Remediating TCE-Contaminated Groundwater in Low-Permeability Media Using Hydraulic Fracturing to Emplace Zero-Valent Iron/Organic Carbon Amendment

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A field pilot test in which hydraulic fracturing was used to emplace granular remediation amendment (a mixture of zero-valent iron [ZVI] and organic carbon) into fine-grained sandstone to remediate dissolved trichloroethene (TCE)-contaminated groundwater was performed at a former intercontinental ballistic missile site in Colorado. Hydraulic fracturing was used to enhance the permeability of the aquifer with concurrent emplacement of amendment that facilitates TCE degradation. Geophysical monitoring and inverse modeling show that the network of amendment-filled fractures extends throughout the aquifer volume targeted in the pilot test zone. Two years of subsequent groundwater monitoring demonstrate that amendment addition resulted in development of geochemical conditions favorable to both abiotic and biological TCE degradation, that TCE concentrations were substantially reduced (i.e., greater than 90 percent reduction in TCE mass), and that the primary degradation processes are likely abiotic. The pilot-test data aided in re-evaluating the conceptual site model and in designing the full-scale remedy to address a larger portion of the TCE-contaminated groundwater plume. © 2012 Wiley Periodicals, Inc.

INTRODUCTION

In situ chemical reduction and bioremediation via anaerobic reductive dechlorination (ARD) are effective and widely applied remediation methods for chlorinated solvent–contaminated groundwater and soils. *In situ* groundwater remediation is often accomplished by injecting liquid or particulate reactive amendments to stimulate biological and/or abiotic degradation mechanisms. This approach is challenging to apply in low- to moderate-permeability media due to the difficulty in distributing amendments in the targeted treatment zone. Amendment delivery methods for *in situ* remediation in low-permeability media include permeation dispersal, soil mixing, electrokinetics (Walden, 1997), direct push, and hydraulic or pneumatic fracturing (Christiansen et al., 2010; Murdoch & Wilson, 1994; Schuring, 2002).

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Published online in Wiley Online Library (wileyonlinelibrary.com). DOI: 10.1002/rem.21310

This article describes a field pilot test in which hydraulic fracturing was used to emplace granular remediation amendments into low-permeability sandstone/siltstone to remediate trichloroethene (TCE)-contaminated groundwater. The amendment used, EHC-G® (Adventus Americas, Inc., Freeport, Illinois), is a mixture of zero-valent iron (ZVI) and organic carbon. The pilot test included:

1. Creating a network of fractures throughout the high-TCE concentration portion of a groundwater plume and filling those fractures with the granular remediation amendment;
2. Determining the location, orientation, and dimensions of the fractures;
3. Monitoring the effect of amendment emplacement on groundwater geochemistry, concentrations of TCE, and abiotic and biotic degradation products; and
4. Predicting the longevity of the remediation amendment.

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Traditional *in situ* remediation approaches would have been challenging at this site due to the low to moderate permeability of the bedrock aquifer and slow groundwater flow velocities. The area affected by each well from which fractures are propagated is much larger than that expected by other methods for injecting granular amendments into the subsurface, which results in a relatively low unit cost for treatment. An important feature of this technology is that it can be applied at virtually any depth.

Hydraulic Fracturing for Environmental Remediation

Hydraulic fracturing originated in the petroleum industry in 1948 and is used to significantly increase oil and gas production rates in petroleum reservoirs. Hydraulic fracturing is the process of creating new fractures by increasing pore pressure so that it exceeds the overburden pressure and tensile strength of rock. Increasing pore pressure also causes existing fractures to dilate. In a typical oil and gas application, coarse sand is injected into the new or existing fractures to "prop" them open when pore pressure declines back to ambient pressure, and the propped fractures act as high-permeability preferential pathways for fluid flow.

In the 1990s, hydraulic fracturing was identified as a promising technique for enhancing *in situ* remediation processes in soils with moderate permeability (i.e., greater than 100 millidarcys or 10^{-6} meters/second equivalent hydraulic conductivity) (Murdoch & Wilson, 1994; Walden, 1997). Environmental hydraulic fracturing was initially applied to accelerate site cleanups with conventional physical remediation technologies, such as soil vapor extraction, multiphase extraction, and pump-and-treat. In the new millennium, hydraulic fracturing has been increasingly used not only for increasing permeability and enhancing physical extraction, but also to improve delivery of chemical and biological treatment amendments into contaminated soil, bedrock, and groundwater aquifers (Martin, Brennan, Sorenson, Peterson, & Bures, 2002; Sorenson, Martin, Brennan, & Bures, 2002). Hydraulic fracturing can aid in overcoming geologic constraints that limit adequate *in situ* delivery of substrates and/or nutrients required for sustained microbial metabolism or oxidative/reductive reactions in the subsurface environment (G. Lu & Zheng, 2003). In particular, a major limitation on the effectiveness of *in situ* treatment processes is achieving adequate distribution of treatment amendments beyond the

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injection point and into the contaminated soil mass and groundwater (Nyer & Page, 2004; Simpkin & Norris, 2010). Hydraulic fracturing has been shown to effectively distribute amendment around an injection zone (Martin et al., 2002; Sorenson et al., 2002); however, the fractures can have a random orientation and may propagate to previously installed monitoring wells that provide a pressure relief during injections (Suthersan, Horst, Nelson, & Schnobrich, 2011). During this pilot test, pressure relief was not observed through completed monitoring wells but rather through open boreholes predrilled for fracturing activities, which served as a method to confirm the radius of influence of fracture propagation and amendment emplacement. An overall limitation of hydraulic fracturing for environmental remediation is the inability to accurately control the final placement of injected treatment amendments relative to the distribution of subsurface contaminants.

Site Description

The F.E. Warren Air Force Base, Former Atlas "E" Missile Site No. 12 (Atlas 12), located outside of Windsor, Colorado, was an operational intercontinental ballistic missile (ICBM) launch facility from October 1960 to March 1965. Periodic missile launch "readiness exercises" included preparing an ICBM for launch by filling both fuel and oxidant tanks. Following missile readiness exercises, missile tanks were drained to remove residual RP-1 rocket fuel, a high-grade kerosene-based fuel, and the tanks and transfer lines were flushed with approximately 25 gallons of TCE to remove residual fuel. Waste TCE and residual rocket fuel were discharged to a wastewater drainage sump that also accumulated storm runoff. Accumulated storm runoff water, TCE, and fuel may have flowed from the sump into the foundation drain system and entered the subsurface, and were also periodically pumped from the sump and released to a drainage pond at the ground surface.

An overall limitation of hydraulic fracturing for environmental remediation is the inability to accurately control the final placement of injected treatment amendments relative to the distribution of subsurface contaminants.

These historical wastewater and runoff disposal activities, along with ongoing irrigation to maintain this site as a recreational facility, resulted in a TCE-contaminated perched groundwater body with a saturated thickness up to 30 feet. The perched groundwater body encircles the missile launch and service building and extends approximately 900 feet from the building. A hydraulic fracturing pilot test was conducted in the high-concentration TCE source area surrounding the building and at two locations in the lower-concentration distal zone (i.e., the portion of the contaminated water body outside the primary source area). TCE concentrations at these locations ranged from 400 to 3,600 μg/L (Exhibit 1). TCE is the primary contaminant of concern, and some of its biodegradation products (*cis*-1,2-dichloroethene [DCE] and vinyl chloride) were also detected. TCE is believed to be present only in the dissolved phase, and no concentrations in soil cores or groundwater are high enough to indicate that TCE is present as a dense nonaqueous-phase liquid.

Geology/Hydrogeology

The Atlas 12 site is underlain by a surficial terrace deposit and/or a layer of loess that overlies the Cretaceous Fox Hills Sandstone Formation. The Fox Hills Sandstone is interlayered fine-grained sandstone and siltstone that extends to a depth of approximately 40 to 60 feet below grade. Unconfined groundwater within the Fox Hills Sandstone is perched above the lower-permeability rocks of the Pierre Shale Transition Zone. Depth to

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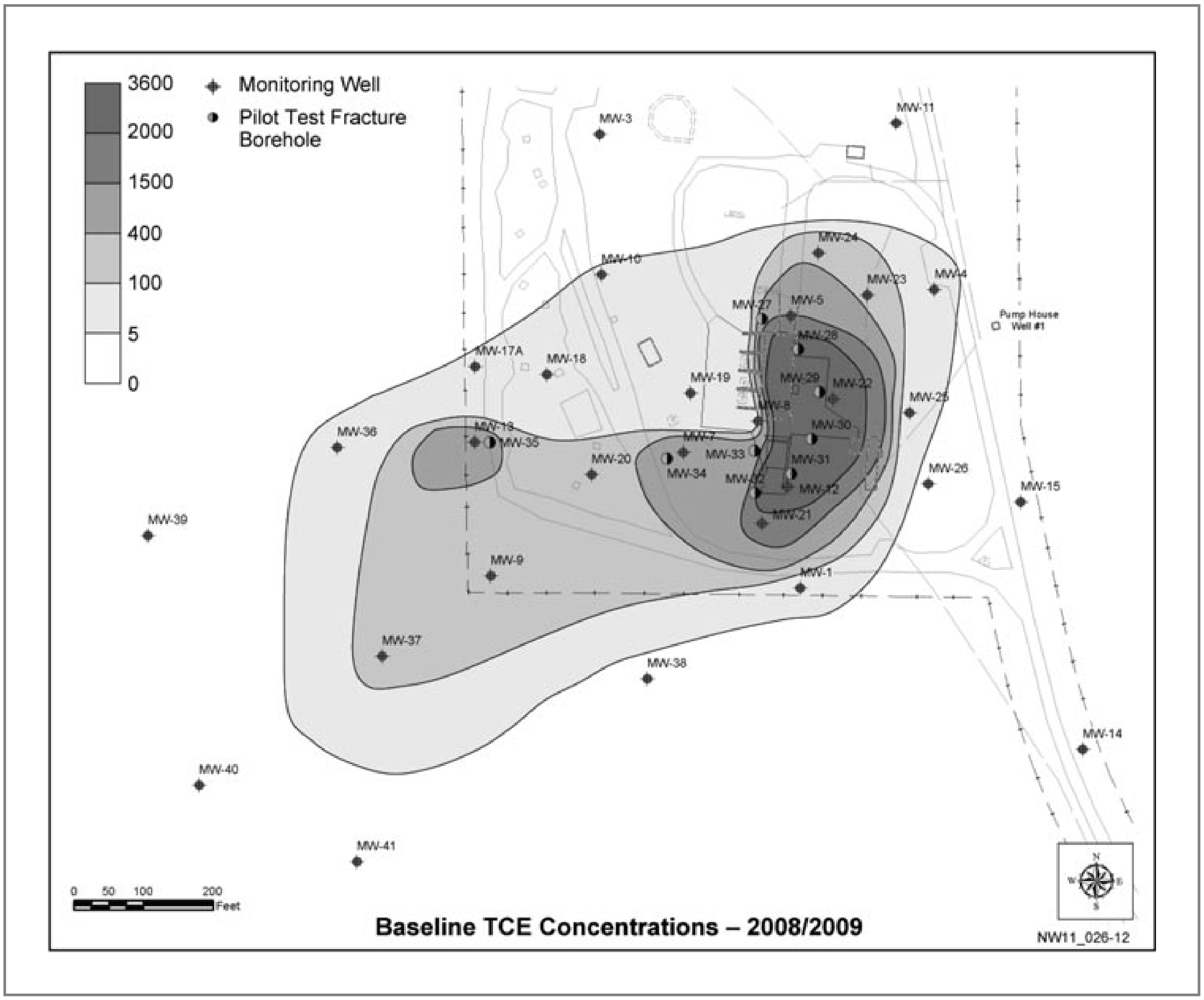

Exhibit 1. Baseline TCE concentrations and locations of pilot-test injection wells

the water table in the Fox Hills Sandstone at the Atlas 12 site ranges from approximately 30 to 45 feet below grade.

Water-table elevations indicate that the perched groundwater system is a radial system with minimal flow velocities centered at the former launch and service building. The site is currently used as a public park and has two septic systems that service the caretaker's residence and restrooms. Recharge is derived primarily from landscape irrigation, storm water runoff, and wastewater discharged to the septic systems. Natural recharge is relatively insignificant (see additional details in the Conceptual Site Model Development and Refinement section).

Geochemistry

The geochemistry of the Fox Hills Sandstone water body at the Atlas 12 site prior to the pilot test indicated that the conditions were aerobic to mildly anaerobic, with low dissolved oxygen (DO) concentrations (i.e., 2.9 ± 1.9 mg/L, average ± standard deviation), variable oxidation-reduction potential (ORP) values (ranging from –238 to

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162 mV), high sulfate concentrations (924 ± 811 mg/L), low ferrous iron concentrations (0.16 ± 0.17 mg/L), and low nitrate concentrations (13.3 ± 10.3 mg/L). Optimal conditions for the biotic ARD of TCE include depleted oxygen, nitrate, and sulfate; elevated ferrous iron; and production of methane (Wiedemeier et al., 1998). Prior to the pilot test, geochemical conditions at the site were generally not favorable for biodegradation of TCE via ARD. *Dehalococcoides*, the genus of bacteria commonly correlated with chloroethene ARD (Löffler, Sun, Li, & Tiedje, 2000), was not detected in groundwater samples collected before the pilot test.

PILOT TEST

During the pilot test, the entire TCE-contaminated source area (TCE greater than 400 μg/L) was targeted for hydraulic fracturing with concomitant emplacement of the ZVI/organic carbon amendment for long-term *in situ* treatment. The objectives of the pilot test were to:

1. Evaluate the effectiveness of hydraulic fracturing for distributing amendment throughout the contaminant source zone;
2. Estimate the amendment utilization rate and amendment longevity; and
3. Determine the TCE mass reduction in the pilot-test targeted source area.

The pilot-test injection was conducted in April and May 2009, and the effect of amendment emplacement was determined by evaluating 24 months of performance monitoring data.

Design and Implementation

The pilot-test injection consisted of creating discrete fractures at nine boreholes within the TCE source area and emplacing ZVI/organic carbon amendment into the induced fractures (Exhibit 1). Fracture boreholes in the source area were placed 60 feet apart, as fractures were originally expected to propagate 30 feet radially from each borehole. The amendment emplaced during hydraulic fracturing, EHC-G®, was a mixture of soluble, controlled-release organic carbon and zero-valent micro-iron particles designed to stimulate reductive dechlorination of chlorinated solvents. The pilot-test design amendment loading rate of 0.27 percent (mass basis) was determined based on the TCE concentration and volume of bedrock sediments to be treated. Surface tiltmeter geophysics were used to map amendment distribution. The fractures were mapped as planar fractures to verify the amendment distribution in the subsurface.

Fracture boreholes were drilled prior to fracturing at each borehole location. Fracturing was conducted using an EF 9300 skid-mounted fracture unit (Frac Rite Environmental LTD, Calgary, Alberta, Canada) used to mix dry ingredients and potable water to create the injection slurry and to pump the slurry into boreholes at pressures sufficient to fracture the formation, downhole fracturing equipment (pneumatic straddle packers and proprietary fracturing tooling), and an amendment/slurry mixture. The amendment slurry consisted of potable water, EHC-G®, and a food grade, biodegradable, linear protein gel carrier that improves the ability of the slurry to transport the dense iron and organic carbon particles. The slurry was injected into the formation using

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high-pressure positive displacement pumps. Straddle packers were used to isolate a four-foot interval of each borehole (within the 35 to 65 feet below ground surface [bgs] targeted treatment zone). A total of 52 individual fractures were initiated and propagated from seven boreholes in the primary TCE source area. The fracture network in the targeted source area vertically covered the entire saturated thickness within the Fox Hills Sandstone with an average of one fracture per 6 feet. The average concentration of the amendment was 2.2 lbs/gal of fracture slurry emplaced in bedrock. The total mass of amendment emplaced into fractures in bedrock in the source area was 188,085 lbs. Approximately 98 percent of the design injection mass was successfully emplaced in the subsurface, and the remaining 2 percent was lost to the ground surface due to hydraulic communication between an injection interval and an open borehole located over 60 feet away that had been predrilled for fracturing. This unequivocally demonstrates that the radius of influence of fracture propagation and amendment emplacement was at least 60 feet.

A total of 10 individual amendment fractures were successfully initiated and propagated to emplace a total amendment mass of 13,864 lbs using methods similar to those used in the source area.

As part of this pilot test, amendment was also emplaced within two boreholes located in the distal zone where TCE concentrations were greater than 400 μg/L (Exhibit 1) but had lower maximum concentrations than those observed in the source area. A total of 10 individual amendment fractures were successfully initiated and propagated to emplace a total amendment mass of 13,864 lbs using methods similar to those used in the source area.

Fracture Mapping

The ground surface deflects during hydraulic fracturing initiation and amendment emplacement. These angular deflections can be measured using a tiltmeter sensor (Cipolla & Wright, 2000; Warpinksi et al., 1997; Wright et al., 1998). Data from an array of tiltmeters, constrained by the known location of the borehole interval from which a fracture originated, can be interpreted using inverse modeling to identify the location, orientation (strike and dip), horizontal and vertical extent, and aperture of individual fractures. In the pilot test, tiltmeter data were collected during fracture propagation from all seven boreholes completed within the primary high-concentration TCE source area. Geophysical data from tiltmeter arrays were analyzed using inverse parameter modeling (Yang & Davis, 1986) to determine the geometry of fractures, which were modeled as planar disk features. The fracture plots were correlated with operational fracturing data (pressure and flow versus time plots) and transformed into three-dimensional, dynamic computer graphics. The entire fracture network was incorporated into three-dimensional graphical output files that depict both individual fractures and the entire fracture network, from any viewing perspective.

Analysis of the fracture map indicated that 60 percent of the fractures tended to propagate toward the south, typically toward the south-southeast. The average vertical extent of fractures was 79 feet compared to 65 feet horizontal extent. Therefore, the average aspect ratio, defined as the average vertical extent divided by horizontal extent, was 1.21. Tiltmeter mapping results indicated that fracture aspect ratios were greater than 1.0 for the majority of fractures. The median aperture of fractures was 0.33 inch and ranged from 0.01 to 1.46 inches. The average fracture dip angle (inclination from horizontal) for all 52 fractures mapped was 35 degrees. Specifically, the dip angles of the fractures included 6 percent of the fractures dipping at less than 10 degrees, 12 percent at

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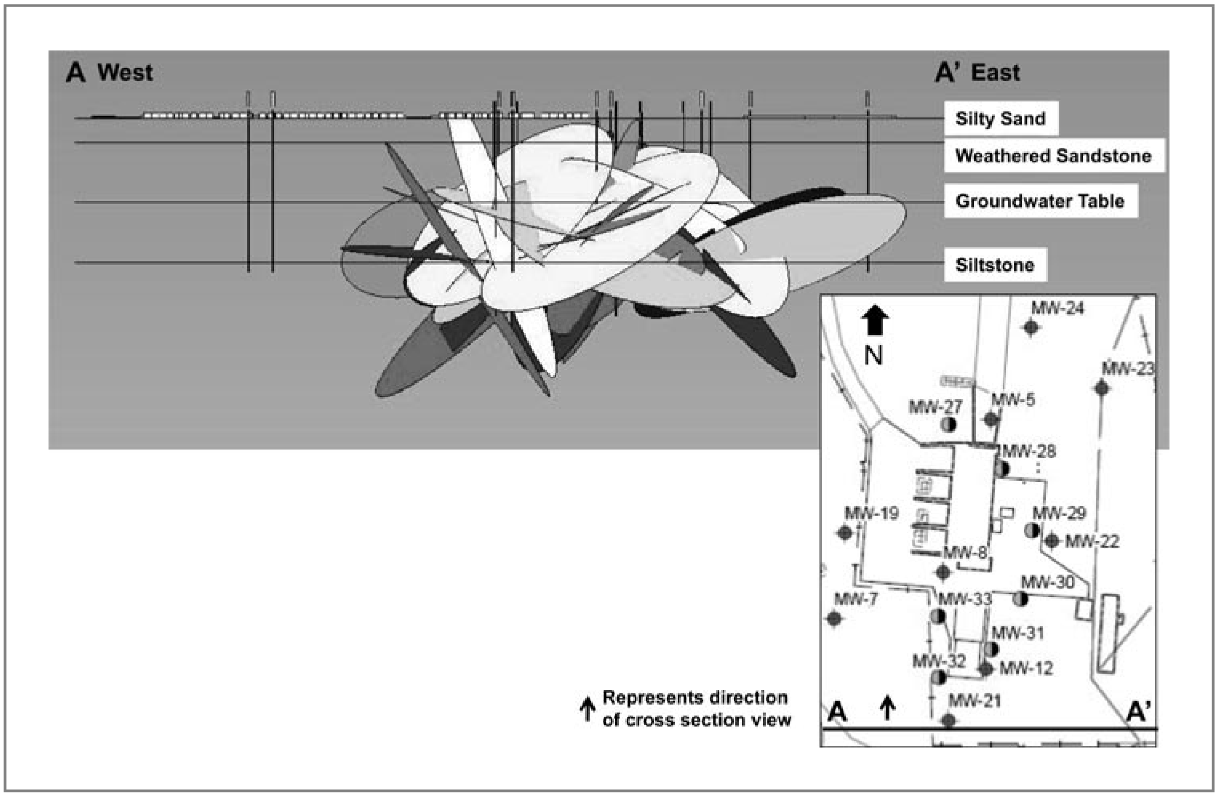

Exhibit 2. Tilt metric mapping of fracture propagation

11 to 20 degrees, 57 percent at 21 to 45 degrees, and 25 percent at 46 to 79 degrees. Therefore, 75 percent of fractures mapped dip 45 degrees or less from the horizontal and none of the fractures were classified as near-vertical (i.e., greater than 80 degrees from horizontal). The preferential direction of fracture propagation, in addition to the moderate dip of most fractures, is likely due to the existing *in situ* stress regime and the horizontal bedding planes in the Fox Hills Sandstone. The average fracture aperture (one-third of an inch) suggests that the amendment was emplaced in sufficient quantity to effectively prop the fractures open and provide fracture longevity over a significant vertical interval of impacted bedrock sediments.

Fracture mapping results were depicted for each individual fracture borehole and the entire fracture network using a 3D graphics model (SolidWorks, Dassault Systèmes SolidWorks Corp., Concord, Massachusetts). Fracture perspectives were aligned for oblique cross-sectional views for individual boreholes (Exhibit 2) and also in plan view for the fracture network (Exhibit 3) emplaced in the source area. Most fractures exhibited aspect ratios close to 1.0, indicating that significant radial fracture coverage was achieved from the point of amendment emplacement.

The hydraulic fracturing conducted during the pilot test created an extensive, overlapping, laterally and vertically interconnected network of 52 individual fractures propagated from seven boreholes in the source area, with some up fractures extending 80 feet from the fracture borehole. This network of fractures provides the potential for significant contact between the TCE-impacted groundwater and the amendment with possible organic carbon diffusion into matrix pores within bedrock sediments.

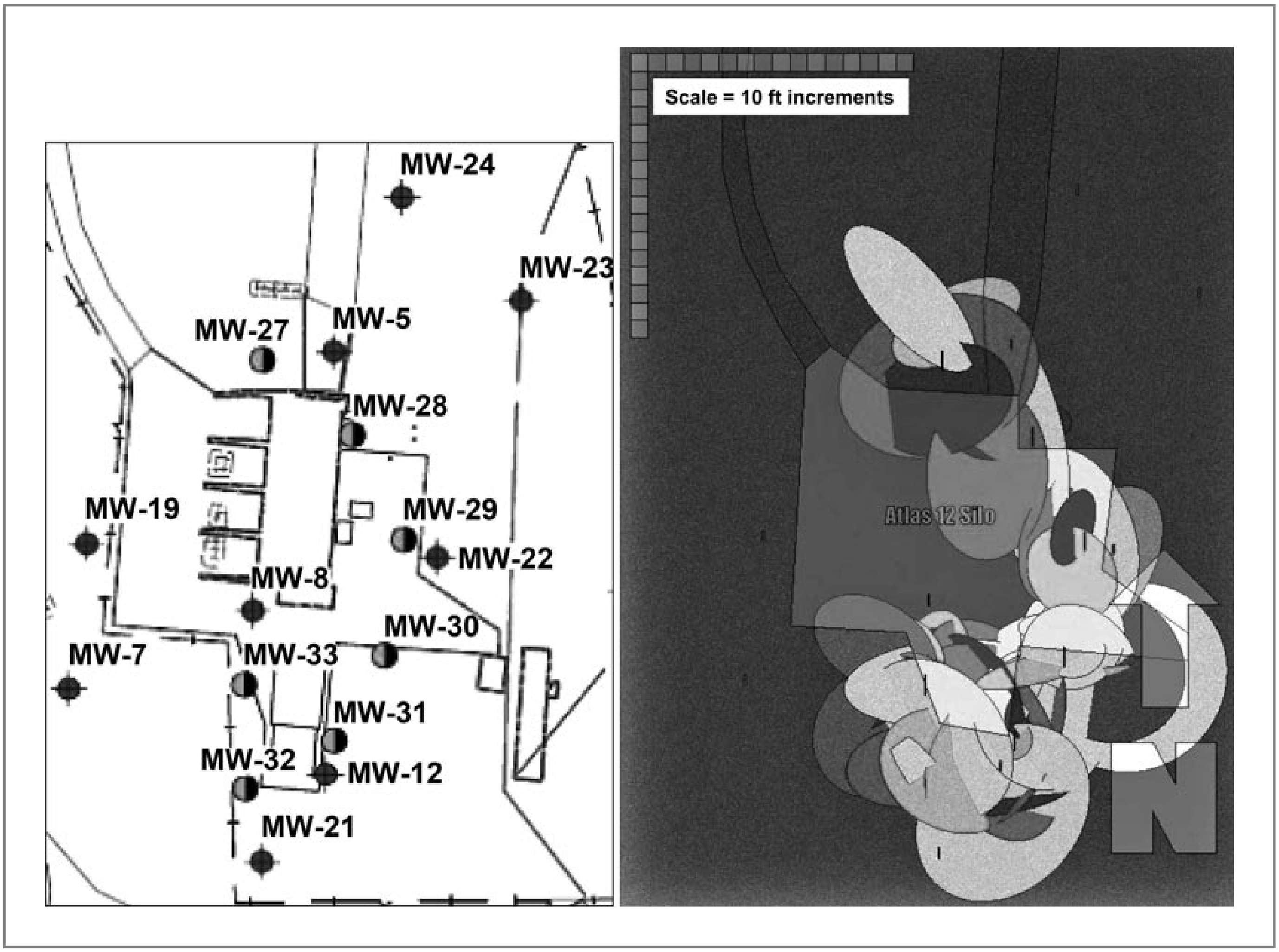

Exhibit 3. Plan view of fracture network

Performance Monitoring and Evaluation

Pre- and post-pilot-test groundwater performance monitoring included routine sampling of 12 to 20 wells inside and outside the pilot-test treatment area. Groundwater samples were collected every three months using low flow sampling techniques. Samples were analyzed for field parameters (dissolved oxygen, oxidation-reduction potential, temperature, pH, and specific conductance), geochemical parameters (dissolved iron, sulfate, nitrate, chloride, phosphate, alkalinity, and total organic carbon [TOC]), volatile organic compounds (VOCs), the microbiology parameter *Dehalococcoides* spp., and dissolved gases (ethene, ethane, and methane). Eight rounds of quarterly monitoring data were collected over the 24 months post-amendment-emplacement time frame.

Emplacement of amendment into the high-concentration TCE source area surrounding the building and the two locations in the lower-concentration distal zone affected groundwater geochemistry by increasing TOC in groundwater, generating more strongly reducing redox conditions, and enhancing TCE degradation. During the 24-month post-injection period, TOC, DO, and ORP decreased in the source area wells

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within the hydraulic fracturing impact area, with concomitant decreases in TCE and production of ethene, while ferrous iron and methane concentrations increased.

Compared to baseline sampling, TOC concentrations were higher after amendment emplacement in areas directly within the fracture network. Specifically, the increase in TOC concentrations observed in the source area wells three months after the pilot-test injection ranged from 500 to 5,500 mg/L, and these increases in concentrations generally corresponded to the amount of amendment injected into nearby boreholes. TOC concentration declines suggest that 84 to 95 percent of the organic carbon in the source area wells had been utilized by nine months after the injection. Dissolved oxygen concentrations decreased to less than 0.5 mg/L by six months after the pilot-test injection and remained below this level over the 24 months of monitoring. Ferrous iron concentrations increased to 2.13 $\pm$ 0.68 mg/L by nine months after the pilot-test injection, while methane concentrations increased from nondetect to 13.71 $\pm$ 4.97 mg/L by 18 months post-pilot-test injection.

Nitrate and sulfate concentrations fluctuated in the source area wells, but nitrate decreased to less than 3 mg/L as nitrogen by 12 months post-injection and sulfate decreased to 118 $\pm$ 137 mg/L by 18 months post-injection. The continued presence of nitrate and sulfate is of concern, as these compounds have been shown to progressively passivate iron surfaces (Li, Benson, & Lawson, 2005; Ritter, Odziemkowski, & Gillham, 2002) or deposit as inorganic species on the iron, thus reducing the overall effectiveness of the treatment and longevity of the remedy. Additionally, the high sulfate concentrations in this water body challenge the effectiveness of the biotic degradation pathways since the organic carbon amendment is short-lived (compared to ZVI), allowing a limited time frame for changing the redox conditions and degrading TCE. However, sulfate has declined or shows concentration fluctuations in the wells directly impacted by hydraulic fracturing activities (11.6 to 245 mg/L). This indicates that the organic carbon amendment likely had a positive impact on the geochemistry to facilitate the success of the abiotic TCE degradation pathway.

In general, VOC concentrations showed significant decline in the source area over the 24 months of monitoring.

In general, VOC concentrations showed significant decline in the source area over the 24 months of monitoring. Pre-pilot-test TCE concentrations within the treatment area ranged from 400 to 3,600 μg/L (Exhibit 1). During the 24 months of post-pilot test monitoring, TCE concentrations declined to between 5 and 110 μg/L in the source area. Plume configurations associated with changes in TCE concentrations over the monitoring period are shown in Exhibit 4. These changes demonstrate initial declines over the first 12 months and slight rebound at month 15; however, concentrations continued to decline by month 18 and remained at the reduced levels. Specifically, monitoring well MW-12, with an initial TCE concentration of 2,300 μg/L, showed reduction to below the TCE maximum contaminant level of 5 μg/L by 15 months after the pilot-test injection and has not shown rebound during the remainder of the 24-month monitoring period. Other significant decreases in TCE concentrations include declines of 92 to 98 percent in wells with the highest initial concentrations of 3,600 μg/L (MW-22), 1,700 μg/L (MW-21), and 1,500 μg/L (MW-5), respectively, within the 24-month monitoring period. Concentrations of *cis*-DCE have declined in some source area wells to below pre-pilot-test concentrations and range from 66 to 97 μg/L; however, concentrations increased in other locations, providing evidence of biotic ARD TCE degradation.

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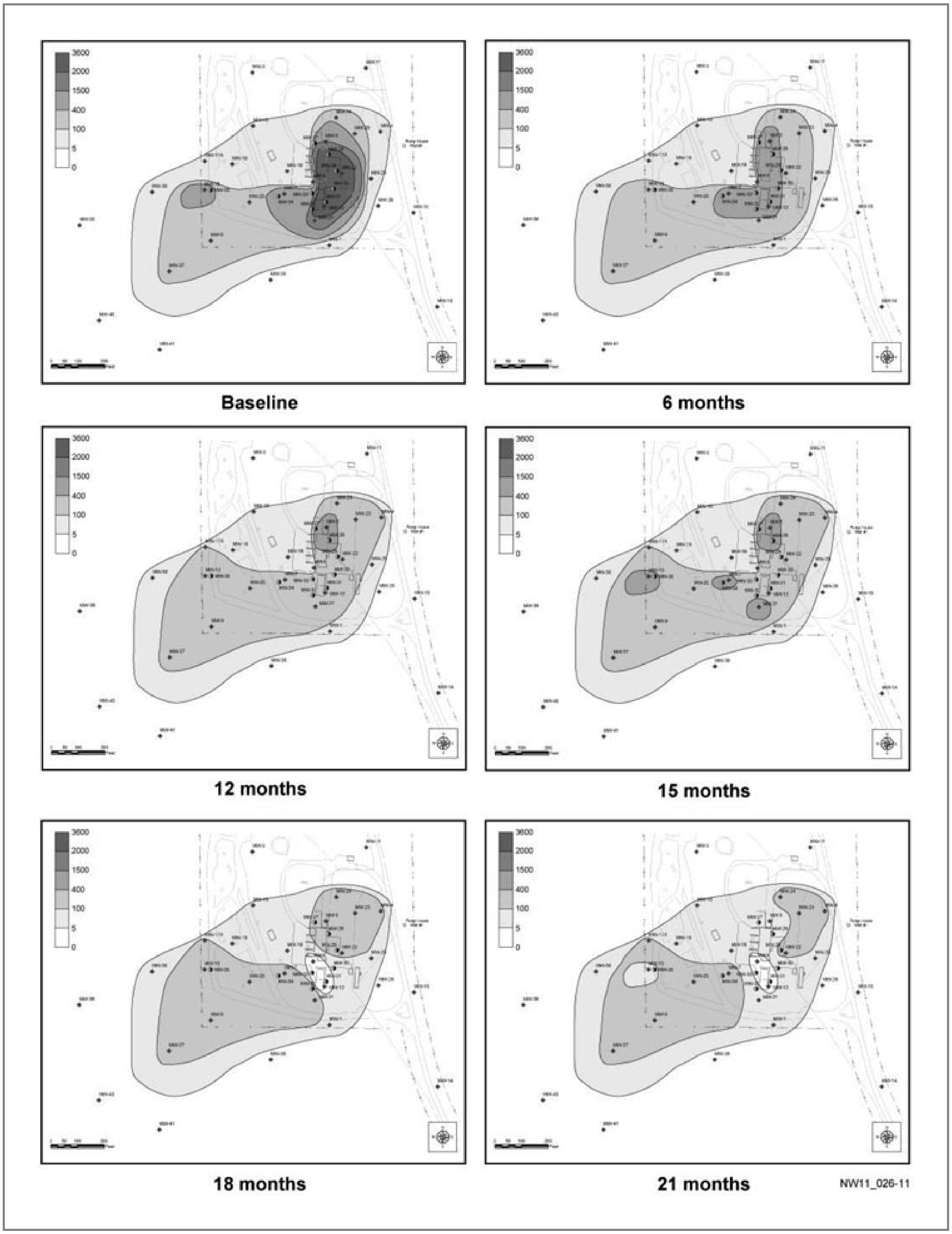

Exhibit 4. Changes in TCE concentrations over time

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Amendment Utilization and Longevity

The two amendment components, ZVI and organic carbon, facilitate different TCE dechlorination pathways. The substantial surface area of active reaction sites on the ZVI particles facilitates chemical reduction (abiotic TCE dechlorination; Arnold & Roberts, 2000; Orth & Gillham, 1996; Roberts et al., 1996; Su & Puls, 1999) and the organic carbon amendment facilitates biotic ARD pathways (Brown, Mueller, Seech, Henderson, & Wilson, 2009). The ZVI amendment longevity and utilization can be estimated based on indirect methods, including sustained contaminant reduction, sustained ethene production, and sustained reducing conditions following utilization of TOC. Based on these indirect lines of evidence, abiotic processes are likely the primary TCE degradation pathway in areas with high amendment loading. This is indicated by simultaneous declines in *cis*-DCE and TCE, production of low levels of ethane and changes in redox conditions from aerobic to anaerobic; however, additional data collection over time is necessary to further evaluate the abiotic processes. In contrast, higher concentrations of *cis*-DCE and ethene would be expected if biotic processes predominated.

The biotic pathway (facilitated by organic carbon) is likely secondary and was observed in areas with lower amendment loading. While *Dehalococcoides* sp. were not detected prior to pilot-test injections, by three and six months post-injections, *Dehalococcoides* sp. were detected at approximately 10^3 to 10^4 gene copies/L and the *vcrA* gene was dominant. The *vcrA* gene is associated with complete TCE dechlorination to ethane (Maymó-Gatell, Anguish, Gossett, & Zinder, 1999; Maymó-Gatell, Chien, Gossett, & Zinder, 1997). Optimal *Dehalococcoides* sp. concentrations for rapid TCE reductive dechlorination are in the range of 10^6 to 10^7 gene copies/L (X. Lu, Wilson, & Kampbell, 2009; van der Zaan et al., 2010). Longevity and utilization of the organic carbon amendment was measured by evaluating TOC concentration trends. The majority of the organic carbon amendment was utilized within nine months following the pilot-test injection (TOC concentrations decreased by 84 to 95 percent in wells impacted by the pilot-test injections); however, one well (MW-5) showed slower utilization and increased longevity with a 95 percent reduction in TOC by 15 months after the pilot-test injection. Since the majority of the organic carbon amendment was utilized within 9 to 15 months after injection, and ZVI has been shown to be active in the field (Henderson & Demond, 2007; Phillips et al., 2010; Wilkin, Puls, & Sewell, 2003) for four to five-plus years, it is expected that the abiotic pathway will continue over the long term. Additionally, no sustained rebound in TCE concentrations has been observed one year post-utilization of the organic carbon in the amendment and up to two years after amendment emplacement.

The combination of injecting ZVI with an organic carbon amendment is beneficial in supporting efficient TCE remediation.

Reducing geochemical conditions are important to support both the abiotic and biotic TCE degradation pathways. For the abiotic pathway, biological processes enhance the reactivity of abiotic materials since the production of ferrous iron (dissolved iron) can create highly reactive sites on iron minerals (the emplaced ZVI amendment; Brown et al., 2009). Therefore, the combination of injecting ZVI with an organic carbon amendment is beneficial in supporting efficient TCE remediation.

Estimating TCE Mass Reduction

Two independent methods, volume-weighted and concentration-weighted averages, were used to estimate TCE mass reduction following the pilot-test amendment injection. Both

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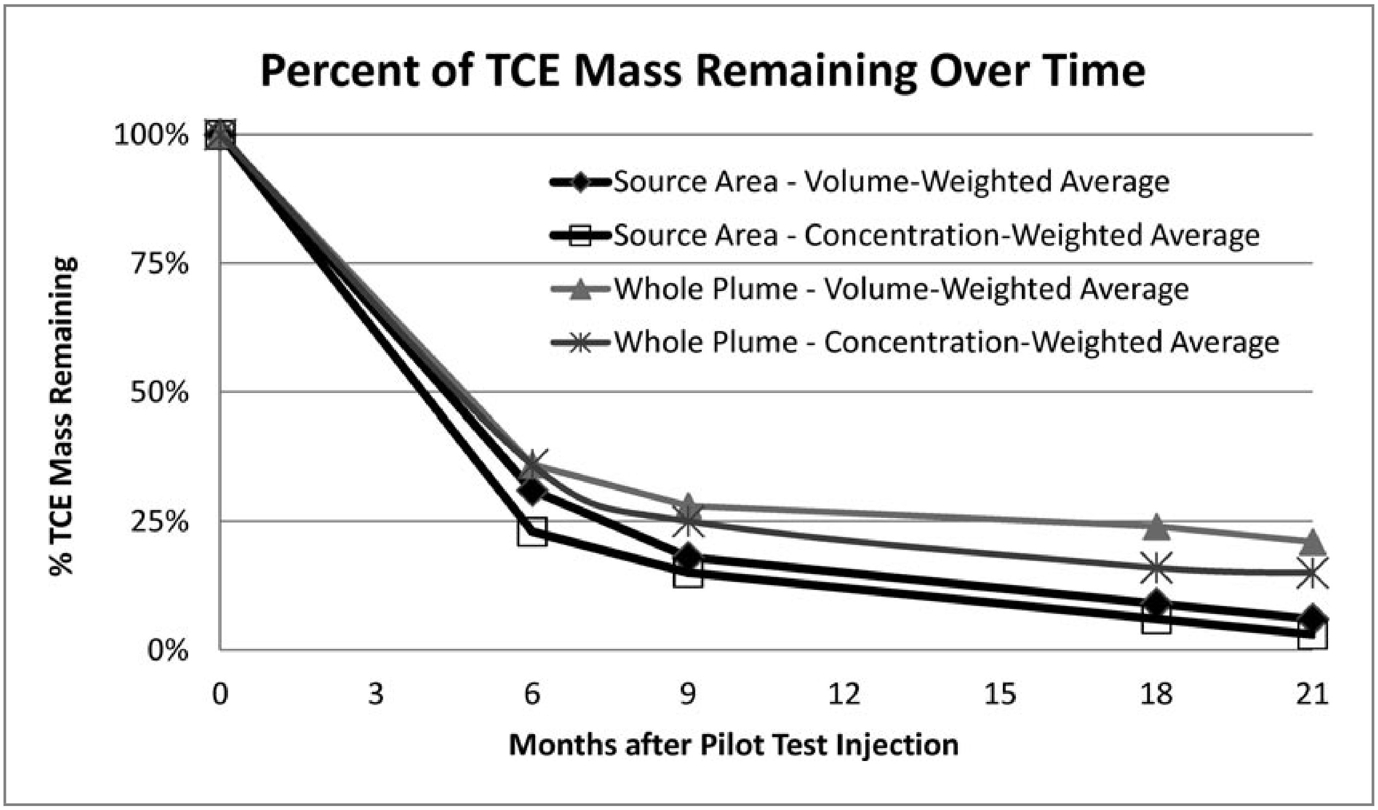

Exhibit 5. Percent TCE mass remaining after pilot test implementation

methods are valid estimates of the total mass of TCE destroyed and, when used in combination, produce values of a similar magnitude to reduce uncertainties associated with each method separately.

The volume-weighted average method used an initial calculation of TCE mass, prior to the pilot-test injection, as a baseline for calculating TCE mass degradation over time. To calculate the volume-weighted TCE mass, the area of the perched water body was divided into a grid to estimate the volume of perched water for each grid cell based on the saturated thickness and effective porosity. The TCE contour maps for the initial and post-pilot-test injection monitoring events were used to assign a TCE concentration to each cell. TCE mass for each cell was calculated as the product of water volume and TCE concentration, and the total TCE mass was calculated by summing over all grid cells. The primary uncertainties associated with this method include: (1) the extent and delineation of the TCE concentration contours, (2) the estimated TCE concentration for each grid cell, and (3) the absolute volume of water within the perched water body. Errors associated with these uncertainties can be minimized over time by consistently using the same method to determine changes in TCE mass. Using this method, a TCE mass reduction of 82 percent by 9 months and 94 percent by 21 months is shown for the source area post-pilot-test injection (Exhibit 5). For the whole plume, this method provided an estimated reduction of 72 percent by 9 months and 79 percent by 21 months.

The concentration-weighted average was also calculated for each source area well. To perform this calculation, the percent reduction in TCE concentration observed at each well was weighted by the initial concentration of TCE observed in that well. For example, this calculation weighted less significantly a 90 percent reduction in TCE from 100 μg/L

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to 10 μg/L in one well and as compared to a more significant weight for a 90 percent reduction in TCE from 3,000 μg/L to 300 μg/L in another well. Using this method, a TCE mass reduction of 85 percent within the source area occurred by 9 months post-pilot-test injection and 97 percent by 21 months post-pilot-test injection (Exhibit 5). For the whole plume, this method provided an estimated reduction of 75 percent by 9 months and 85 percent by 21 months.

Pilot-Test Conclusions

This pilot test demonstrates that *in situ* remediation using the combination of hydraulic fracturing and EHC-G® amendment can be cost-effectively implemented to achieve significant TCE mass reduction. The extensive distribution of massive quantities of amendment using few borings highlights the passive and efficient nature of this approach. The estimated cost of fracturing, geophysics, and the amendment was approximately $8 per ton of bedrock treated for the pilot test. In addition, the pilot test provided critical data to re-evaluate the conceptual site model and improve the design and efficiency of the final implementation strategy.

CONCEPTUAL SITE MODEL DEVELOPMENT AND REFINEMENT

Refining a conceptual site model (CSM) as additional data are developed throughout the lifetime of a multiphase remediation project is a critical activity that can have a significant impact on remedial design. The Atlas 12 CSM was initially developed prior to the pilot test based on historical data and was refined after collection of additional site characterization data. Refinement of the CSM while designing the full-scale remedy led to an important lesson learned: the initial appearance of plume configuration is not always a good indication of contaminant fate and transport in groundwater.

The pilot test provided critical data to re-evaluate the conceptual site model and improve the design and efficiency of the final implementation strategy.

Initial CSM Development

Historic Atlas 12 data identified a local perched water table flow system in the Fox Hills Sandstone, above deeper flow systems in the Pierre Shale. The configuration of the perched water table and knowledge of traditional flow systems were used to assume mounding and radial groundwater flow from the contaminant source areas. This view of a traditional system for Atlas 12 included multiple sources of recharge, flow through a porous medium, and subsequent discharge, perhaps to deeper saturated flow systems. The hydraulic gradient and estimated hydraulic parameters were used to calculate a groundwater seepage velocity of approximately 0.32 feet/day.

CSM Refinement

As part of designing the full-scale remedy and evaluating natural attenuation effectiveness, a groundwater flow and transport model was developed. The flow system was modeled as an equivalent porous medium with three-dimensional transient flow. Recharge was assumed to be primarily derived from on-site landscape irrigation and disposal of wastewater from septic system leach fields. Discharge could occur at escarpments that bound three sides of the site, across a specified head boundary at the fourth side of the

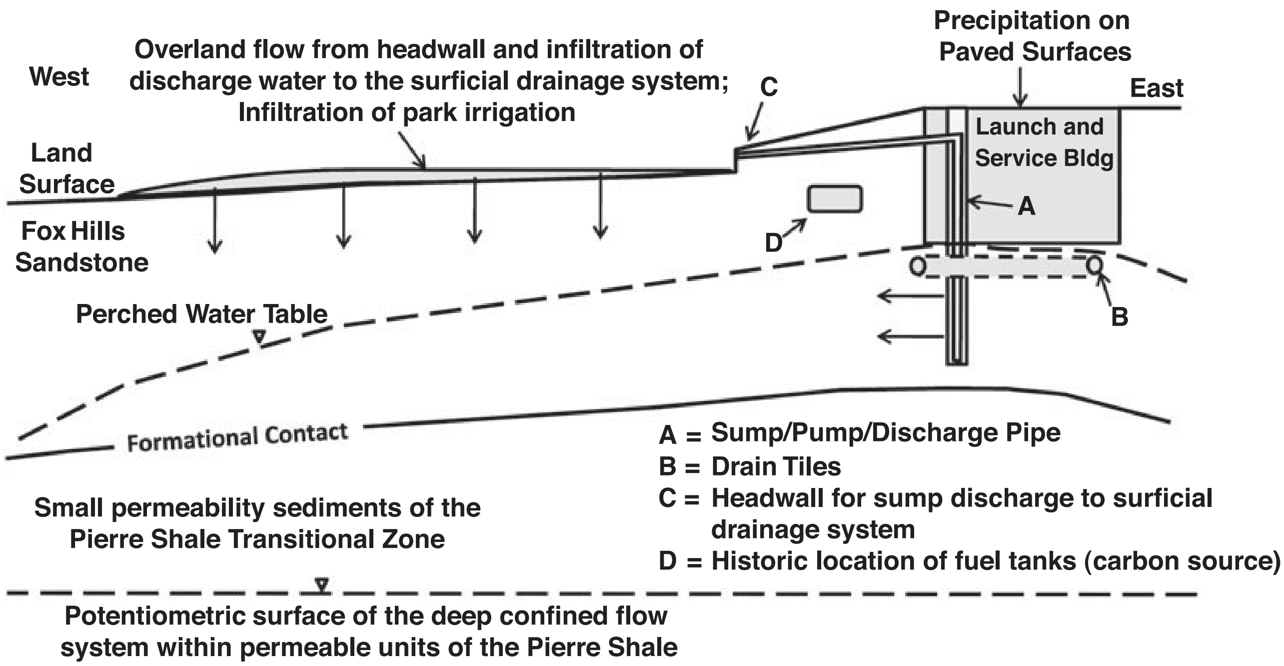

Exhibit 6. Cross-section illustration of the Atlas 12 2011 conceptual site model

model domain, and via vertical flow into the lower-permeability Pierre Shale sediments below the Fox Hills Sandstone. Simulation results demonstrated that most recharge water moves into storage in previously unsaturated sediments in the Fox Hills Sandstone near recharge sources, creating an artificial perched water body with limited areal extent characterized by short flow paths and minimal flow velocities. In particular, advective flow was determined to be too slow to account for the extent of the TCE plume if the source of dissolved contamination was only at the Launch and Service Building. Based on this refined conceptual model of the groundwater flow system, the TCE plume configuration was likely due to two source release areas: (1) discharge of waste and residual storm runoff to the Launch and Service Building's subsurface drainage system forming a "bull's-eye" around the building and (2) discharge of contaminated water pumped from the wastewater sump to a surficial drainage system with overland flow and infiltration being the primary source of the distal portion of the plume (Exhibits 6 and 7).

The previously anticipated rates of groundwater flow and contaminant transport in the perched groundwater system would have had beneficial impacts on future remedial efforts and natural attenuation since traditional remediation strategies commonly rely on groundwater flow and contaminant transport to facilitate distribution of the injected remediation amendments or, as in the case of natural attenuation, take advantage of dilution, dispersion, and degradation. However, groundwater flow velocities at this site are minimal (approximately 0.02 ft/day) and indicate that advective transport within the newly saturated sediments is negligible. The observed contaminant distribution supports this limited flow system since advective transport of TCE from the source areas typically

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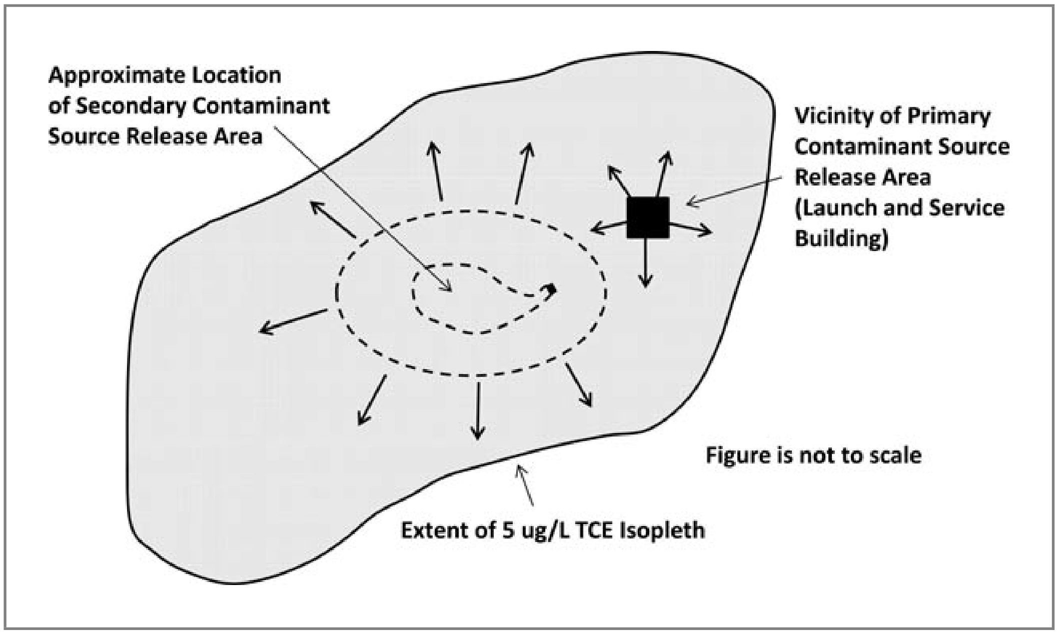

Exhibit 7. Plan view illustration of the Atlas 12 2011 conceptual site model

have been less than 300 feet in the last 50 years. This understanding supports the selected remedy, hydraulic fracturing, as an appropriate remedy to distribute amendment to as much of the subsurface area as possible without assistance of amendment distribution from groundwater flow.

FULL-SCALE IMPLEMENTATION AND FUTURE MONITORING

The results, successes, and lessons learned from the pilot test, combined with the refined CSM, were used to design the full-scale remedy, which was implemented in July and August 2011. The full-scale remedy used hydraulic fracturing (same as the pilot test) to emplace the ZVI/organic carbon amendment by creating discrete fractures at six borehole locations in the distal plume where TCE concentrations were greater than 100 μg/L. Two key lessons learned from the pilot test were taken into consideration for designing the full-scale remedy.

Lesson #1: Correlation of Amendment Loading Rates/Distribution With TCE Reduction

During the pilot test, the predicted fracture propagation radius was 30 feet; however, tiltmeter mapping showed an actual radius greater than 60 feet with an average of 79 feet (vertical) and 65 feet (horizontal). Since fractures propagated further than anticipated, the actual amendment loading rate was lower than the planned loading rate of 0.27 percent; however, TCE mass was reduced by 94 percent following 21 months of treatment. Using this information, the full-scale remedial design anticipated a fracture radius of 60 to 80 feet, and amendment loading rates were determined based on correlation of the actual

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pilot-test loading rates (corrected for volume due to larger fracture radius) with corresponding initial TCE concentrations.

Lesson #2: Effectiveness of TCE Degradation Pathways

The two amendment components facilitate abiotic (ZVI) and biotic (organic carbon) degradation. The abiotic pathway likely dominated during the pilot test, as indicated by simultaneous declines in *cis*-DCE and TCE. Based on this abiotic degradation success, the same amendment ratio of ZVI to organic carbon was used during full-scale injections.

Hydraulic fracturing for the full-scale injection was successful in emplacing greater than 99 percent of the total design mass of 134,260 lbs of amendment within TCE-impacted bedrock sediments for locations with TCE concentrations greater than 100 μg/L. The final fracture-emplacement depths at each borehole were slightly adjusted prior to fracturing in order to optimize amendment distribution within the saturated interval of bedrock within the Fox Hills Sandstone. A total of 31 discrete fractures were created to distribute the amendment across the target treatment interval of 35 to 63.5 feet depth.

Full-scale remedial activities will also include ongoing performance monitoring of the pilot test and full-scale injections and continued evaluation of natural attenuation in the plume beyond the areas where amendment was emplaced. TCE degradation will be monitored on a quarterly basis for the first year following the injection, followed by semiannual monitoring for the long term. Assessment of natural attenuation for Atlas 12 has included analysis of three independent lines of evidence (bulk degradation rates, compound-specific isotope analysis, and microbial enzyme activity probes) currently demonstrating that aerobic TCE degradation is occurring in the plume outside the area where amendment was emplaced, with an estimated degradation half-life range of 2 to 20 years. Long-term data collection and analysis for natural attenuation will continue.

ACKNOWLEDGMENTS

The authors of this article would like to acknowledge the support of the regulatory agencies involved with the project. This project is funded through the United States Army Corps of Engineers, Omaha District.

REFERENCES

Arnold, W. A., & Roberts, A. L. (2000). Pathway and kinetics of chlorinated ethylene and chlorinated acetylene reaction with Fe(0) particles. Environmental Science & Technology, 34, 1794–1805.

Brown, R. A., Mueller, J. G., Seech, A. G., Henderson, J. K., & Wilson, J. T. (2009). Interactions between biological and abiotic pathways in the reduction of chlorinated solvents. Remediation, 20(1), 9–20.

Cipolla, C. L., & Wright, C. A. (2000). Diagnostic techniques to understand hydraulic fracturing: What? why? and how? Presented at the SPE/CERI Gas Technology Symposium, Calgary, Alberta, Canada.

Christiansen, C. M., Damgaard, I., Broholm, M., Kessler, T., Klint, K. E., Nilsson, B., & Bjerg, P. L. (2010). Comparison of delivery methods for enhanced in situ remediation in clay till. Ground Water Monitoring & Remediation, 30(4), 107–122.

 Remediation DOI: 10.1002/rem © 2012 Wiley Periodicals, Inc.

Henderson, A. D., & Demond, A. H. (2007). Long-term performance of zero-valent iron permeable reactive barriers: a critical review. Environmental Engineering Science, 24, 401–423.

Li, L., Benson, C. H., & Lawson, E. H. (2005). Impact of mineral fouling on hydraulic behavior of permeable reactive barriers. Ground Water, 43, 582–596.

Löffler, F. E., Sun, Q., Li, J., & Tiedje, J. M. (2000). 16S rRNA gene-based detection of tetrachloroethene-dechlorinating Desulfuromonas and Dehalococcoides species. Applied and Environmental Microbiology, 66, 1369–1374.

Lu, G., & Zheng, C. (2003). Natural attenuation of fuel hydrocarbon contaminants: Hydraulic conductivity dependency of biodegradation rates in a field case study. International Groundwater Modeling Center, Colorado School of Mines, Golden. Paper No: LBNL-53443.

Lu, X., Wilson, J. T., & Kampbell, D. H. (2009). Comparison of an assay for Dehalococcoides DNA and a microcosm study in predicting reductive dechlorination of chlorinated ethenes in the field. Environmental Pollution, 157, 809–815.

Martin, J. P., Brennan, R. A., Sorenson, K. S., Peterson, L. N., & Bures, G. H. (2002). Enhanced CAH dechlorination in a low-permeability, variably saturated medium. Presented at the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds Battelle Conference, Monterey, California.

Maymó-Gatell, X., Chien, Y. T., Gossett, J. M., & Zinder, S. H. (1997). Isolation of a bacterium that reductively dechlorinates tetrachloroethene to ethene. Science, 276, 1568–1571.

Maymó-Gatell, X., Anguish, T., Gossett, J. M., & Zinder, S. H. (1999). Reductive dechlorination of chlorinated ethenes and 1,2-dichloroethane by "Dehalococcoides ethenogenes" 195. Applied and Environmental Microbiology, 65, 3108–3113.

Murdoch, L., & Wilson, D. (1994). Alternative methods for fluid delivery and recovery. USEPA/625/R-94/003. Washington, DC: US Environmental Protection Agency.

Nyer, E. K., & Page, G. B. (2004). Special delivery. Ground Water Monitoring and Remediation, 24(1), 34–40.

Orth, W. S., & Gillham, R. W. (1996). Dechlorination of trichloroethene in aqueous solution using Fe0. Environmental Science & Technology, 30, 66–71.

Phillips, D. H., Van Nooten, T., Bastiaens, L., Russel, M. I., Dickson, K., . . . Kalin, R. M., (2010). Ten year performance evaluation of a field-scale zero-valent iron permeable reactive barrier installed to remediate trichloroethene contaminated groundwater. Environmental Science & Technology, 44, 3861–3869.

Ritter, K., Odziemkowski, M. S., & Gillham, R. W. (2002). An in situ study of the role of surface films on granular iron in the permeable iron wall technology. Journal of Contaminated Hydrology, 55, 87–111.

Roberts, A. L., Totten, L. A., Arnold, W. A., Burris, D. R., & Campbell, T. J. (1996). Reductive elimination of chlorinated ethylenes by zero valent metals. Environmental Science & Technology, 30, 2654–2659.

Schuring, J. R. (2002). Fracturing technologies to enhance remediation. Technology Evaluation Report TE-02-02 prepared for GWRTAC Ground-Water Remediation Technologies Analysis Center, Pittsburg, Pennsylvania.

Simpkin, T. J., & Norris, R. D. (2010). Engineering and implementation challenges for chlorinated solvent remediation. In H. F. Stroo & C. H. Ward (Eds.), In situ remediation of chlorinated solvent plumes (pp. 109–143). New York, NY: Springer Science + Business Media, LCC.

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Sorenson, K. S., Martin, J. P., Brennan, R. A., & Bures, G. H. (2002). Development of a chitin-fracing technology for remediation of chlorinated solvent source areas in low permeability media. Final Report to U.S. National Science Foundation. Report No. AN0109868.

Su, C., & Puls, R. W. (1999). Kinetics of trichloroethene reduction by zero valent iron and tin: Pretreatment effect, apparent activation energy, and intermediate products. Environmental Science & Technology, 33, 163–168.

Suthersan, S., Horst, J., Nelson, D., & Schnobrich, M. (2011). Insights from years of performance that are shaping injection-based remediation systems. Remediation, 21(2), 9–25.

van der Zaan, B., Hannes, F., Hoekstra, N., Rijnaarts, H., de Vos, W. M., . . . & Gerritse, J. (2010). Correlation of *Dehalococcoides* 16S rRNA and chloroethene reductive dehalogenase genes to different geochemical conditions in chloroethene-contaminated groundwater. Applied and Environmental Microbiology, 76, 843–850.

Walden, T. (1997). Summary of processes, human exposures, and technologies applicable to low-permeability soils. Ground Water Monitoring Review, 16(1), 63–69.

Warpinksi, N. R., Branagan, P. T., Engler, B. P., Wilmer, R., & Wolhart, S. L. (1997). Evaluation of a downhole tiltmeter array for monitoring hydraulic fractures. International Journal of Rock Mechanics and Mining Sciences, 34(3–4), 108.e1–108.e13.

Wiedemeier, T. H., Swanson, M. A., Moutoux, D. E., Kinzie Gordon, E., Wilson, J. T., . . . Chapelle, F. H. (1998). Technical protocol for evaluating natural attenuation of chlorinated solvents in ground water. EPA/600/R-98/128. Washington, DC: United States Environmental Protection Agency Office of Research and Development.

Wilkin, R. T., Puls, R. W., & Sewell, G. W. (2003). Long-term performance of permeable reactive barriers using zero-valent iron: geochemical and microbiological effects. Ground Water, 41, 493–503.

Wright, C. A., Davis, E. J., & Weijers, L. (1998). Downhole tiltmeter fracture mapping: A New tool for directly measuring hydraulic fracture dimensions. Presented at the SPE Annual Technical Conference and Exhibition, New Orleans, Louisiana.

Yang, X., & Davis, P. M. (1986). Deformation due to a rectangular tension crack in an elastic half-space. Bulletin of the Seismological Society of America, 76, 865–881.

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