Substrate Flood-Injection Approach to Treat the Source Area of a Thin Discontinuous Aquifer

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ABSTRACT: An in situ groundwater remedial program is ongoing in the contaminant source area located beneath a currently inactive Titan missile launch complex known as Space Launch Complex 4 East (SLC-4E) at Vandenberg Air Force Base (VAFB), California. Here, trichloroethene (TCE) and ammonium perchlorate both source a contaminant plume extending over 1 mile (1.6 kilometers [km]) from the launch pad. Maximum concentrations of TCE and perchlorate detected in groundwater have ranged toward 2,500 and 900 micrograms per liter (μg/L), respectively.

Unconfined groundwater lies on the upper weathered bedrock surface of a subhorizontal paleomarine terrace comprised of marine shale. The aquifer is thin, on the order of only 1 to 8 feet (ft) (0.3 to 2.4 meters [m]) thick and is discontinuous due to intermittent bedrock highs approaching or exceeding aquifer thickness; a result of historical erosion of the terrace surface. Groundwater is naturally aerobic with dissolved oxygen (DO) in the 5 to 7 milligrams per liter (mg/L) range, a generally positive oxidation-reduction potential (ORP), and sulfates in the 50 mg/L range.

A recently completed groundwater pilot test program at SLC-4E featuring injections of an amended sodium lactate solution with bromide tracer followed by microbial inoculation, successfully transitioned the groundwater to strongly anaerobic, with documented destruction of perchlorate and sequential dechlorination of TCE and daughter products through to ethene within 4 to 6 months. Pilot test findings indicated that substrate distribution is controlled by an irregular bedrock topography, which, coupled with considerable access limitations, presents challenges towards addressing the entire source area.

Based on pilot test findings, a subsequent site-wide well installation program was conducted in support of full-scale interim removal action (IRA) implementation. Wells were installed in the limited accessible areas overlying the groundwater source area, with planned injection and monitoring well pairs generally spaced 30 to 60 ft apart. Dilute batches of amended soluble sodium lactate solution were then mixed on site and gravity-fed through manifolds into injection wells. This strategy was designed to create transient flooding of the aquifer around each injection well, allowing substrate to overcome bedrock highs, fill in bedrock lows, and move with the prevailing groundwater flow. Operation, maintenance, and reporting are ongoing.

Use of the soluble substrate sodium lactate afforded effective transport with natural groundwater flow, reaching out well beyond injection wells to target treatment of the greater source area. Efforts are currently geared towards an expanded clean-up effort in the final quarter of the program, to treat plume margins not originally scoped in the IRA and ultimately exceed program objectives while meeting the project schedule and budgetary constraints.

INTRODUCTION

Environmental investigations conducted at an inactive, aboveground gantry launch facility at VAFB, known as SLC-4E or Installation Restoration Program (IRP) Site 8, indicate that previous missile launch activities have impacted groundwater quality. A concrete-lined deluge water channel terminating in a retention basin extends toward the south (Figure 1). This feature channeled deluge water used during launches to suppress heat and noise. TCE, used as a degreaser of missile components, leaked into the underlying vadose zone through cracks and joints in the deluge channel and retention basin concrete lining, eventually reaching groundwater. In addition, a low altitude launch failure in 1986 caused widespread deposition of ammonium perchlorate debris, which is believed to have sourced perchlorate in groundwater.

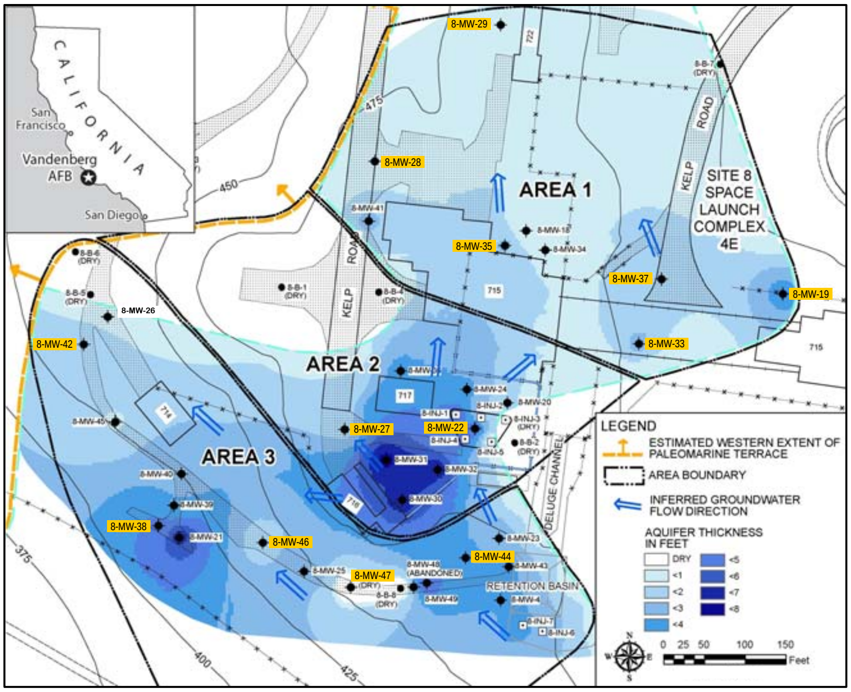

FIGURE 1. Site map showing well locations, aquifer thickness, and interpreted groundwater flow direction. Monitoring wells are highlighted yellow.

Results of a human health risk assessment indicated that if left untreated, concentrations of TCE, *cis*-1,2-dichloroethene (cDCE), and perchlorate would pose an unacceptable risk for the hypothetical use of groundwater for potable purposes. In addition, contaminated groundwater daylights along the sea cliffs bordering the Pacific Ocean approximately 1 mile (1.6 km) to the west, potentially posing a risk to ecological receptors.

An engineering evaluation/cost analysis (EE/CA) was performed to evaluate removal alternatives for an IRA to reduce concentrations of chloroethenes (CEs) and perchlorate in groundwater from the source area (Tetra Tech 2005a). The EE/CA recommended an initial bench scale microcosm study designed to assess whether indigenous bacteria are capable of degrading CEs and perchlorate, followed by implementation of an emulsified soybean oil (ESO) injection program, a technology which has proven effective at other sites at VAFB (Springer et al., 2006). Mixed results from the microcosm study, coupled with the successful application of sodium lactate at an adjacent remediation site, motivated a change of substrate to an amended sodium lactate solution in lieu of the ESO selected in the EE/CA.

A pilot test using sodium lactate solution was subsequently conducted to assess the post-injection substrate distribution pattern (Tetra Tech 2008). Pilot test results were used to refine well-field geometry, lactate substrate strength, and injection frequency for the full-scale IRA. Pilot test results showed that strongly reducing conditions can be achieved and maintained in the naturally aerobic aquifer at Site 8 via targeted substrate injections, resulting in sequential reductive dechlorination of CEs, and rapid destruction of perchlorate. However, as opposed to an originally expected quasi-radial flow distribution pattern influenced by regional groundwater flow, a strongly linear direction of transport was observed, influenced primarily by bedrock topography. Substrate movement was tracked by analyzing groundwater samples for bromide and total organic carbon (TOC), which, along with electrical conductivity (EC), DO, and ORP field testing, proved to be cost effective alternatives over other more expensive laboratory testing parameters. Figure 2 illustrates the linear post-injection distribution of substrate injected into well 8-MW-22 in relation to the interpreted regional groundwater flow direction (black arrow). Site lithology logs indicate an undulating bedrock surface beneath Site 8, with vertical relief in some areas approaching or exceeding the thickness of groundwater observed (Figure 3). Under such a hydrogeologic regime, groundwater pools in bedrock depressions during dry periods, while flowing over bedrock highs during wet periods.

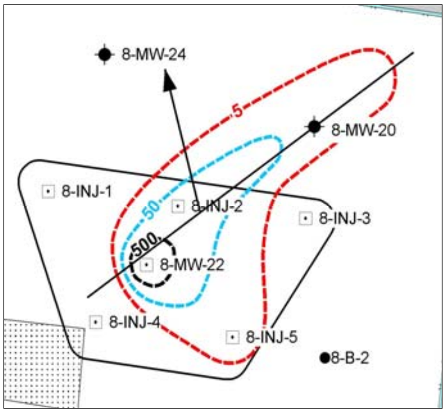

FIGURE 2. Bromide distribution following second injection event during pilot test.

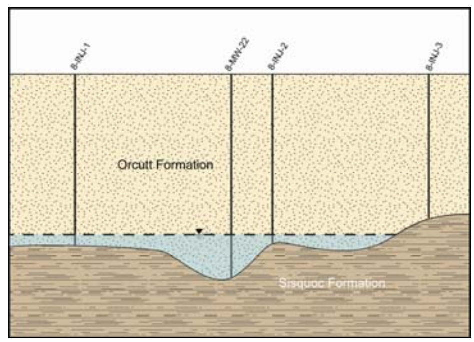

FIGURE 3. Cross section illustrating bedrock topography. Sketch not to scale.

Consequently, Tetra Tech revised its approach by considering each injection event as a temporal wet period, with a transient substrate mound dissipating along the natural pathways followed by groundwater. Bedrock highs would be effectively circumvented by supplying sufficient volume to overwhelm the local bedrock topography. The full-scale well-field that was installed following completion of the pilot test program is shown on Figure 1, with monitoring wells highlighted in yellow.

Site 8 Hydrogeology. Site 8 is located within a wide paleomarine terrace commonly known as the Lompoc Terrace, which is bounded on the north by the Santa Ynez River and on the south by the Santa Ynez Mountains. The terrace consists predominantly of regressive paleomarine sediments overlain by dissected stream terrace, alluvial fan, and eolian deposits (Dibblee 1988).

The sedimentary deposits at Site 8 are characterized as dune sand sediments of the Pleistocene Orcutt Formation unconformably overlying Sisquoc Formation shale. A series of three uplifted paleomarine terraces is interpreted to form the bedrock base of the unconfined aquifer beneath and downgradient of Site 8. The Site 8 area is underlain by the upper terrace, the upper surface of which has been altered to clay, forming an effective aquitard. Bedrock topography undulates locally and is interpreted to dip to the northwest approximately two to three degrees.

Groundwater occurs above the undulating bedrock surface in relatively limited quantities, ranging from less than 1 to 8 ft (0.3 to 2.4 m) in thickness (Figure 1). The average hydraulic gradient is approximately 0.07. The calculated groundwater velocity at Site 8 is approximately 0.6 ft/day (0.2 m/day) (Tetra Tech 2009), but can vary locally from 0.4 ft/day (0.1 m/day) or lower in the south to 1.4 ft/day (0.4 m/day) in the north.

INJECTION AND MONITORING SCOPE AND METHODS

After four injection events and pilot test completion in November 2007, three targeted injection events were conducted to maintain the reducing conditions attained during the pilot test. During February and March 2008, wells 8-MW-29 through 8-MW-49 (Figure 1) were installed in accordance with the IRA Work Plan (Tetra Tech 2005b). The first full-scale injection event (injection event 8) was conducted during May 2008.

Substrate injections were conducted once every one to two months and targeted an optimized well list based on ongoing evaluation of monitoring data. In addition, groundwater samples were collected quarterly from 13 monitoring wells (Figure 1) and a limited list of targeted injection wells.

The sodium lactate injectate solution was created by mixing Wilclear (a proprietary blend consisting of 60 percent lactate in purified water) with potable water into 5,400 gallon (gal) (20,400 liter [L]) polyethylene tanks via hydraulically-driven proportional pumps until a 1 to 3 percent by volume solution was obtained. Amendments added during mixing included sodium bromide as a tracer and sodium bicarbonate to provide aquifer buffering. After mixing, DO and ORP levels were allowed to drop sufficiently before injecting, so as not to compromise the prevailing geochemical environment created in the treatment zone.

In situ monitoring of water quality parameters was conducted periodically using a handheld, down-well multiparameter water quality sonde that measured temperature, EC, pH, DO, and ORP, with the purpose of identifying areas requiring additional substrate for maintenance and/or enhancement of reducing conditions in the groundwater aquifer.

Geochemical proxy indicators (e.g., bromide, TOC, metabolic acids, sulfate) were monitored periodically for evidence of substrate presence and breakdown and indications of the onset and degree of reducing conditions. Contaminant concentrations were monitored for trends that are consistent with progressive reductive dechlorination, as opposed to dilution and/or displacement, neither of which would produce degradation daughter products. Observed trends for these indicators were used to assess the post-injection distribution of substrate and the state of the reductive dechlorination process.

Microbiological Sampling. Various anaerobic microorganisms are capable of direct metabolic reductive dechlorination of CEs (Haas 2007). However, only *Dehalococcoides ethenogenes* (DHE) have the demonstrated ability to completely dechlorinate TCE through cDCE and vinyl chloride (VC) to the harmless end product ethene. Selected samples were analyzed by real-time quantitative polymerase chain reaction (qPCR) analysis for the presence of DHE during a baseline sampling event and again during a post-inoculation sampling event. During the baseline sampling event all sampled wells showed presence of DHE in the 10^5 to 10^6 organisms per liter (org/L) range. Following inoculation, population density is shown to have increased 1 to 3 orders of magnitude into the 10^7 to 10^8 org/L range, indicating a successful inoculation.

RESULTS AND DISCUSSION

Biodegradation and fermentation of organic substrates in groundwater aquifers generates hydrogen, which acts as an electron donor in the reaction that reduces CEs and drives the reductive dechlorination of TCE through to ethene (Parsons 2004). Real-time evaluation of various geochemical proxy indicators allowed for optimization of the injection and monitoring programs as the transport and breakdown of the injectate in the subsurface became progressively better understood. Over the course of the Site 8 IRA, groundwater data were evaluated for: 1) evidence of substrate presence and breakdown, indicated by increases in TOC, bromide, alkalinity, and EC levels and the presence of metabolic acids; 2) evidence of the onset and maintenance of anaerobic, reducing conditions, indicated by sustained low DO and ORP levels, increases in ferrous iron and methane, and decreases in the alternate electron acceptors nitrate and sulfate; 3) reductions in perchlorate concentrations; and 4) evidence of sequential reductive dechlorination of CEs, indicated by decreases in TCE with attendant production of sequential daughter products cDCE, VC, and ethene.

As expected, injection wells showed rapid conversion from aerobic to anaerobic, methanogenic conditions with attendant contaminant destruction within weeks of the initial injections. With respect to monitoring wells, the interpreted arrival of substrate generally was followed by perchlorate destruction within 2 weeks and the onset of reductive dechlorination of TCE after 3 to 5 weeks.

Figure 4 illustrates geochemical changes associated with the arrival of substrate in monitoring well 8-MW-27. A reduction in perchlorate concentrations was first observed when the ORP became negative and DO had decreased to 1 mg/L in September 2008. A nascent reductive dechlorination process became evident one month later with the arrival of increasing amounts of substrate, evidenced by the spike in bromide and EC. Concurrently, the presence of metabolic acids (acetic and propionic), increases in TOC, and reductions in sulfate document conversion to sulfate reducing conditions. Where substrate presence has been confirmed in other site monitoring wells, geochemical proxy indicators of substrate presence and reductive dechlorination have exhibited similar behavior.

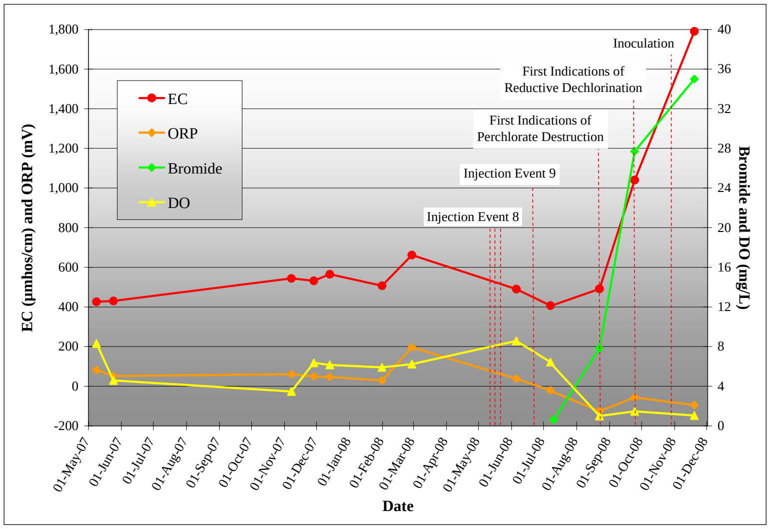

FIGURE 4. Geochemical indicators of substrate presence in monitoring well 8-MW-27 (Area 2).

Figure 5 illustrates perchlorate destruction and classic sequential dechlorination of CEs in monitoring well 8-MW-29. Perchlorate decreased from 196 µg/L to below the detection limit between August and November 2008, six months after the first full-scale IRA injection event conducted during May 2008. During the same period, on a molar equivalent basis, TCE decreased from 3.12 to 0.16 micromoles per liter (µmol/L) with an increase in cDCE concentrations from 0.09 to 3.20 µmol/L, suggesting full molar conversion of parent to daughter product. During the February 2009 sampling event, cDCE had almost completely been replaced by VC and ethene. Evidence of dechlorination of VC to ethene is documented for other monitoring wells located closer to their associated injection wells, where reducing conditions were established earlier in the program (e.g., 8-MW-35).

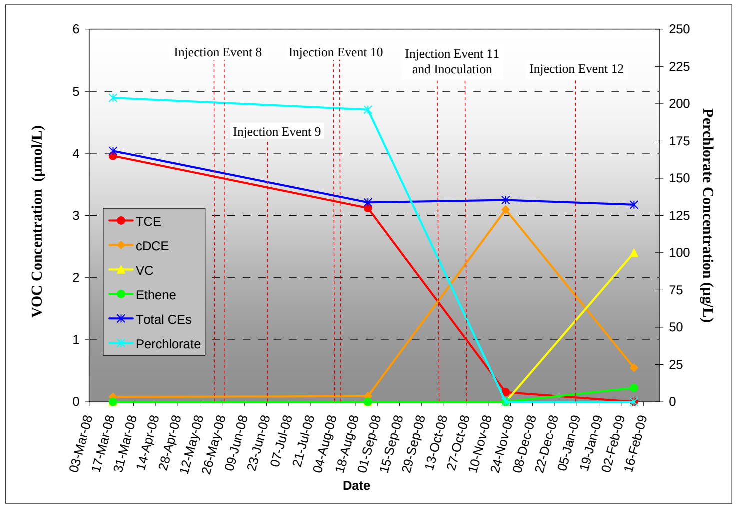

FIGURE 5. Destruction of perchlorate and sequential dechlorination of CEs in monitoring well 8-MW-29 (Area 1).

The stated IRA program objective was an 80 to 90 percent reduction in concentrations within that portion of the source area that contained TCE and/or perchlorate at concentrations greater than 500 and 300 µg/L, respectively (i.e., target concentrations of < 100 µg/L for TCE and < 60 µg/L for perchlorate) (Tetra Tech 2005a). Figure 6 shows TCE concentrations as interpreted from three post-injection monitoring events. The red dashed outline represents the original

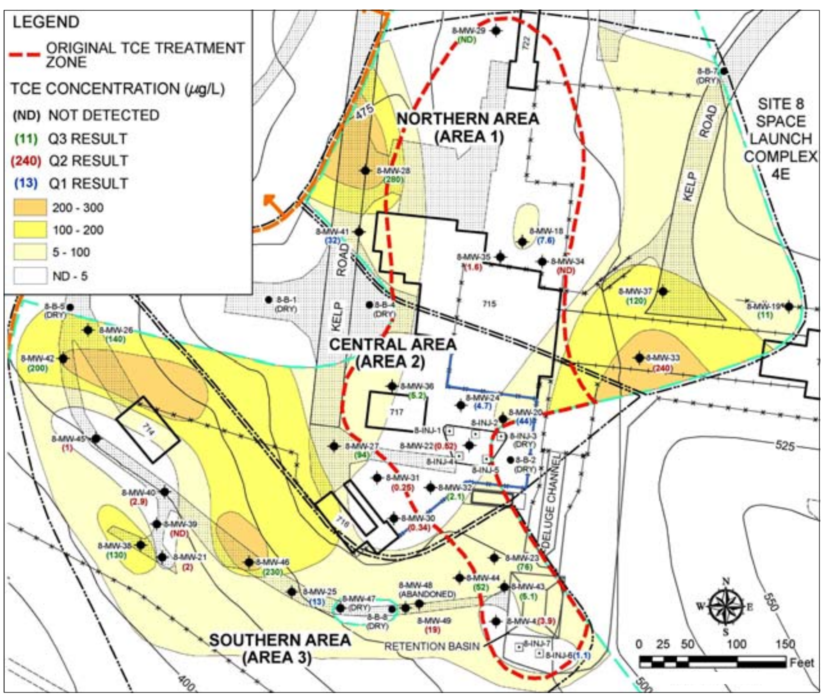

FIGURE 6. Interpreted TCE concentrations at Site 8, generated from three quarters of post-injection monitoring data, with the original baseline TCE treatment area (TCE > 500 µg/L) shown in red.

targeted TCE treatment area, where TCE concentrations ranged from 500 to 2,500 µg/L prior to the pilot test. Northernmost well 8-MW-29 is located 250 feet (76 m) downgradient from associated injection wells 8-MW-18 and 8-MW-34 in Area 1. Relatively high hydraulic conductivity, coupled with an aquifer thickness of approximately 1 ft (0.3 m) (Figure 1) allowed for extensive northward distribution of the substrate, effecting clean-up of a large portion of the originally targeted TCE plume. The action of substrate on such a distal monitoring well illustrates the effectiveness of sodium lactate as a soluble electron donor substrate that can be transported considerable distances following injection (Tetra Tech 2009).

Figure 7 shows the current perchlorate distribution, where the eastern half of the original treatment area has been cleaned up. Substrate movement is slower to the west near monitoring well 8-MW-27 and to the south, where recalcitrant monitoring wells 8-MW-38 and 8-MW-46 continue to show relatively elevated perchlorate and TCE concentrations (Figures 6 and 7). Monitoring well 8-MW-44 is located at the southern extent of the original TCE treatment area, more than 50 ft (15 m) distant from associated injection wells, and shows conclusive evidence of reductive dechlorination, indicating that despite more limited substrate movement in the south the substrate flood-injection approach remains effective.

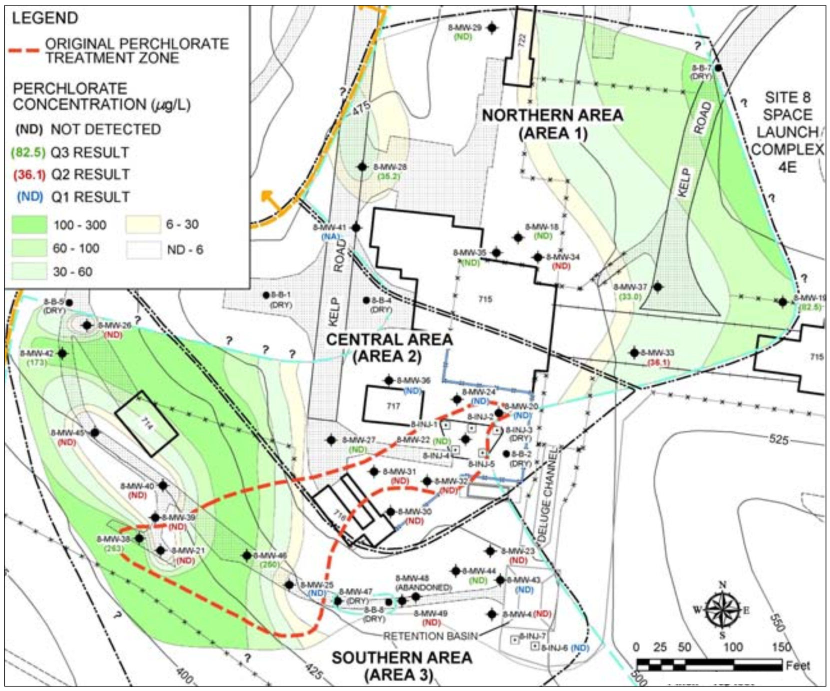

FIGURE 7. Interpreted perchlorate concentrations at Site 8, generated from three quarters of post-injection monitoring data, with the original baseline perchlorate treatment area (perchlorate > 300 µg/L) shown in red.

The degree to which this approach was successful relied largely on post-injection monitoring of geochemical conditions, where use of the bromide tracer emerged as a cost-effective laboratory analytical means of establishing the success of substrate migration between well pairs. Sequencing soluble substrate injections over a one year period enabled a pulsing of substrate addition, which served to maintain the geochemical changes and successively expand the reactive zone over time. To date, approximately 210,000 gal (800,000 L) of substrate have been injected into the roughly 1,000,000 gal (3,800,000 L) portion of aquifer underlying the Site 8 source area (i.e., 21 percent of the estimated aquifer volume). The originally defined treatment area has been cleaned up to below targeted destruction levels of 80 to 90 percent, while current efforts are geared towards addressing the lower concentration plume margins not originally scoped within the cleanup program.

The Way Ahead. In an effort to expand site cleanup efforts, the remaining recalcitrant wells 8-MW-33 (Area 1) and 8-MW-38 and 8-MW-46 (Area 3) have recently been converted to injection points following State regulatory approval. One more planned injection event is scheduled for April 2009 and will include inoculation of these three wells with DHE culture. Fourth quarter sampling is scheduled for May 2009, after which point the IRA will be completed. Continued operation, maintenance, and monitoring at the site will be transferred to another base contractor.

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