TECHNOLOGY NEWS AND TRENDS

A newsletter about soil, sediment, and groundwater characterization and remediation technologies

Issue 50 **October 2010**

This issue of Technology News and Trends *highlights accelerated remediation of contaminant source areas containing dense nonaqueous phase liquid (DNAPL). Treatment typically involves conversion of contaminants, most commonly trichloroethene, from the nonaqueous phase to the dissolved phase where degradation occurs more readily through chemical or biological processes.*

Dual-Reagent ISCO "Fast-Tracks" Cleanup of Orlando Brownfield

The City of Orlando initiated a three-phase plan in the summer of 2007 to accelerate remediation of VOC-contaminated groundwater. Contamination was found beneath a former industrial site scheduled to reopen in 2010 as the city's events center. The first phase of the plan employed in situ chemical oxidation (ISCO) with catalyzed hydrogen peroxide (CHP) to target the suspected contaminant source area, located directly below the center's proposed athletic arena. The second phase involved additional ISCO using sodium permanganate to target residual contaminants, and the third phase focused on offsite disposal of shallow impacted soil. Sequentially applying two oxidants, rather than combining single-oxidant ISCO with a time-intensive polishing technology such as bioremediation, met the project's cleanup goals within nine months. To meet a tight schedule calling for 2008 startup of building construction, field work was guided by daily rounds of injector and monitoring well sampling to optimize reagent and catalyst dosing. Frequent measurements of off-gases and degradation end products also were made to quickly determine when chemical oxidation was complete.

An investigation in early 2007 confirmed source-area tetrachloroethene (PCE) in concentrations reaching 14,600 µg/L in groundwater above a clay-confining layer 40 feet below ground surface (bgs). Concentrations of PCE degradation products included 57 µg/L of trichloroethene (TCE) and 98 µg/L of *cis*-1,2-dichloroethene (DCE) without detectable levels of vinyl chloride. The presence of DNAPL was suspected due to the high PCE concentrations in sand and silt zones immediately on top of the area's dense clay aquitard. Remediation goals were set at the Florida groundwater cleanup target levels (CTLs) of 3 µg/L for PCE and TCE and 70 µg/L for DCE.

Shallow soil at depths of 2-4 feet bgs also was contaminated in two discrete areas near a concrete pad with an underlying sewer from past operation of a garage and machine shop. The highest identified PCE concentration in soil at these areas was 0.49 mg/kg, which exceeded the 0.03 mg/kg CTL for leachability.

In early November 2007, field preparations for ISCO began by installing 72 injection wells spaced on 20-foot centers in an 80- by 130- foot area of concern (AOC) under the proposed arena. Each well extended to one of three intervals between 10 and 40 feet bgs. Shallow and deep nested injectors were screened from 15 to 20 feet and 35 to 40 feet bgs, respectively, and interspersed intermediate-depth zone injectors were screened at 25 to 30 feet bgs. Use of a direct-push (DP) instead of conventional drilling rig allowed for construction of the well network in two weeks. The grout seals were allowed to cure for two weeks.

CHP was selected as the primary oxidant due to its efficiency in destroying DNAPL and sorbed-phase contamination. The first-phase injection was conducted in January 2008 using two trailers connected by chemical hoses to inject low-pressure CHP solution into the full array of injection wells. Using a top-down injection approach, each injection rig initially deployed four injectors to fully blanket the AOC.

A photoionization detector (PID) and multi-gas meter were used to measure VOCs, oxygen,

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CLU-IN Resources

Dense Nonaqueous Phase Liquids is one of several *Contaminant Focus* areas of the U.S. Environmental Protection Agency (EPA) CLU-IN web host *www.clu-in.org/contaminantfocus/*. Information includes introductory discussion and additional web links for DNAPL policy and guidance, chemistry and behavior, environmental occurrence, toxicology, and treatment technologies.

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and carbon dioxide in the well headspace as indicators of treatment progress. PID readings from four monitoring wells in the source area showed an initial VOC spike related to contaminant desorption from the aquifer matrix, followed by subsequent VOC destruction to non-detectable levels over the remainder of treatment. CHP injection was terminated after 23 days, when PID and other in situ data indicated completed chemical oxidation. Residual catalyzed peroxide from the 85,000-gallon injection was allowed to degrade for another week before the second injection phase began.

Sodium permanganate was selected as the secondary reagent due to its ability to treat residual contaminants that slowly diffuse out of the fine-grained aquifer matrix after the peroxide had removed bulk contamination. In early February 2008, approximately 21,000 gallons of 4% sodium permanganate solution was injected through the same well network over 7 days. The volume was anticipated to again blanket the full AOC. Injection and post-injection monitoring included groundwater sampling for visual analysis to ensure uniform permanganate distribution. Permanganate in its characteristic purple color was found throughout the treatment area.

In the third phase of remediation during late February, approximately 94 tons (1,800 ft^3) of surface soil were excavated to a depth of 4 feet near the concrete pad. The two-day excavation targeted all vadose zone soil documented to contain detectable VOCs during earlier delineation of the AOC. It also revealed a PVC pipe connected to a former floor drain system, which contained residual sludge above the source area. Elevated PID readings in the pipe vicinity suggested this jointed sewer was the source of solvent discharge. Following extraction of the pipe and associated bedding, the concrete pad was removed and the area was backfilled. Confirmatory sampling in early March did not detect PCE in soil surrounding the excavated area.

Groundwater was sampled in five treatment-area monitoring wells beginning four days after the permanganate injection and in mid- April and mid-July. Results indicated that total VOCs immediately decreased after the first injection (Figure 1) and remained below the CTLs except at one well (MW-5) close to the former pad and excavation area. The increase in PCE concentrations at MW-5 prompted injection 7 days later of 150 additional pounds of sodium permanganate via shallow injectors within 20 feet of the well. Confirmatory sampling in early August showed a PCE concentration below 1.0 µg/L in MW-5, which supported earlier suspicion that the observed VOC rebound was caused by the preceding excavation activities.

July and subsequent monitoring events in five wells within the treatment area showed a total VOC concentration of less than 3 µg/L, a 99.98% decrease from maximum pre-treatment levels. More recent investigations by the Florida Department of Transportation in an adjacent offsite area documented a presence of permanganate that likely continues to polish onsite groundwater and groundwater downgradient of the AOC.

The injectors and monitoring wells were abandoned shortly after MW-5 confirmation sampling and when all treatment-area wells exhibited non-detectable levels of PCE, within 290 days after the city executed the cleanup contract. Field work was completed in 101 days, and the remaining project time involved regulatory review and post-treatment monitoring. Costs totaled $596,000 for remediation (approximately $34/yd^3) and $85,395 for soil and groundwater confirmatory sampling during and after the injections. Building construction began on schedule in July 2008 for opening of the city's new events center this October.

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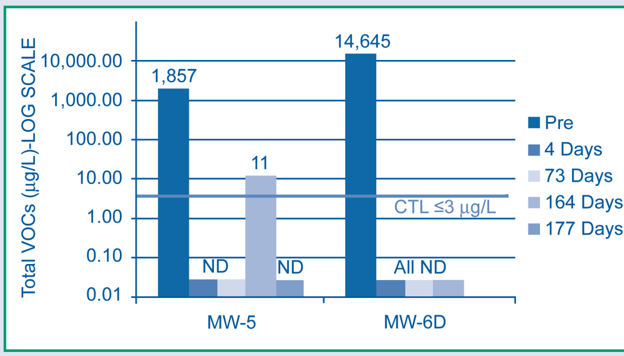

***Figure 1.** Monitoring at two onsite wells with the highest VOC concentrations prior to remediation showed reductions to below Florida CTLs within four days after injecting CHP.*

In Situ Thermal Desorption Minimizes Cleanup Duration at Dunn Field BRAC Site

Full-scale in situ thermal desorption (ISTD) was initiated in 2008 for areas of Dunn Field at the Memphis Defense Depot Superfund site to destroy chlorinated VOCs (CVOCs). ISTD was selected to replace soil vapor extraction (SVE) in the top 30 feet of soil, a clay-rich loess, after SVE pilot testing suggested that its exclusive use in the loess could take up to 235 years to reach remediation goals (RGs). Thorough delineation of the CVOC hotspots minimized the areas needing treatment, which lowered ISTD costs while significantly reducing the overall cleanup cost and duration.

The Memphis Depot closed in 1997 under the Base Realignment and Closure Act (BRAC) after approximately 55 years of use for military material distribution/storage and maintenance services. Upon closing, the 64-acre Dunn Field housed multiple areas used for mineral and waste storage and disposal. The underlying stratigraphy consists of the relatively low-permeability loess which grades, with depth, to a high permeability fluvial unit consisting of sand, silt, and gravel. Groundwater depth is approximately 75 feet bgs.

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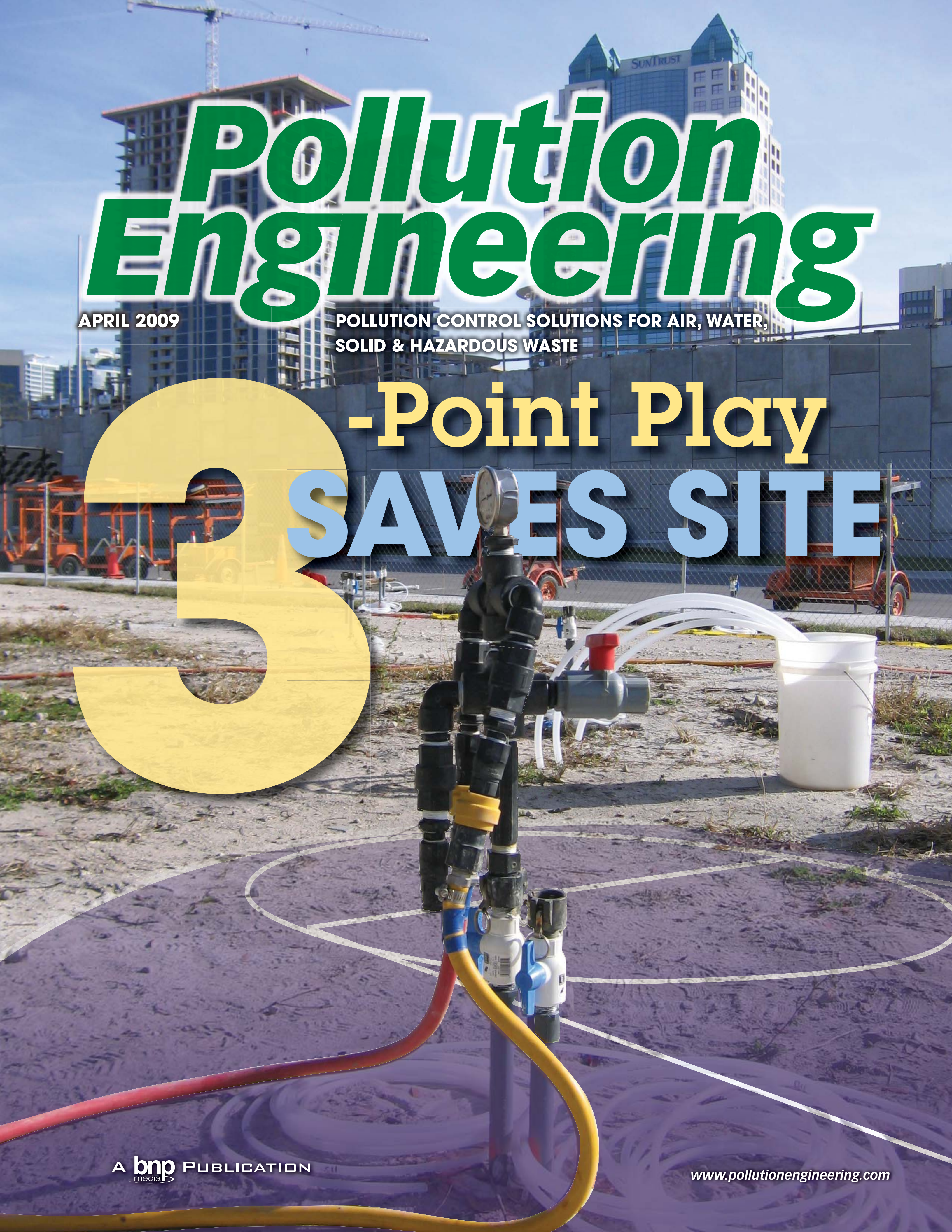

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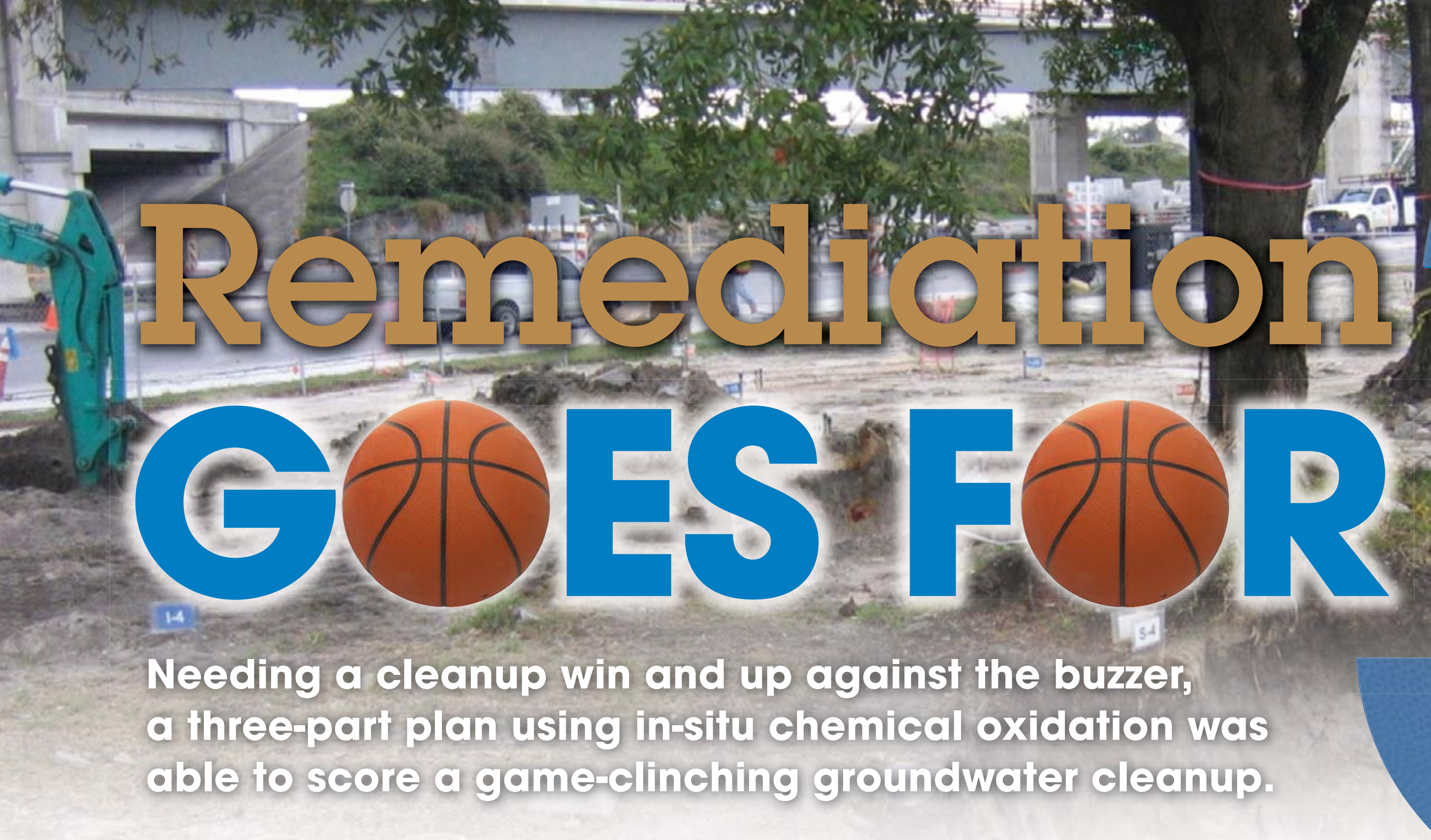


Remediation GOES FOR

Needing a cleanup win and up against the buzzer, a three-part plan using in-situ chemical oxidation was able to score a game-clinching groundwater cleanup.

By **DAN BRYANT**, Geo-Cleanse Intl. Inc., and
ED KELLAR, MACTEC Engineering and Consulting Inc.

In 2007, the NBA's Orlando Magic and their host city unveiled the design for the Orlando Events Center as the professional basketball team's new downtown venue. Due diligence by the city identified a groundwater tetrachloroethene (PCE) plume with a source area located beneath the proposed arena footprint (see **Figure 1**).

The maximum PCE concentration found in the source area groundwater was 14,600 ug/L, which exceeded the Florida groundwater Cleanup Target Level (CTL) of 3 ug/L. Trichloroethene (TCE; maximum concentration of 57 ug/L) and cis-1,2-dichloroethene (DCE; maximum concentration of 98 ug/L) were also detected at concentrations exceeding their CTLs of 3 ug/L and 70 ug/L, respectively. Shallow soil (2 to 4 feet below grade) was also impacted in two discrete areas. The maximum soil PCE concentration was approximately 0.49 mg/kg, which exceeded the Florida soil CTL for leachability of 0.03 mg/kg.

The aquifer was primarily sand, with some finer-grained (silty sand) zones to a depth of approximately 40 feet below grade, underlain by a dense clay aquitard in the treatment area.

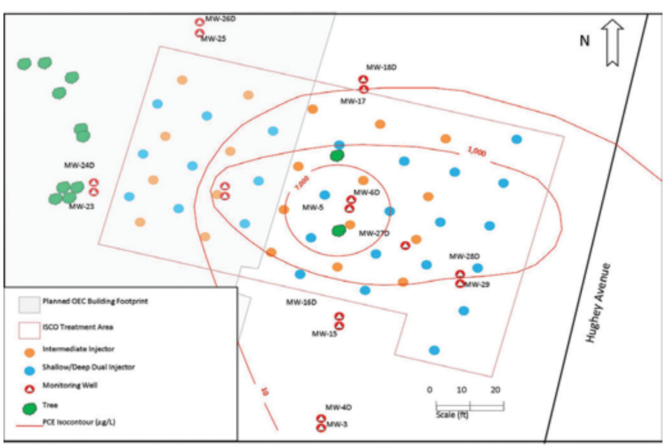
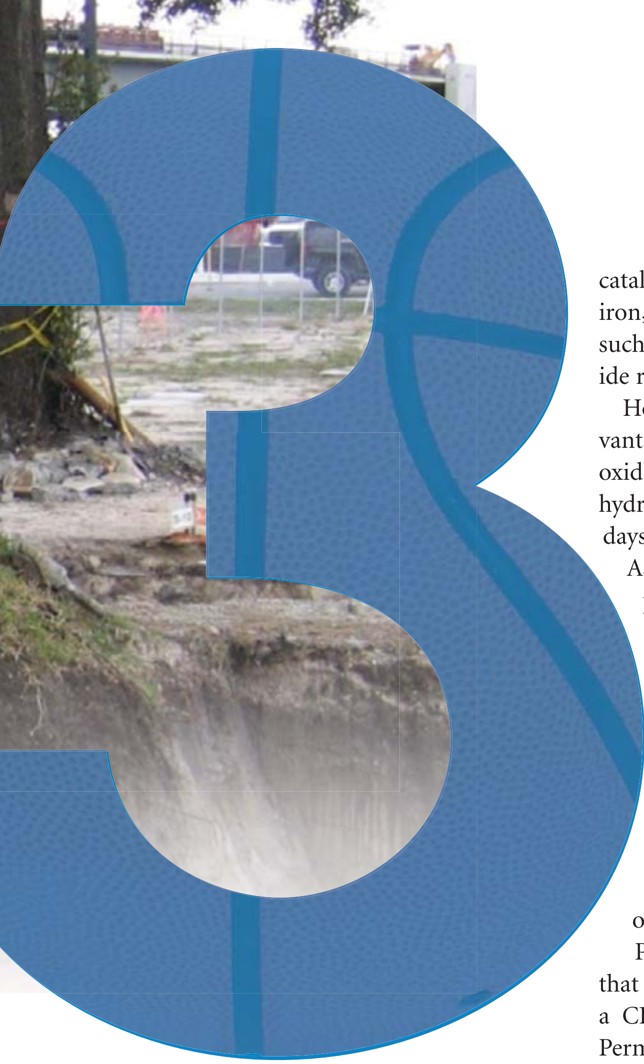


Figure1: The above drawing shows the location of the injection points, monitoring wells and other points of interest on the site.

Drawing up the play

The city issued a request for proposal for a source area remedy with a fast-tracked, performance-based contract on Aug. 30, 2007. Construction was scheduled to begin in the late summer 2008, thus a very rapid and aggressive response was required to prevent any construction delay. Geo-Cleanse International Inc., Matawan, N.J., and Mactec Engineering and Consulting Inc., Newberry, Fla., agreed to partner for the project and developed a three-phase remediation plan.

The first phase consisted of in-situ chemical oxidation (ISCO) with catalyzed hydrogen peroxide (CHP) to target the concentrated source area. The second phase consisted of additional ISCO using sodium permanganate to target residual contaminants potentially remaining after the catalyzed peroxide application. The third phase consisted of removal with offsite disposal of impacted shallow soil.



Stacking the court

One of the novel components of the team's approach was the sequential application of different oxidants to achieve the CTLs. Plume management strategies typically employ ISCO in concert with other methods, such as engineered or natural bioremediation, extraction or air sparge/soil vapor extraction. However, most of these secondary technologies require longer periods of time to achieve cleanup goals (months or years). When time is a pressing issue, an alternative approach is to couple different ISCO technologies to more rapidly achieve low cleanup standards. Each general chemical compound such as catalyzed hydrogen peroxide (CHP), activated persulfate, or permanganate, has advantages and disadvantages. But in certain cases different oxidants can be applied together or in succession to rapidly reduce contaminant concentrations, as was shown in this application.

CHP includes a range of chemical reactions responsible for degradation of organic compounds such as PCE. When catalyzed by a transition metal such as iron, H_2O_2 generates powerful radicals such as the hydroxyl radical and superoxide radical.

However, the chemical also has disadvantages. One is the short lifetime of the oxidant in the subsurface. In most cases, hydrogen peroxide will persist for several days to perhaps a week in the subsurface. As a result, residual oxidant may not persist long enough to address contaminants slowly diffusing out of fine-grained (silt or clay) aquifer matrices, and the oxidant itself does not survive long enough to diffuse into those matrices. Long-term diffusion of contaminants from fine-grained aquifer matrices may pose a rebound problem, and prevent achievement or maintenance of the CTLs.

Permanganate exhibits characteristics that make it an excellent choice to follow a CHP treatment for PCE remediation. Permanganate is generally a less aggressive oxidant than CHP and not as efficient as CHP at rapidly destroying sorbed- or NAPL-phase contaminants. Permanganate is also a more costly oxidant than CHP in terms of cost per unit mass of contaminant destroyed. However, due to the slower reaction, permanganate has a much longer lifetime in the subsurface than CHP. Residual permanganate may last for months to address contaminants slowly diffusing from fine-grained matrices. Permanganate also diffuses directly into finer-grained aquifer matrices to directly attack those contaminants.

Executing the play

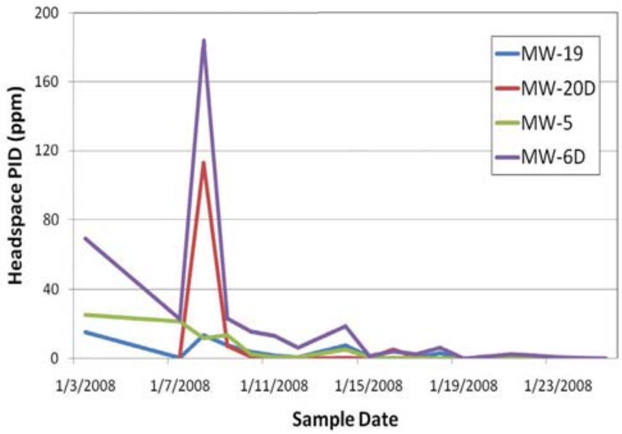
The design called for 72 injection wells installed across three depth intervals between approximately 10 to 40 feet below grade, in an 80-foot by 130-foot area (see Figure 1). Injector installation was conducted from Nov. 27 to Dec. 15, 2007. The injector seals were then allowed to cure for two weeks.

The first phase of remediation consisted of injecting 85,000 gallons of CHP solution over the period from Jan. 2 to 26, 2008. Measurements of volatile organic compounds (VOCs) in the headspace over groundwater samples, as taken with a photoionization detector (PID), provided a semi-quantitative measure of VOC concentration in the groundwater.

Figure 2 is a chart of the PID readings of groundwater samples from the four monitoring wells in the source area. The readings showed an initial spike in headspace PID measurements related to desorption of VOCs from the aquifer matrix, followed by subsequent destruction to non-detectable levels during the treatment. These data were used to determine when to cease CHP injection and confirm that the first treatment phase was complete.

One week was allowed for residual peroxide to degrade before beginning permanganate injection for the second phase. The same network of injection wells installed for the CHP injection was also utilized for the permanganate. This second phase of remediation consisted of injecting 21,000 gallons of 4-percent sodium permanganate solution over the period from Feb. 4 to 10, 2008. Field monitoring for sodium permanganate injection consisted of collecting groundwater samples for visual analysis to ensure uniform distribution of the permanganate. Permanganate (recognized by its characteristic purple color) was found throughout the treatment area following the injection. The post-injection groundwater monitoring period began after completion of the permanganate injection.

The third phase of remediation consisted of soil removal at two areas impacted with PCE. A total of 94 tons of soil was removed from Feb. 25 to 27, 2008. During the removal, a PVC pipe and apparent floor drain system were discovered (see **Figure 3**). The pipe was found to contain residual sludge and exhibited elevated PID readings, and was located directly over the groundwater source area, and thus was the presumed discharge source. The piping and associated bedding were also removed. The excavation was backfilled on March 7, 2008 after receipt of post-excavation sampling results.



The chart to the left is of readings from the four monitoring wells in the source area. The readings showed an initial spike in headspace PID measurements related to desorption of VOCs from the aquifer matrix, followed by subsequent destruction to non-detectable levels during the treatment.

Figure 3 shows a floor drain system that was unearthed during excavation of 94 tons of soil. This was considered the source of the contamination.

Post-game wrap-up

The post-treatment performance sampling program consisted of three groundwater sampling events, conducted on Feb. 14, 2008 (four days after injection), April 23, 2008, and July 23, 2008, with a supplemental sampling event on Aug. 5, 2008. With one exception, the VOC concentrations in all five of the performance monitoring wells were reduced to below the CTLs.

The total VOC concentration (consisting of the summed PCE, TCE and DCE concentrations) is plotted in Figure 4 for the two monitoring wells exhibiting the highest pre-injection VOC concentrations. During the July 23 event, PCE was detected at 11 ug/L in MW-5 and was confirmed with a second analysis. MW-5 was a shallow well located adjacent to the soil removal area, thus the VOC detection was likely associated with the soil removal. Additional permanganate treatment was focused in the area of MW-5, and a confirmatory sample was collected on Aug. 5, 2008. All VOCs were below CTLs. The injection and monitoring wells were then abandoned in accordance with Florida regulations by Aug. 8, 2008.

Rarely can one single technology provide a complete remedy for a contaminated site. The combination of CHP with sodium permanganate provided a one-two ISCO punch to rapidly eliminate a concentrated PCE source area and reduce the dissolved concentrations below the regulatory standard.

Monitoring has also demonstrated that permanganate had diffused down gradient from the treatment area, providing additional benefit. The total time required from contract execution to injection well abandonment was 286 calendar days (about nine months). The field remediation component (drilling, injection and soil removal) required 101 calendar days, and the remainder was a regulatory review period and post-remediation monitoring. The total remediation cost (excluding post-remediation groundwater sampling conducted by another contractor) was $584,299. Construction was not delayed, and the opening horn of Magic basketball at the Orlando Events Center is moving ahead as planned for October 2010. ***PE***

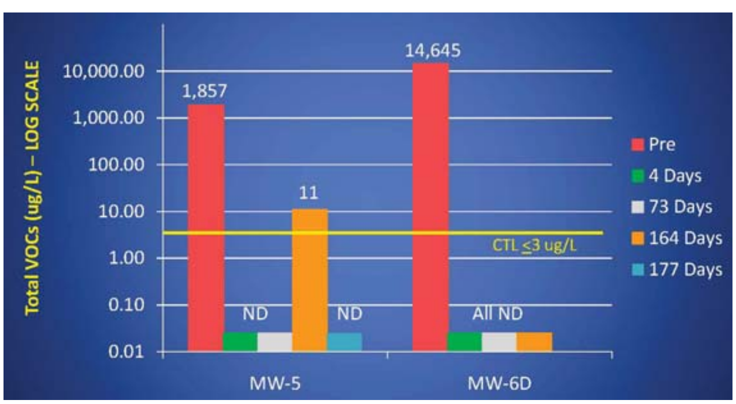


Figure 4 - Monitoring wells MW-5 and MW-6 exhibited the highest levels at the start of the project. The chart above shows the results after ISCO injections.

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