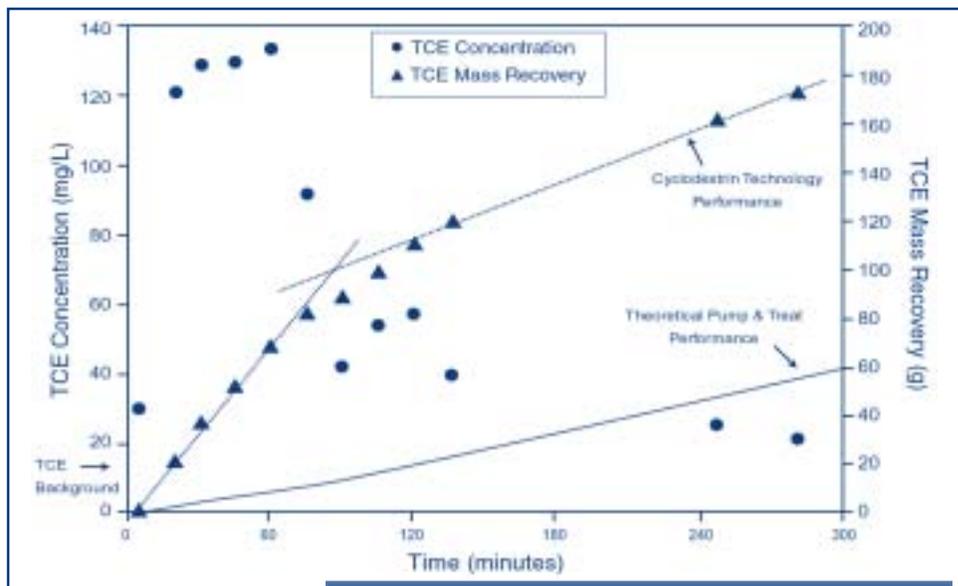


Figure 1. TCE solubility achieved through cyclodextrin treatment was enhanced 9- to 12-fold at NABLC when compared to conventional pump and treat technology.

Chitin/Fracturing Used to Stimulate Microbial Degradation of Chlorinated Solvents

The National Science Foundation sponsored a pilot-scale field test of enhanced bioremediation at the Distler Brickyard site near Louisville, KY, from October 2001 to January 2002. The pilot test technology combined the use of hydraulic fracturing (“fracing”) with anaerobic bioremediation enhanced by the addition of chitin, a solid, natural polymeric organic material consisting of shrimp and crab shells. The primary objectives of the field test were to determine if fracing would enhance the geologic formation’s permeability and if the addition of chitin would impact the aquifer’s geochemistry in ways conducive to anaerobic reductive dechlorination (ARD). Field data indicate that active ARD of trichloroethene (TCE) continues to occur in the treatment area as a result of chitin/fracing.

As a result of past waste-handling activities, ground water at the Distler Brickyard site contains TCE and *cis*-1,2-dichloroethene (DCE) at concentrations reaching nearly 100 and 500 $\mu\text{g/L}$, respectively. The underlying

stratigraphy consists of approximately 40 ft of silty-sand and silty-clay overlaying shale bedrock. The ground-water table is approximately 30 ft below ground surface (bgs). Horizontal hydraulic conductivities range from 10^{-8} to 10^{-4} cm/sec. Although monitoring data indicate that natural biodegradation via ARD was occurring, the rate and extent of ARD reactions are limited by a lack of sufficient electron donor and the low permeability of the formation. Earlier laboratory studies conducted by the University of Illinois at Urbana/Champaign (UIUC) demonstrated that chitin produces volatile fatty acids (VFAs) shown to be high-quality electron donors for ARD.

Hydraulic fracturing was conducted at the Distler Brickyard through a single borehole within the contaminant source area, near the bedrock surface. By injecting sand slurry with chitin, three sets of highly permeable fractures were created in the borehole at depths of 25, 33, and 38 ft bgs. Approximately 250 gallons of the (1:4 ratio) chitin/sand slurry were

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delivered into each frac. The borehole subsequently was completed as a monitoring well.

The hydrologic system evaluation included tiltmeter monitoring to measure the orientation of fractures, pre- and post-fracing slug tests, and a pumping test. Results indicated that fracing produced a network of three permeable zones with a modeled effective radius of 4 ft for the uppermost frac (within the silt/sand unit) and 13 ft for the two lower fracs (within the silt/clay unit). As anticipated, the extent of fracture propagation depended upon the site's lithology, degree of soil consolidation, presence and orientation of bedding planes, and presence of geologic heterogeneities. Despite the heterogenous propagation of fractures, the pumping test showed that all four of the monitoring wells were in direct hydraulic connection with the fracing well.

Ground-water sampling in the fracing well and surrounding monitoring wells was conducted to determine the effect of chitin emplacement on the electron donor concentrations, oxidation-reduction (redox) conditions, and ARD. The breakdown of chitin as an electron donor was measured by the production of individual VFAs such as acetate, propionate, isobutyrate, butyrate, isovalerate, and formate. Monitoring well data showed that the dominant VFAs produced from chitin were acetate and butyrate, which reached maximum concentrations of greater than 600 and 300 mg/L, respectively. Acetate concentrations of greater than 200 mg/L persisted in the treatment cell nine months following chitin emplacement.

Pilot test results indicated that conditions became more reducing following chitin

emplacement. Redox conditions were assessed using concentrations of ferrous iron, sulfate, and methane. Strong methanogenic conditions, which are required for successful ARD, were indicated by the increased concentrations of methane and ferrous iron and by the absence of sulfate. Ferrous iron concentrations increased and sulfate dropped within the first month after chitin emplacement, indicating an immediate impact to redox conditions. Methane concentrations began increasing steadily approximately two months after chitin emplacement and reached up to 12,000 µg/L within nine months.

Concentrations of TCE and breakdown products *cis*-1,2-DCE, vinyl chloride, and ethene were monitored to further evaluate the ARD process (Figure 2). Data indicated an initial decrease in *cis*-1,2-DCE following chitin emplacement, followed by a three-month rebound. In contrast, ethene concentrations initially increased but subsequently decreased. (These trends may be attributed to higher ground-water levels and dilution effects.) After nine months, however, *cis*-1,2-DCE concentrations dropped below detection (5 µg/L), and a nearly stoichiometric increase in ethene concentrations was observed.

These results indicate the persistence of ARD reactions as long as nine months after chitin

emplacement. Overall concentrations of chloroethene contaminants in the source area decreased to or below maximum contaminant levels (MCLs) in three of the five wells within nine months. TCE and *cis*-1,2-DCE concentrations in the remaining wells decreased from a maximum of 59 µg/L to 11 µg/L and 450 to 99 µg/L, respectively.

Region 4 of the U.S. EPA, which provided analytical services and technical assistance, estimates a cost of \$140,000 for implementing this pilot project. Full-scale application of chitin/fracing technology at the Distler Brickyard during 2003 will focus on evaluating the technology's cost-effectiveness, achieving adequate distribution of chitin in-situ, and evaluating the long-term performance of chitin as a slow-release electron donor for ARD of chloroethene contaminants in low-permeability systems.

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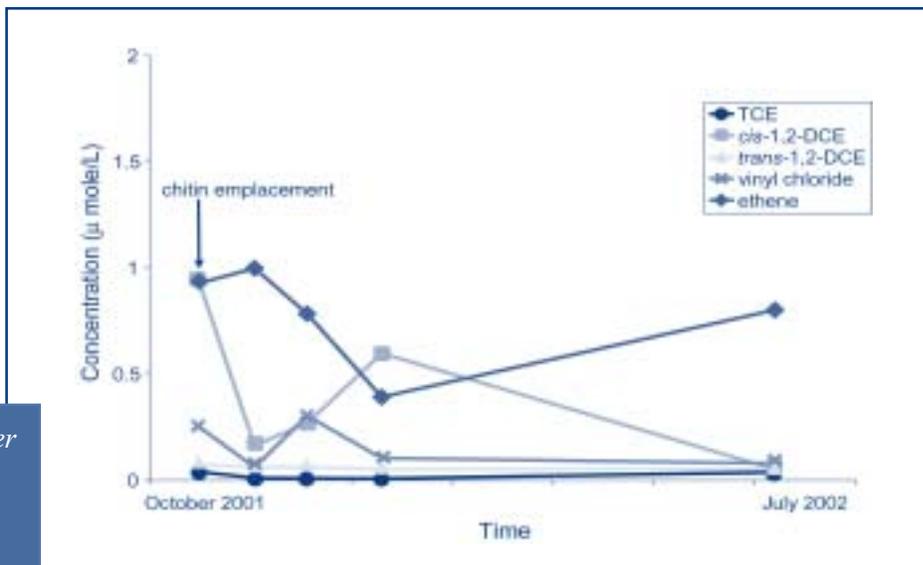


Figure 2. Chitin/fracing at the Distler Brickyard site resulted in significant break-down of *cis*-1,2-DCE within nine months.

Field Tests Conducted on Use of Potassium Permanganate for In-Situ Oxidation

The U.S. Air Force (USAF) is collaborating with researchers from the University of Arizona and Raytheon to study the effectiveness of large-volume injections of potassium permanganate (KMnO_4) solution for remediating ground-water contamination sources. In-situ oxidation (ISO) field studies were conducted recently at Air Force Plant 44 (AFP 44), located within the Tucson Airport Area Superfund site in Tucson, AZ, as part of extensive efforts to remove trichloroethene (TCE) and 1,1-dichloroethene (DCE) from the aquifer as dense non-aqueous phase liquid (DNAPL). A two-square-mile pump and treat system has operated at the facility since 1987, and soil vapor extraction (SVE) and dual-phase extraction systems were added in 1995 for source control at five former disposal sites. Based on the field study results, ISO using KMnO_4 will be implemented on a larger scale in 2003 as a follow-up technology to SVE.

AFP 44 is located in the central part of the Tucson Basin. The area is underlain by unconsolidated to semi-consolidated alluvial basin fill sediments consisting of thin (less than 20-ft-thick) permeable beds of sand and gravel separated by thick, low-permeability beds of sandy clay and clay. Ground water in the area occurs under semi-confined conditions at depths of 135-150 ft below ground surface (bgs). Transmissivities in test locations are on the order of 10,000-50,000 gal/day/ft.

Two methods of KMnO_4 injection were compared during the study. In August 2001, 15,000 gallons of 2% KMnO_4 solution (2,500 lbs of KMnO_4) were injected into the subsurface in an area known as "Site 2." The solution was injected into the vadose zone above a fine-grained unit, 20-30 feet above the water table. The injection was designed to provide a vertical flood allowing the solution to migrate laterally in the unsaturated permeable zone along the top of the fine-

grained unit suspected to contain the DNAPL, and then downward through this unit and into the ground water (Figure 3).

At "Site 3," 12,000 gallons of the solution (2,000 lbs of KMnO_4) were injected directly into the ground water at depths of 140-160 ft bgs, within a permeable sand and gravel bed bounded by low-permeability, fine-grained units. This injection was intended to provide a horizontal flood, allowing the solution to migrate horizontally and to contact the TCE and DCE DNAPL in the lower portion of the overlying fine-grained unit.

Nine and twelve wells were used at Sites 2 and 3, respectively, to monitor ground water for six months. Monitoring parameters included TCE, DCE, chromium, major anions and cations, pH, temperature, conductivity, and oxygen reduction potential. (Chromium monitoring was performed due to the trace amounts of chromium present in potassium permanganate and the possibility of mobilizing trivalent chromium potentially present in the aquifer.) The characteristic purple color of KMnO_4 served as the most useful indicator of its presence; KMnO_4 concentrations as low as 10 mg/L could be detected on color alone. Movement of KMnO_4 solution within the aquifer was controlled by pumping ground water from selected wells to induce the flow of injected solution toward the wells.

Bench-scale testing prior to field injections indicated that KMnO_4 concentrations of 50 mg/L or more could oxidize TCE. To determine the effectiveness of breakdown reactions under site conditions, tests were performed using TCE-contaminated ground water in columns containing AFP 44 aquifer material derived from a site core. Testing indicated that aquifer materials did not inhibit the TCE breakdown reaction.

Field study results showed that distribution of the KMnO_4 was most effective at Site 3, where solution was injected directly into the aquifer and spread through horizontal flow. Ten of the 12 wells were impacted by KMnO_4 concentrations greater than 50 mg/L. At Site 2, however, much of the solution remained absorbed to the fine-grained unit above the water table and only three of the wells were impacted.

Results indicated that all impacted wells experienced reductions in TCE concentrations during the period when active KMnO_4 ISO was observed, with some wells experiencing a 100% reduction. DCE, where present, also decreased in concentration. The period of time when the active KMnO_4 was present varied among wells, with active solution residing in some wells for up to six months. Three months after injection, TCE

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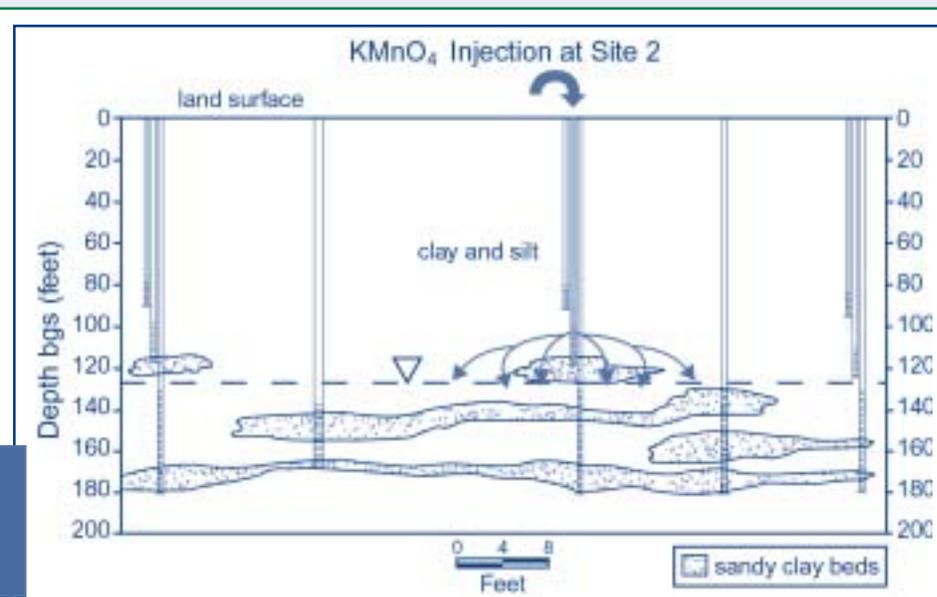


Figure 3. Fine-grained clay and silt prevented complete distribution of KMnO_4 through vertical flooding at AFP 44 Site 2.

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concentrations in most wells began to rebound as a result of contaminated ground water migration into the study area from upgradient contamination zones. Most of the impacted wells continued to experience rebound over the following three months, but TCE concentrations remained lower than pre-test concentrations. Average pre-test TCE concentrations in two benchmark wells at Site 2 ranged from 900 to 1,200 µg/l, while average pre-test TCE concentrations in three benchmark wells at Site 3 ranged from 90 to 475 µg/l range. Sampling data collected from these wells 12 months after the injections indicated concentrations had decreased approximately 65% at Site 2 and 30-70% at Site 3.

Since previous studies at Site 3 suggested that full rebound of TCE and DCE concentrations would occur within 20 days of injection if no TCE DNAPL had been

oxidized, the extended period of rebound observed during these field tests indicated DNAPL was destroyed in the treated areas. Field results showed that the KMNO₄ solution remained viable in the aquifer for up to six months, in contrast to the two months predicted by bench-scale tests. The unusual persistence of the KMNO₄ solution was attributed partially to the low organic carbon content of soil at AFP 44. Although bench-scale tests also suggested that MnO₂ precipitation may cause a loss of soil permeability, no loss was encountered. Chromium concentrations were found to decline as KMNO₄ was consumed and as ground water returned to a lower redox potential.

This study cost approximately \$125,000, including \$9,000 for KMNO₄. Field experiences suggest that a similar injection could be implemented for approximately \$35,000 by eliminating unnecessary field monitoring and sample analysis. Researchers

concluded that a combination of vertical flood and horizontal flow injection methods are needed to remediate the source area completely.

In December 2002, the USAF initiated an expanded injection test involving both vertical and horizontal flooding with KMNO₄ solution across the entirety of Site 2, into both the vadose zone and aquifer. Located at the upgradient end of the TCE plume, Site 2 is expected to produce unambiguous test results due to the absence of TCE-contaminated ground water migration. Modifications to the technology will include vertical flooding using greater volumes of more dilute solutions injected into multiple wells.

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Co-Oxidation Used to Remove PCE DNAPL at Drycleaner Site

The Florida Department of Environmental Protection (FDEP) is conducting pilot tests to remediate contaminated ground water at a drycleaning facility in Jacksonville, FL. Following the limited success of in-situ chemical oxidation (ISCO) testing at this site, co-oxidation technology is being tested to improve remedial effectiveness, reduce cleanup costs, and accelerate overall cleanup.

As a result of past releases of tetrachloroethene (PCE), dense nonaqueous phase liquid (DNAPL) exists immediately adjacent to the drycleaning facility in a source area located 10-15 feet below ground surface (bgs). The dissolved-phase plume emanating from the source extends across an area of approximately 670 by 150 feet. The site is underlain primarily by sandy soil with interbedded layers of silt and clay. Within these units, the measured hydraulic conductivity is approximately 5 ft/day. The water table is approximately 6 feet bgs, and the hydraulic gradient is 0.01 ft/ft.

From September 1999 through December 2000, ISCO tests were conducted by injecting potassium permanganate (KMnO₄) directly into the DNAPL zone (10-15 ft bgs). A total of 4,000 pounds of KMnO₄ was injected through screened wells into the source area during four 3-week events. Results indicated an initial reduction of dissolved-phase PCE concentrations, followed by consistent PCE rebound in source area monitoring wells. Rebound was attributed to limitations in pore diffusion and interfacial mass transfer between the DNAPL and ground water.

The pilot was modified to incorporate in-situ co-oxidation technology. Co-oxidation was selected due to its ability to:

- ◀ Employ a co-solvent for addressing mass transport limitations,
- ◀ Reduce the solvent's aqueous concentration, thereby maximizing the rate of chemical oxidation,

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- ◀ Allow for retention of co-oxidant solution in the aquifer for a short time without the need for hydraulic control,
- ◀ Reduce treatment costs for the extracted fluid, due to destruction of contaminant once it transfers to the aqueous phase, and
- ◀ Reduce overall remediation costs through accelerated, in-situ contaminant destruction.

Co-oxidation testing began at the site in May 2001. This phase of pilot testing involved a single source-area injection of 1,000 gallons of co-oxidant solution containing tertiary butyl alcohol and $KMnO_4$. The solution was extracted 10 days later and disposed offsite.

Preliminary results from ground-water monitoring and direct-push soil samples collected in April 2002 indicated an 80-90% reduction of source-area DNAPL following co-oxidation. PCE concentrations in a

representative monitoring well decreased from pre-treatment levels of 15,000-20,000 $\mu g/L$ to less than 750 $\mu g/L$.

Testing of alternative co-oxidants is underway to enhance performance of the process.

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Update on the State Coalition for Remediation of Drycleaners

For the past four years, the State Coalition for Remediation of Drycleaners has worked to address problems posed by soil and ground-water contamination at drycleaning sites. It is estimated that contamination exists at more than 25,000 drycleaning sites across the country. Under sponsorship of the U.S. EPA's Technology Innovation Office, representatives from 11 states with established drycleaner remediation programs have joined the coalition to provide a forum for:

- ◀ Exchanging information on existing state drycleaner programs,
- ◀ Sharing information and lessons learned with states having no drycleaner-specific programs, and
- ◀ Encouraging the use of innovative technologies in drycleaner remediation.

More information about the coalition's work, including development of more than 60 site-specific cleanup profiles, is available on the web at www.drycleancoalition.org.