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ORIGINAL ARTICLE

Multiple remediation strategies for halogenated hydrocarbons in fractured limestones at a 9.3 hectare site

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Abstract Between 1975 and 2006, drilling rigs and utility trucks were assembled at the site. The geology and hydrogeology at the site was defined based on subsurface data, soil descriptions and geophysical logs from 38 wells and 3 coreholes. The results of the water samples collected from shallow and deep wells indicate that many wells have concentrations of halogenated hydrocarbons above regulatory standards and that contaminant migration has occurred vertically, laterally, and along strike. Impacted groundwater covers most of the property and has migrated to 68.5 m below land surface. Two pilot studies (one bench-scale and one on-site) have been completed to evaluate the application of technologies in addressing contamination of shallow and deep groundwater at the site underlain by the Conasauga Formation.

Keywords Karst · Halogenated hydrocarbons · Hydrogeology · Remediation

Introduction

Two areas of groundwater contamination were identified at the site: the Paint Building Area and the Southwest Corner (Fig. 1). Because of the variable movement of groundwater contamination in these two areas (laterally, vertically, and along strike), different alternatives were selected for consideration for remedial design: accelerated in situ bioremediation in the Paint Building Area, and a combination of in-well technologies of air sparging, air stripping with vacuum extraction Accelerated Remediation Technologies (ART), LLC (ART) (personal communication) in the Southwest Corner.

Geology

The site is located in the Birmingham–Big Canoe Valley Physiographic District of the Alabama Valley and Ridge Physiographic Section. Structure is characterized by large thrust fault ramps and associated folding. The most prominent structural features in the area include the Birmingham Anticlinorium, the Cahaba Synclinorium and the Coosa Synclinorium. Published mapping (Kidd 1979), shows that the site is approximately 0.40 km southeast of the hinge of the Murphrees Valley Anticline.

The Cambrian age Conasauga Formation with thickness ranging between 335 and 580 m underlays the site and consists of finely crystalline limestone with minor quantities of interbedded dolomite and shale. The shale of the Conasauga usually occurs as thin beds/laminae separating carbonate units (Rindsberg et al. 2003). At the site the limestone strike is N 25° E–N 30° E, and dip is 8°–23° SE (Ponta and George 2008).

The Conasauga Formation is comprised of beds of low-porous limestone with groundwater occurrence and movement along secondary features (bedding planes and fractures). Small vugs and some fractures containing calcite and stylolites are common in the Formation. A thin residuum (0.6–9 m thick) of clay and silty clay covers the Conasauga Formation (Ponta and George 2008).

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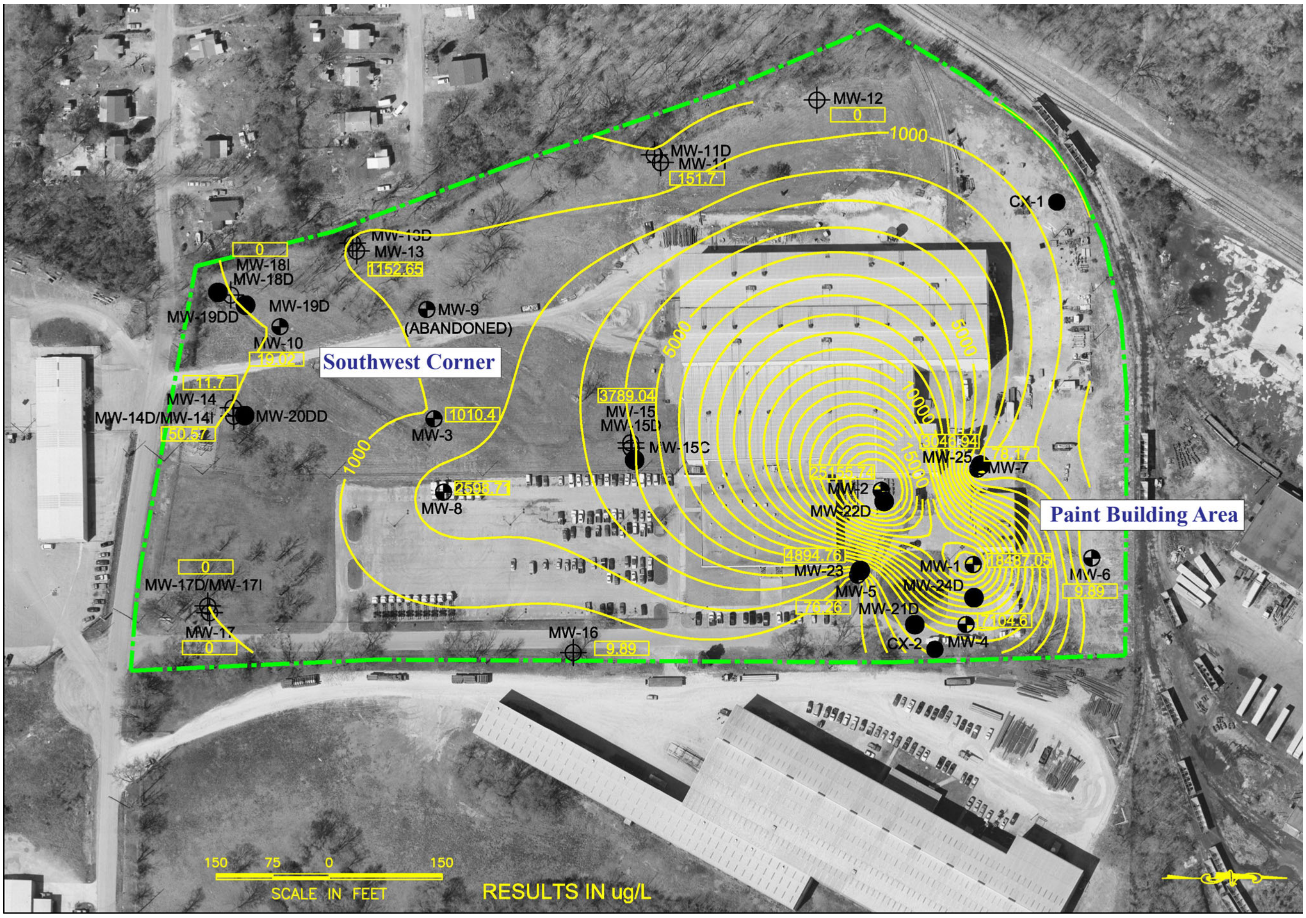


Fig. 1 Total organic compounds in groundwater: shallow wells, January 2007

Site characteristics (hydrology and contamination)

Groundwater contour maps generated using water levels measured in monitoring wells indicate that the direction of groundwater movement is generally towards to the south/southeast, consistent with the bedrock dip. Groundwater quality data, from multiple and iterative rounds of sampling, indicate that the migration of halogenated hydrocarbons has occurred along strike. The contaminated groundwater encompasses most of the site and has migrated downward to at least 68.5 m below land surface (Ponta and George 2007).

VOCs have been identified in groundwater in two general locations at the site. The location with the most significant concentrations is the former paint shop area in the northeast portion of the property (Paint Building Area). VOCs are present in shallow groundwater at 10 s of milligrams per liter (mg/L) concentrations, with concentrations decreasing with depth. The groundwater data indicates the presence of source solvents PCE, TCE, and 1,1,1 TCA and also indicates the presence of significant amounts of degradation products of these compounds. The presence of these degradation products indicates that an active, naturally-occurring anaerobic degradation process is occurring in this area.

VOCs have also been detected in groundwater at the southwestern property boundary. This area is an "along strike" or "down strike" location of the property (i.e., groundwater is migrating to this location from other locations on the property). VOCs have been detected in the shallow groundwater at relatively low concentrations, but concentrations of total VOCs within the deeper zones exceeds 1 mg/L in certain wells and the VOCs are dominated by the degradation products of PCE, TCE and 1,1,1-TCA.

The results of groundwater analysis are illustrated in contour maps of total organic compounds (TOC) from sampling events in January 2007 and June 2010 (Figs. 1, 2, 3, 4). Illustrated are results for both the shallow and deep wells. The TOC is the sum of the organic compounds detected in groundwater samples from each well (shallow and deep).

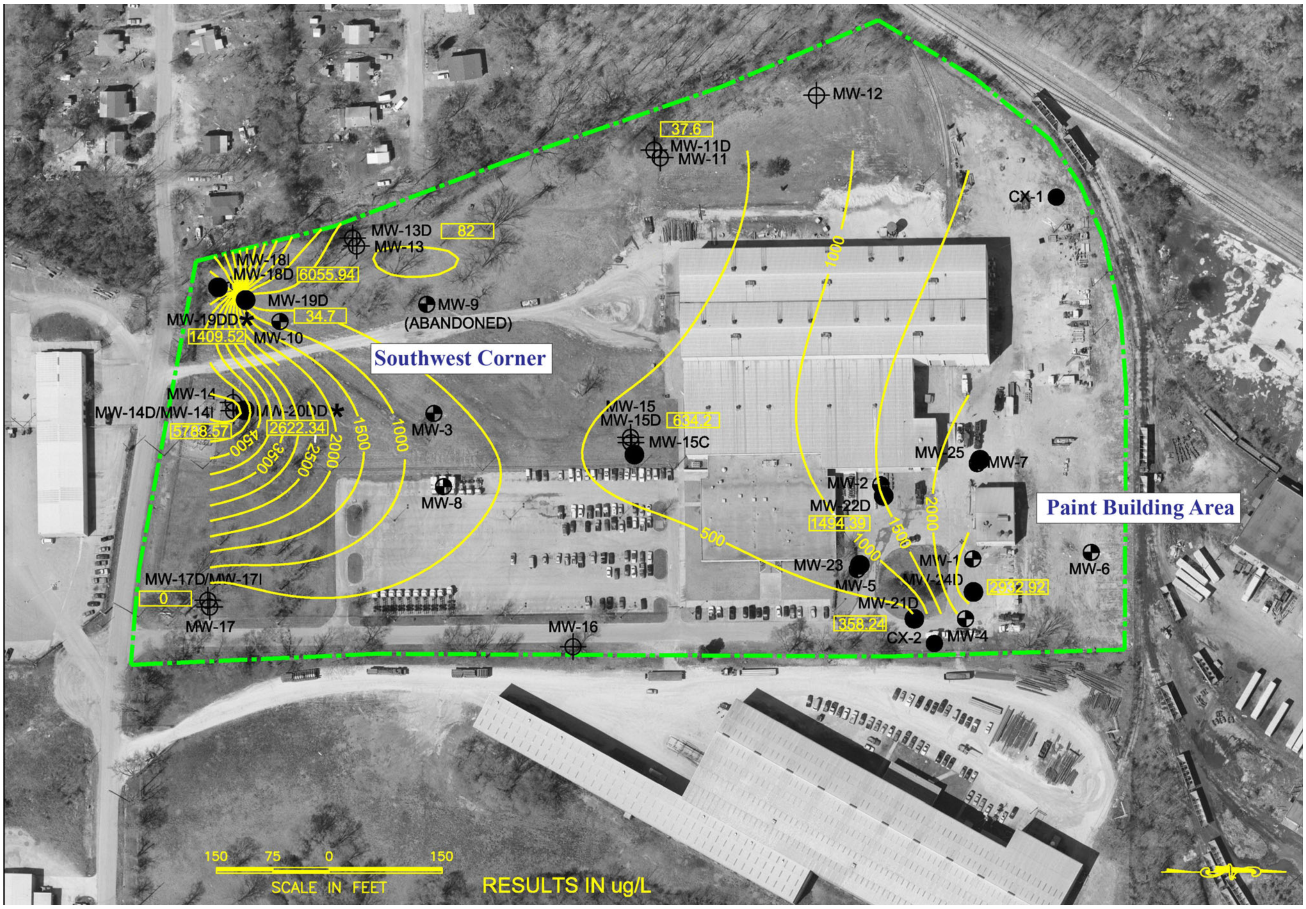


Fig. 2 Total organic compounds in groundwater: deep wells, January 2007

Remediation alternatives

Because of the heterogeneous characteristics of the Conasauga Formation, and the varying lateral and vertical nature of groundwater contamination as indicated at the Paint Building Area and the Southwest Corner, a single method is not appropriate for groundwater remediation at the site. Based on an evaluation of the site conditions, potential receptors at and adjacent to the site and the review of the available remedial technologies for the contaminants identified different alternatives for the Paint Building Area and the Southwest Corner serve as the best remedial actions. The following remedial alternatives have been considered: accelerated in situ bioremediation at the Paint Building Area, and a combination of in-well technologies of air sparging, air stripping with vacuum extraction (ART Technology) in the Southwest Corner.

The phased approach to achieving this goal was first the completion of bench-scale testing at the Paint Building Area and on-site pilot testing (Southwest Corner).

Bench-scale testing

Groundwater data demonstrates that degradation of contaminants is occurring naturally, and a healthy population of microorganisms is present in the shallow groundwater at the source area of contamination at the Paint Building Area. Acceleration of natural attenuation of contaminants such as TCE, PCE and 1,1,1-TCA via subsurface injection of a substrate "recipe" [promotes stimulation of the indigenous microbes] to enhance the in situ bioremediation of contaminants through a process called anaerobic reductive dechlorination (ARD). The treatment is designed and implemented by Environmental Alliance, Inc. (personal communications) to promote expedited remedial results in treating such contaminated groundwater. A bench-scale treatability study was completed to determine the viability of ARD and provide recommendations for design and full-scale implementation.

The results of the microcosm study for groundwater samples from MW-1 (see Figs. 1, 3 for location) indicated that Dehalo-coccoides (dechlorinating bacteria) are present in the

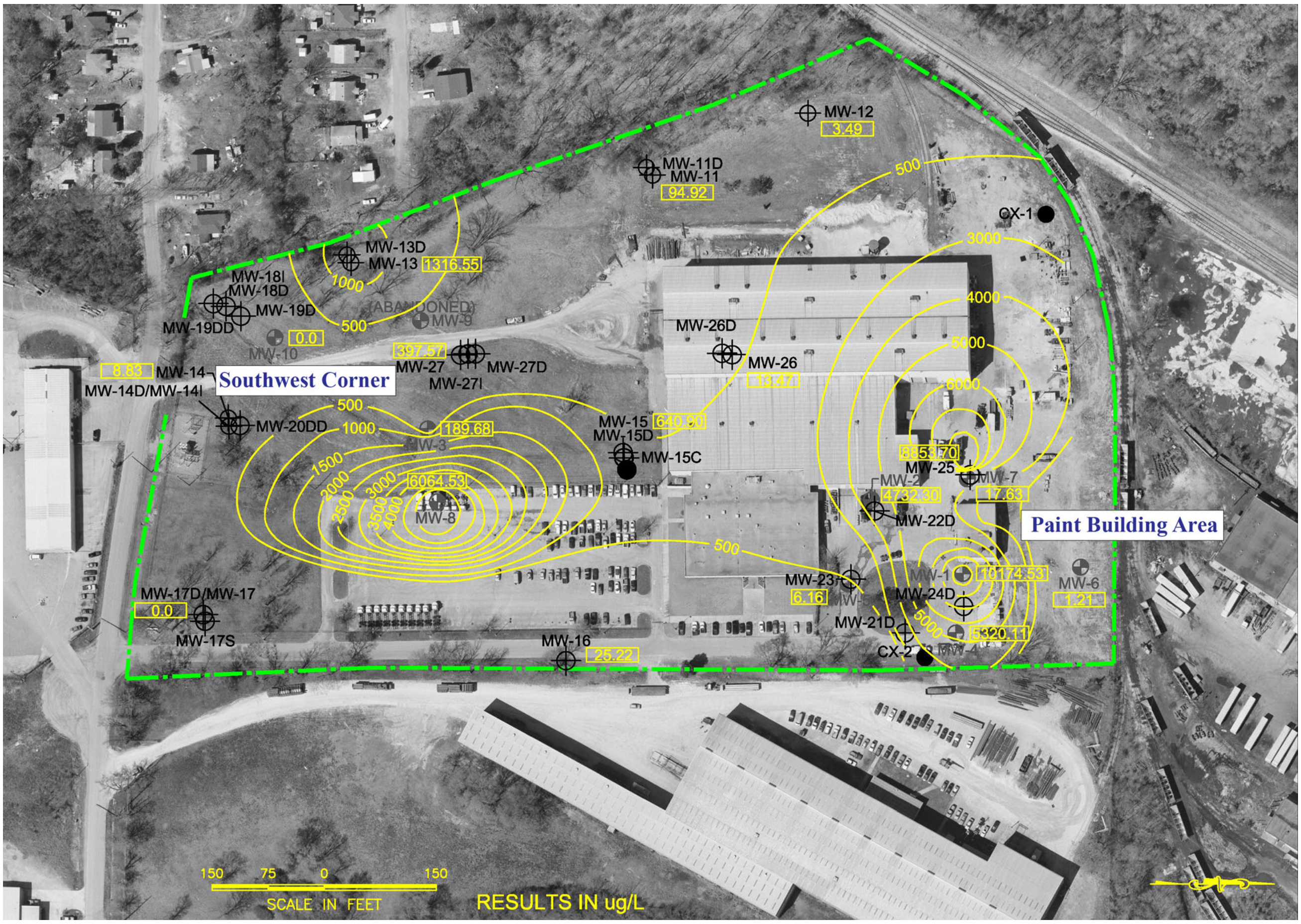


Fig. 3 Total organic compounds in groundwater: shallow wells, June 2010

aquifer and capable of dechlorinating the identified PCE and TCE to ethene provided the proper donor substrate (lactate or corn sweet) can be delivered to the aquifer. However, TCA-dechlorinators were not active throughout the study, therefore affecting no dechlorination of TCA in the microcosm. Results of the bioaugmented microcosm for MW-1 demonstrated successful degradation for all of the constituents of concern to ethane within 85 days. These results demonstrate that the site conditions for the shallow aquifer (representative of the conditions for MW-1—screen interval from 2. 8 to 5.8 m below land surface) are suitable for ARD without bioaugmentation for PCE and TCE. The results further demonstrate that the site conditions are suitable for the implementation of ARD, including TCA, as long as bioaugmentation is also included in the ARD program.

The microcosm results for MW-22D (see Figs. 2, 4 for location) provided materially different results from the results for MW-1. The groundwater from MW-22D (screened interval from 28.7 to 31.7 m) was reported at a pH of 9.8, versus a pH of 7.1 for the groundwater from MW-1. This elevated pH required that the microcosm study for MW-22D be modified (relative to the microcosm study for MW-1) to allow for the adjustment of the pH to approximately neutral. Results of the microcosm performed on MW-22D demonstrated that the microbes capable of dechlorinating the identified contamination are not likely present in the deeper aquifer. Dechlorination was not observed in any of the microcosms with the exception of the bioaugmented microcosm with the pH adjusted to 7.0 standard units. These results indicate that in order for ARD to be successful in the deeper part of the aquifer, bioaugmentation and adjustment of the pH would be required.

Based on the results of the microcosm studies on the shallow (to about 9 m below land surface) and deep (from about 10 to 68.5 m below land surface) water-bearing zones, it has been determined that ARD can be implemented on the shallow water-bearing zone represented by MW-1. ARD can be implemented by injecting a suitable substrate to generate anaerobic conditions in the shallow water-bearing zone, followed by bioaugmentation. The results of the microcosm study for MW-22D documented that ARD can only be implemented through the injection of suitable substrates, bioaugmentation and the adjustment of the pH in the deeper water-bearing zone to a

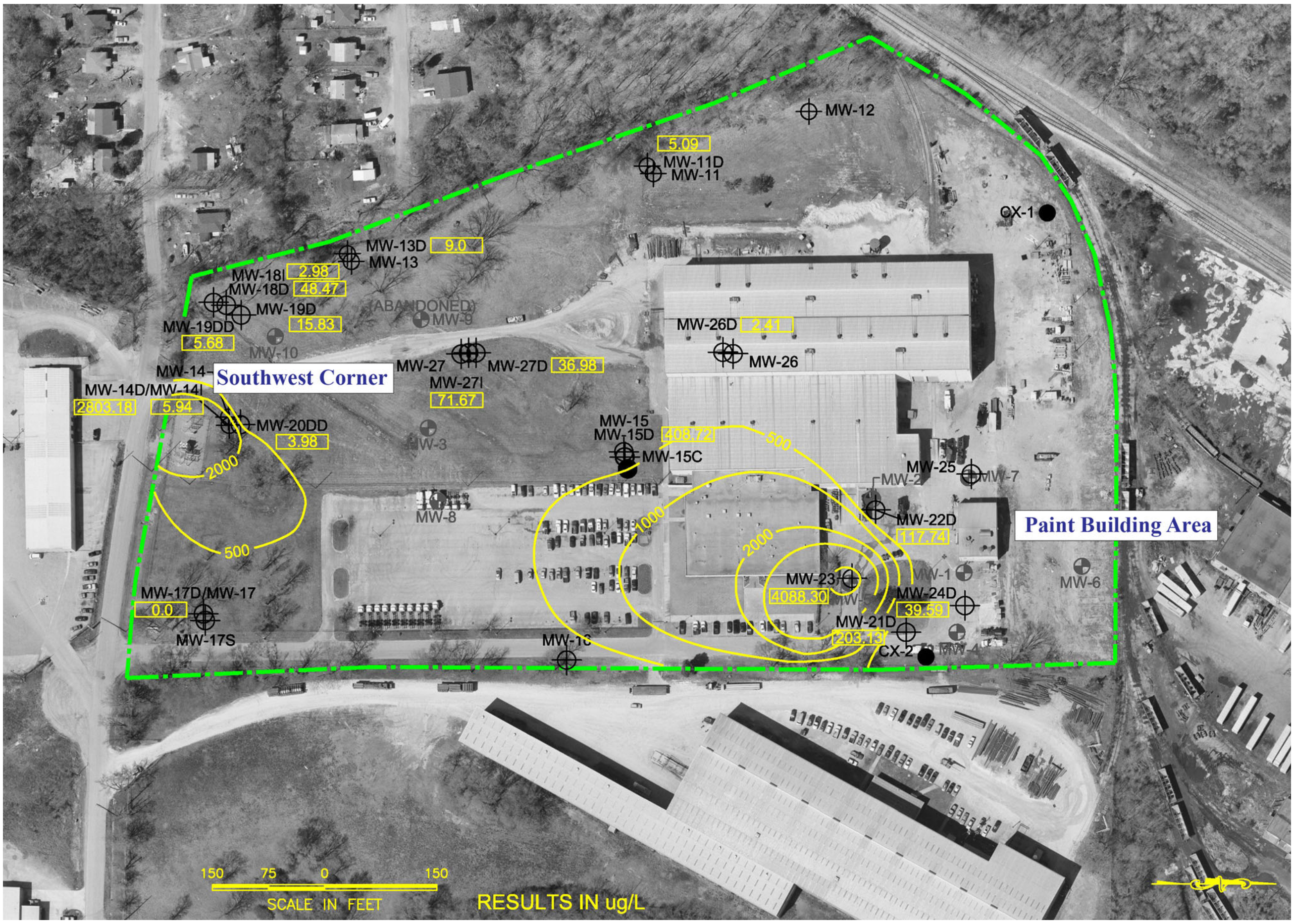


Fig. 4 Total organic compounds in groundwater:deep wells, June 2010

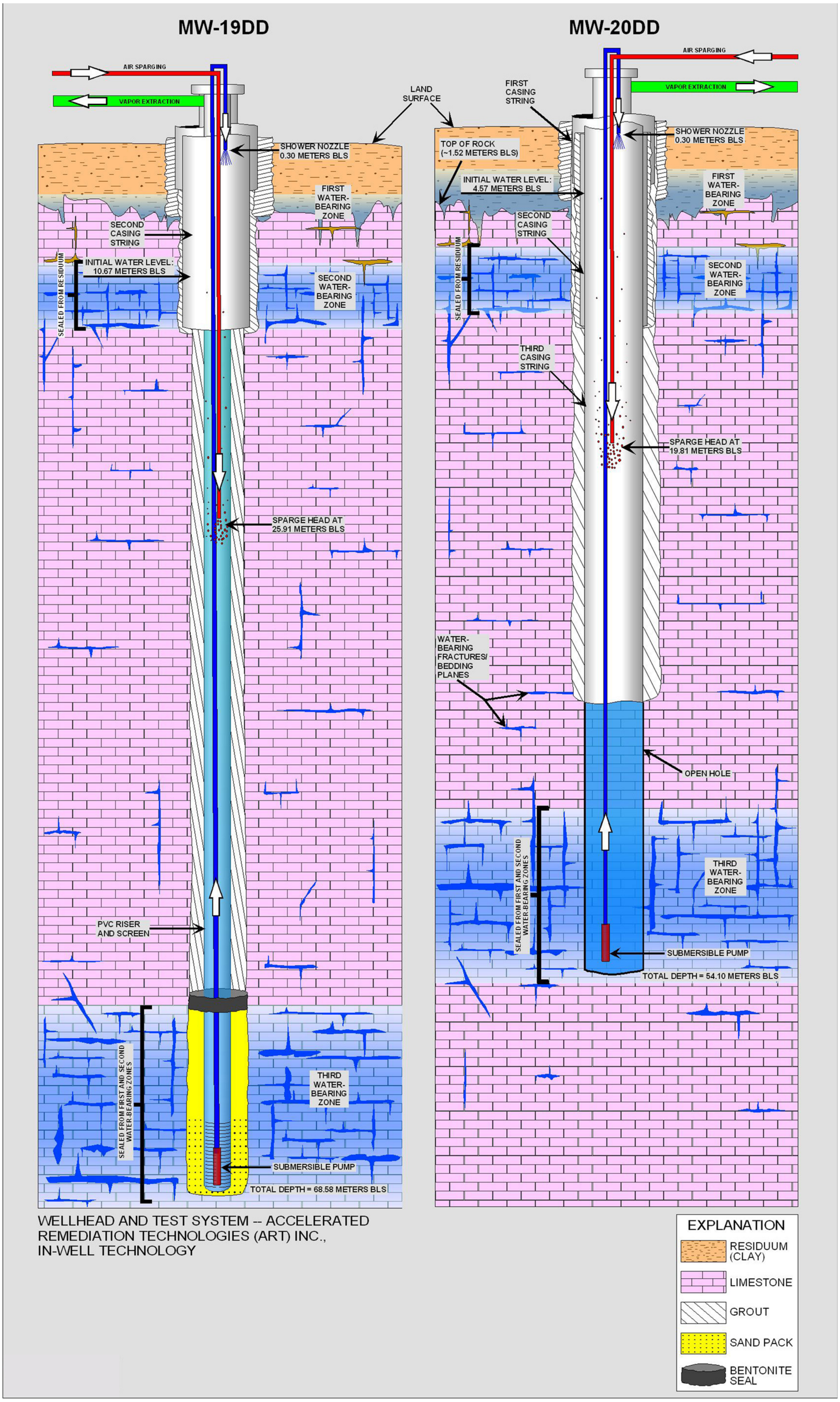
neutral pH. Attempting to lower the pH of the deeper water-bearing zone to something approaching neutral is not considered feasible.

Based on the results of the microcosm study, substrate injections using a lactate based substrate and bioaugmentation of the aquifer are planned for the shallow water-bearing zone. The substrate injections would be performed to stimulate the growth of the native bacteria population and facilitate the development of appropriate anaerobic aquifer conditions in preparation for bioaugmentation. Bioaugmentation would be performed to increase the development of a microbial population capable of degrading PCE, TCE and TCA to their end products. The ARD technologies are considered for implementation at strategically located injection points in the source material, in the shallow aquifer in the vicinity of the Paint Building Area.

On-site pilot testing/in-well technologies

In keeping with the recommended action of applying multiple remedial methods to address the VOCs in groundwater, on-site pilot testing employing an integration of technologies was completed at the Southwest Corner in wells MW-19DD and MW-20DD (see Figs. 2, 4). The Accelerated Remediation Technologies, Inc. (ART Technology) combines in situ air stripping, air sparging, and soil vapor extraction. A schematic of the well head and in-well test system is provided in Fig. 5. The system is designed to accommodate a four inch well and is cost effective when compared with other remediation technologies.

The air sparging component results in reduced water density and lifting (mounding) of the groundwater in the vicinity of the well. This causes a negative gradient to the well resulting in water flowing back towards the well. Vacuum pressure (the vapor extraction component) is applied atop of the well point to extract vapor from the subsurface. The negative pressure from vacuum extraction creates additional water mounding, and removes vapors from the well annulus. The soil vapor extraction (SVE) and sparging technologies combined in the same well further enlarge the radius of influence (Odah 2005).


MW-19DD
MW-20DD
AIR SPARGING
VAPOR EXTRACTION
LAND SURFACE
FIRST CASING STRING
SHOWER NOZZLE 0.30 METERS BLS
TOP OF ROCK (~1.52 METERS BLS)
INITIAL WATER LEVEL: 4.57 METERS BLS
FIRST WATER-BEARING ZONE
SECOND CASING STRING
SECOND WATER-BEARING ZONE
INITIAL WATER LEVEL: 10.67 METERS BLS
SEALED FROM RESIDUUM
THIRD CASING STRING
SPARGE HEAD AT 19.81 METERS BLS
SPARGE HEAD AT 25.91 METERS BLS
WATER-BEARING FRACTURES/ BEDDING PLANES
OPEN HOLE
THIRD WATER-BEARING ZONE
SEALED FROM FIRST AND SECOND WATER-BEARING ZONES
SUBMERSIBLE PUMP
TOTAL DEPTH = 54.10 METERS BLS
PVC RISER AND SCREEN
TOTAL DEPTH = 68.58 METERS BLS
WELLHEAD AND TEST SYSTEM -- ACCELERATED REMEDIATION TECHNOLOGIES (ART) INC., IN-WELL TECHNOLOGY
EXPLANATION
RESIDUUM (CLAY)
LIMESTONE
GROUT
SAND PACK
BENTONITE SEAL

◀**Fig. 5** Schematic of pilot test wells

As shown in Fig. 5, a submersible pump was installed at the bottom of each well to re-circulate water to the top and discharge downward through a spray head. The water then cascaded down the interior of the wells. Enhanced stripping via air sparging at depth in each well occurred simultaneously. In essence, each well served as a subsurface air stripping tower. In addition to the air stripping resulting from the pumping/cascading, the pumped, stripped, highly oxygenated water flowed down the well and over the mounded water back into the aquifer, hydraulically enhancing the radius of influence. These combined synergistic technology effects set up a circulation zone surrounding each well to further enhance remediation.

Contour maps of TOCs in deep groundwater before and after the pilot test illustrate the vertical and horizontal migration/degradation of the constituents (Figs. 2, 4). The analysis of samples from the two wells during the 3 months pilot test period indicated TOCs diminishing from over 2000 ug/L to near non-detected. The ART Technology was considered for implementation at a system of wells at the Southwest Corner to contain/control and treat the deep groundwater contamination.

Conclusions

1. Groundwater data demonstrates that degradation of contaminants is occurring naturally, and a healthy population of microorganisms is present in the shallow groundwater at the source area of contamination. A bench-scale treatability study was completed to determine the viability of ARD and provide recommendations for full-scale implementation in the source material in the northern portion of the property (Paint Building Area).
2. The analysis of groundwater samples from wells during the pilot test period indicated TOC concentrations diminishing to near analytical detection limits. The pilot study results provide sufficient data for development of remedial design for a system of wells at the Southwest Corner to contain/control and treat the deep groundwater contamination.

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