
Cost and Performance Summary Report

In Situ Chemical Reduction at the Marshall Space Flight Center, Source Area 2, Huntsville, Alabama

Summary Information [1, 2, 5, 7]

The Marshall Space Flight Center (MSFC) is a federal research and development facility located within the Redstone Arsenal (RSA) in Huntsville, Alabama. During the 1940's, RSA was used for manufacturing munitions and from 1949 to 1960 for developing rockets and guided missile systems. Since 1960, when the civilian rocketry and mission activities were transferred to the National Aeronautics and Space Administration (NASA), MSFC has been used to support the space program, including developing spacecraft and rocket engines. Historical solvent waste management practices from rocket engine testing operations at MSFC resulted in contamination of soil and groundwater at the facility, primarily with chlorinated volatile organic compounds (cVOCs). MSFC was placed on the National Priority List (NPL) with RSA in May 1994.

Site investigations identified five major cVOC plumes at MSFC along with 14 contaminant source areas that may act as continuing sources of groundwater contamination. Several pilot tests of *in situ* treatment technologies are ongoing or planned, with the results to be used in completing a feasibility study for groundwater remediation at MSFC.

This report presents the results of the pilot test of *in situ* chemical reduction technology using the FerroXSM process, patented by ARS Technologies, Inc. (ARS). This process involves the subsurface injection of a reactive, colloidal, zero-valent iron (ZVI) powder, normally in a water-based slurry. Pneumatic fracturing preceded the injections and the Liquid Atomized InjectionSM (LAI) system (also an ARS patent) was used to deliver the ZVI into both saturated and unsaturated subsurface media.

Source Area 2 (SA-2) was selected for testing this technology. In the past, an existing pond (CERCLA Site MSFC-005) located within SA-2 received trichloroethene (TCE) from engine cleaning operations. The pond overflowed through a concrete trough to surrounding soils.

The focus of this pilot test project was to assess the application of this *in situ* chemical reduction technology to treat dissolved TCE in the residuum groundwater beneath the SA-2 area. According to NASA, this pilot study was not intended to assess the extent of contamination in the underlying bedrock groundwater, or to evaluate the use of this technology to treat the contamination that might occur within it.

Figure 1 shows the distribution of TCE in the SA-2 area as of July 2000, and the layout of the injection locations. TCE and dichloroethene (DCE) were found in the residuum groundwater at SA-2 in the dissolved phase. The general distribution of dissolved contaminants was defined mainly with groundwater

samples collected from direct-push techniques. Eight permanent monitoring wells also were installed in SA-2. TCE was identified in the groundwater at concentrations as high as 72,800 micrograms per liter ($\mu\text{g/L}$). Approximately 55 pounds of contaminants were estimated to be located in the residuum groundwater at SA-2.

This mass of contaminant was estimated by using a computerized kriging algorithm contained in the data visualization software (EVS®) used to develop the three-dimensional view of the dissolved plume in the residuum groundwater beneath SA-2. The mass estimate involved using the spatial distribution of dissolved groundwater concentrations, measured from direct-push sampling and monitoring well locations that could be installed in the area, and the estimated properties (such as thickness) of the rubble zone layer at the base of the residuum. NASA reported that this value is an order-of-magnitude estimate, and that there are difficulties in, and uncertainties associated with, developing contaminant mass estimates, especially in a complex, heterogeneous subsurface environment.

The pilot test of *in situ* chemical reduction began in July 2000 with data available from July 2000 to March 2002. Groundwater monitoring is planned to continue until either TCE concentrations reach apparent steady-state conditions, or other parameters suggest a decline in overall treatment effectiveness.

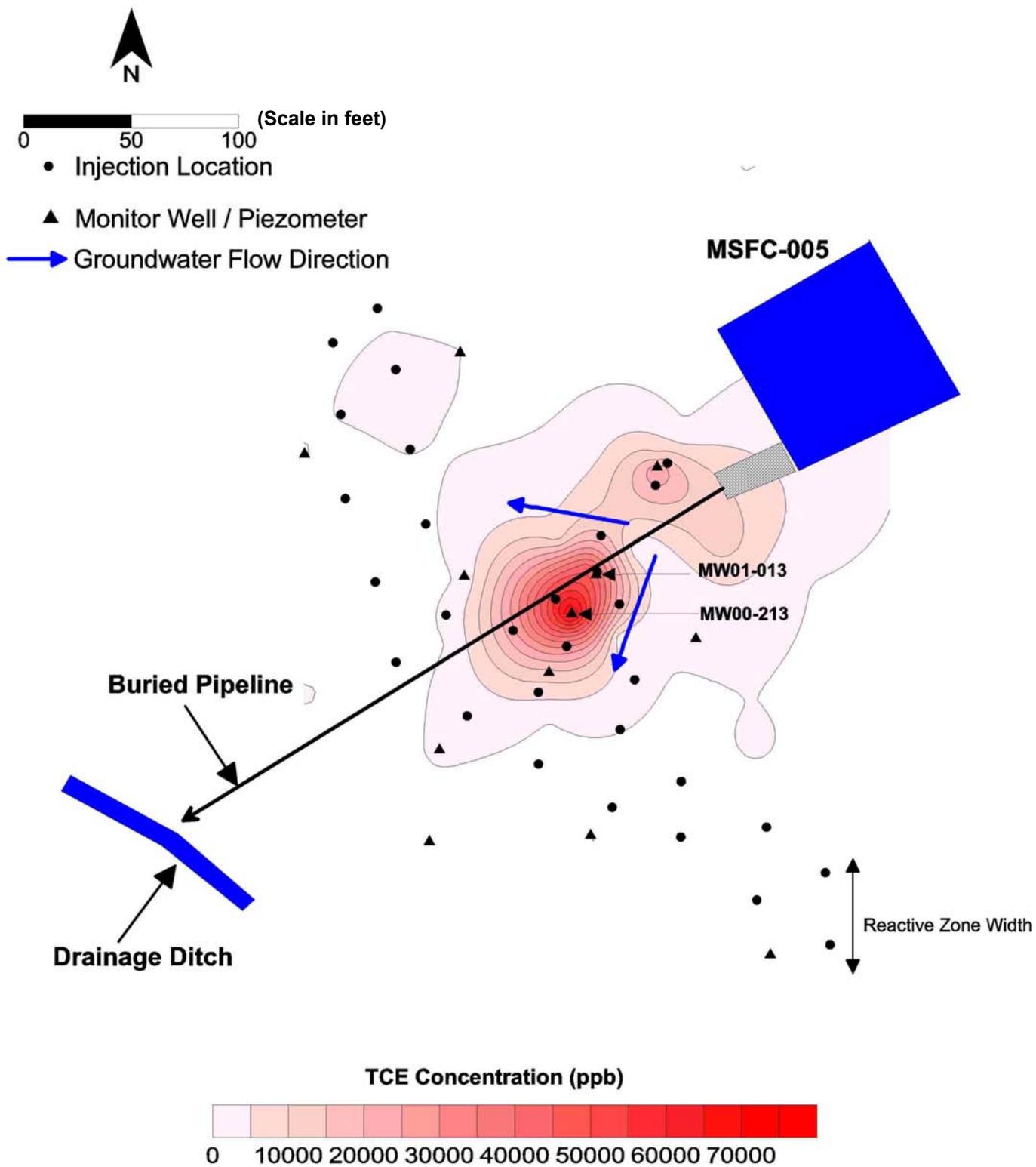
CERCLIS ID Number:	AL1800013863
Type of Action:	Remedial
Lead:	PRP

Factors That Affected Cost or Performance of Treatment [1, 2, 3, 5, 7]

The presence of unexploded ordnance (UXO) within the subsurface beneath the SA-2 area affected the design and operation of the pilot test. Clearance of all subsurface sampling, injection and permanent groundwater monitoring points was required because of the presence of UXO.

RSA had identified all areas of MSFC south of Fowler Road (that includes the SA-2 area) as having potential UXO buried beneath the surface. RSA is currently reevaluating the ordnance and explosive (OE) designation across all the arsenal; however, at the time of the pilot test, the area at SA-2 was designated as a potential UXO area requiring an UXO clearance survey.

Figure 1. SA-2 Pilot Test Layout [5, 7]



The subsurface of the SA-2 test area consists of low permeability clayey residuum overlaying fractured bedrock. The bedrock is Tusculumbia limestone with karst features; the depth to bedrock varies from 22 to 34 feet beneath the site. The residuum transitions into the bedrock through a weathered, saturated interval of higher permeability, consisting mainly of gravel, chert and clayey media. This interval, called the rubble zone, is of varying thickness and generally forms a main pathway for groundwater and contaminant migration to downgradient areas.

The degree of vertical hydraulic connection between the rubble zone and underlying bedrock appears variable throughout the area, and is considered by NASA to be low to moderate beneath SA-2.

The characteristics of the groundwater within the rubble zone are presented below.

Matrix Characteristics (Rubble Zone Groundwater) [1,2,3,5]

Parameter	Value
Soil Classification:	Mostly gravel and clays with large pieces of chert
Groundwater Velocity and Directions of Flow:	0.14 ft/day, with primary flow directions spanning from southwesterly to northwesterly
Dissolved Oxygen Content:	5-7 mg/L
Oxidation-Reduction Potential:	130 mV
Depth to Bedrock:	22-34 feet
pH:	6-7
Temperature:	19 °C

Treatment Technology Description [1, 2, 3, 5, 7]

In situ chemical reduction using a ZVI slurry (FeroxSM process) with pneumatic fracturing was pilot tested at SA-2. ZVI chemically reduces TCE through reductive dechlorination reactions in which hydrogen ions, released from the corrosion of iron in groundwater, displace chloride ions in the parent compound (TCE), and reduce it to lower forms (such as DCE isomers, vinyl chloride (VC), and ethene).

Pneumatic fracturing was performed using nitrogen gas injected into the ground at 120 pounds per square inch (psi). The fracturing was used to create preferential pathways in the low permeability, capillary fringe media above the rubble zone.

Following fracturing, ZVI powder was mixed with water under pressure to form a slurry. The slurry was then injected into subsurface target intervals using the patented LAISM system. A specialized nozzle (capable of delivering the atomized fluids in up to a 360-degree pattern) was used to atomize the injected fluids to improve dispersal into the target zone. The average slurry delivery pressure was 60 psi. A total of 11,000 pounds of ZVI was injected during the pilot test at SA-2 to reduce 55 pounds of TCE. The field ratio of iron to TCE by weight was 200:1, consistent with results from previous bench-scale studies.

An inflatable packer system was used to isolate discrete subsurface intervals for slurry injection. The system used an inflatable bladder to expand a packer (drop ball or tubing) against the well casing at specific depths. Each packer consisted of a relatively-thick, rubber-like membrane about a foot in length, with the ends clamped and fixed to a rod. Tubing was connected to the packers that went back to land surface. Typically, two packers were fixed to the rod at pre-spaced intervals (e.g., 1-foot). The entire assembly was lowered into a borehole or screened well interval to the target zone depth. The tubing was connected to an above-ground compressed gas source (air or nitrogen), and the packers were pressurized and inflated to expand against the borehole wall or well screen to seal off and isolate the target interval for subsequent injection of fluids.

As discussed previously, UXO was present throughout the areas of highest TCE contamination at the test site. Direct injection of ZVI could not be done in many of these areas, and a permeable reactive zone was created downgradient to treat the groundwater as it flowed from the source area. As shown in Figure 1, the reactive zone consisted of two rows of injection points. The radius of influence of each point was between 20 to 60 feet, creating overlapping zones at each injection point. In addition, direct injection of ZVI was performed in those areas where UXO was not present.

To help determine the width of the reactive zone, a sensitivity analysis was performed that compared the estimated retention time for contaminants in the reactive zone based on projected values for contaminant concentrations entering the zone, groundwater velocity, and degradation half-life. The time needed to degrade contaminant to an effluent value of 5 µg/L was estimated for projected scenarios (required retention times [R_{tr}]), and compared with the estimated retention time (R_{te}) within the reactive zone. The assessment considered the best-to-worst case range of values for determining factors, such as the groundwater concentrations (C_{inf}) and velocities (V_s) that might enter the zone, the reported half-lives (T_{1/2}) of the contaminants in contact with ZVI, and the possible reactive zone widths (W) that may be created with the injections. As shown in Table 1, the estimated retention times for all three scenarios are greater than the required retention times, suggesting that contaminated groundwater should have sufficient retention time in the zone even under worst-case assumptions.

Table 1. SA-2 Reactive Zone Design Considerations [5]

Case	C _{inf} (µg/L)	V _s (ft/day)	W (ft)	T _{1/2} (days)	R _{tr} (reqd) (days)	R _{te} (estd) (days)
Worst case	70000	1	35	2.3	31.2	35
Likely case	35000	0.1	50	1.6	20.1	500
Best case	3000	0.01	60	0.9	8.1	6000

$$C_{\text{eff}} = 5 \mu\text{g/L}$$

$$R_{\text{tr}} = ([\ln C_{\text{eff}}/C_{\text{inf}}] / \ln 0.5) \times T_{1/2}$$

$$R_{\text{te}} = W/V_s$$

These equations are for the first-order reactions that are typically used to describe degradation processes associated with estimating retention time in reactive ZVI walls (see generally *In Situ Treatment Technology*, E.K. Nyer, et al., Chapter 9, Lewis Publishers, 1996).

The half-life estimates used in the tabulated calculations were based on the range of values reported for TCE and its degradation products for commercially-available, granular ZVI, as summarized in Table 1-1, *Design Guidance for Application of Permeable Barriers to Remediate Dissolved Chlorinated Solvents*, A. Gavaskar et al., Battelle Memorial Institute, AL/EQ-TR-1997-0014, February 1997. Research by ARS Technologies, Inc., indicated that the reactivity of the ZVI iron powder is higher than that of granular ZVI. This higher reactivity was expected by NASA to provide an additional factor of safety in the retention time estimates.

Operating Parameters [1, 5]

Listed below are the key operating parameters for this technology and the values measured for each.

Operating Parameter	Value
Pneumatic Fracture Pressure	120 psi (average)
ZVI Injection Pressure	60 psi (average)
Radius of Influence	20 to 60 feet
Iron to TCE ratio	200:1 by weight

Performance Information [1, 5, 6]

The objective of the pilot test was to evaluate the effectiveness of *in situ* chemical reduction using the ZVI FeroxSM process to treat TCE in SA-2. No specific cleanup targets were identified for the pilot test.

Several target parameters were measured during the pilot test to evaluate the effectiveness of the process in treating TCE in

residuum groundwater. These include groundwater concentrations of TCE, DCE, VC, ethene, ethane, carbon dioxide, methane, iron, chloride (Cl), and additional field parameters.

Seven sets of post-injection groundwater monitoring data are available as of March 2002. Figures 2 and 3 show groundwater concentrations for TCE, DCE, VC, and Cl in the two source area monitoring wells, MW00-213 and MW01-013, respectively, for the period from July 2000 to March 2002. According to NASA, at a minimum, semi-annual monitoring is planned until either TCE concentrations reach apparent steady-state conditions, or other parameters suggest a decline in overall treatment effectiveness. Parameters to be monitored include TCE and its degradation products.

Figure 2 shows that the pre-injection TCE concentration in MW00-213 was approximately 73,000 µg/L. After 13 months of treatment, the concentration had been reduced by about 95% (to 3,400 µg/L). In March 2002 (after about 20 months of treatment), the concentrations had increased (to 7,600 µg/L) but still reflected nearly a 90% reduction. NASA's contractor reported that this rebound could have been related to effects from groundwater fluctuations.

This figure also shows that the concentration of DCE and Cl increased over this time. According to the contractor, this was attributed to the reductive dechlorination of TCE. Increasing concentrations of VC also were observed after the first year of post-injection monitoring, to nearly 100 µg/L.

In March 2002, the following additional degradation products of TCE were measured for the first time: ethene (560 µg/L), ethane (240 µg/L), carbon dioxide (3,900 µg/L), and methane (150 µg/L). These constituents likely were not present at significant concentrations prior to treatment.

Figure 3 shows that the pre-injection TCE concentration in MW01-013 was 50,200 µg/L. After 13 months of treatment, the concentration had been reduced by about 87% (to 6,600 µg/L). In March 2002 (after about 20 months of treatment), significant increases in concentrations were observed (to 24,000 µg/L) indicating only a 52% reduction. According to the contractor, this rebound may reflect an insufficient amount of ZVI placement near this well, due to the UXO constraints.

Figure 2. MW00-213 Rubble Zone Groundwater VOC and CI Concentrations (log-scale) [5]

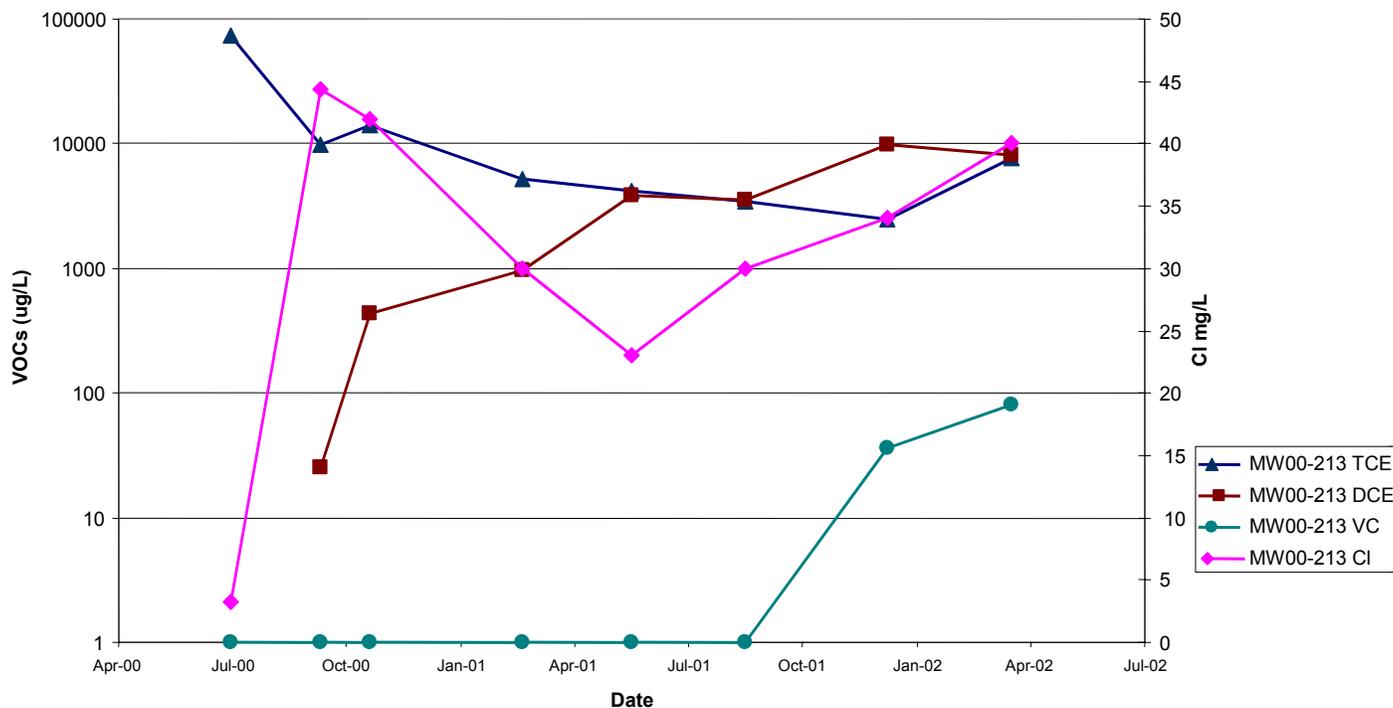


Figure 3. MW01-013 Rubble Zone Groundwater VOC and CI Concentrations (log-scale) [5]

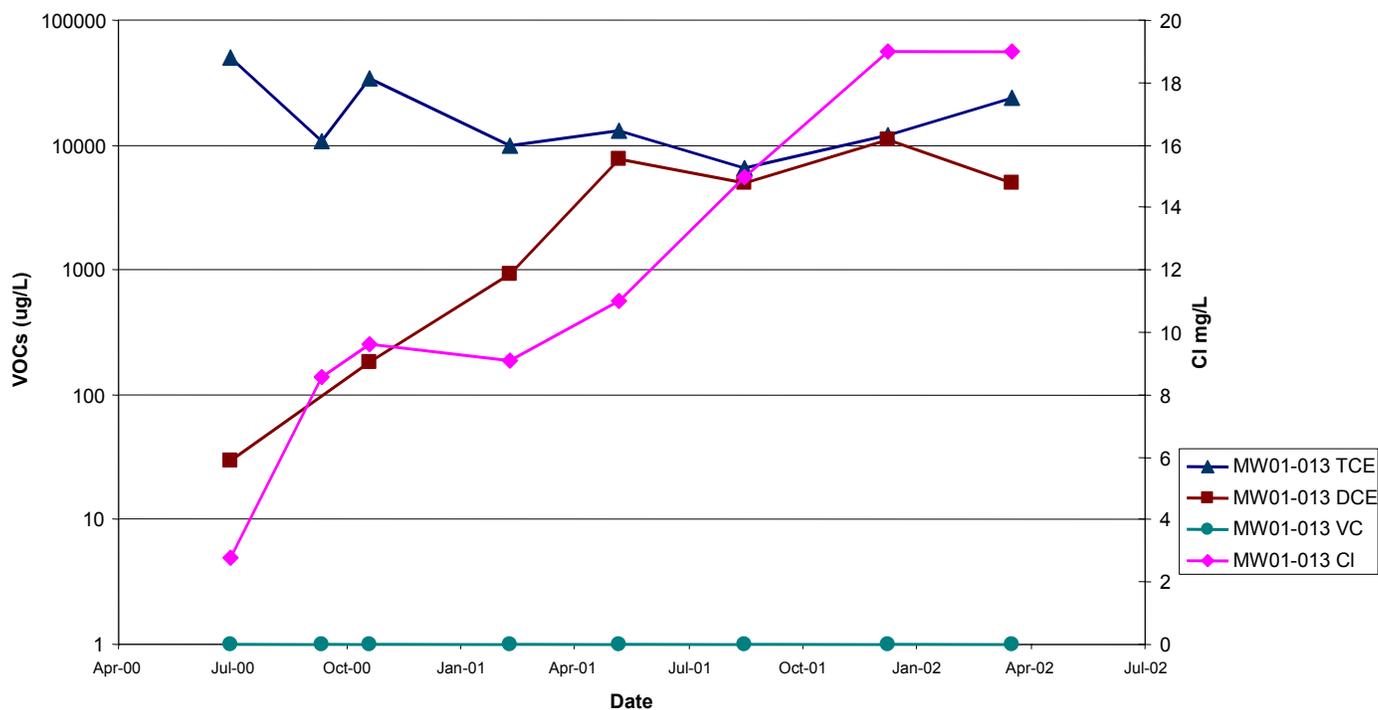


Figure 3 also shows increases in the expected degradation products at MW01-013, but at lower concentrations than for the other source area well. As of March 2002, VC had not been observed above its detection limit at this location. The March 2002 sampling detected the following degradation products of TCE: ethene (96 µg/L) and methane (700 µg/L); others were below their detection limits. As with MW00-213, these constituents likely were not present prior to treatment.

The available groundwater monitoring data were used to assess the chloride balance at SA-2. The chloride balance was used to confirm that TCE was reduced to its degradation products, and not redistributed at the site. According to the contractor, the data indicate that about 97% of the TCE reductions can be accounted for stoichiometrically by the corresponding increase in DCE and chloride ions in the rubble zone groundwater. The remaining amount likely involved the increased production of other degradation products.

In situ groundwater monitoring probes were used to continuously record indicator field parameters in MW00-213 for a 30-day period during February and March 2001. Dissolved oxygen concentrations had decreased from background levels of 5-7 mg/L to around 2 mg/L; oxidation-reduction potential had also decreased from 140 millivolts (mV) to around -450 mV. These results showed that conditions had been established in the rubble zone which were more conducive to *in situ* chemical reduction reactions.

Cost Information [1]

CH2M Hill was NASA's prime contractor for the SA-2 (and other) *in situ* pilot test. ARS was subcontracted by CH2M Hill for the bench-scale testing and field implementation components of the study. As indicated in Table 2, a total capital cost of \$428,800 was incurred between 1999 and 2001, of which \$299,800 were for related services by ARS, for the following tasks: work plan preparation, site characterization costs, bench-scale testing, utility surveying and video-logging, pneumatic fracturing and ZVI injections (including mobilization and demobilization), royalty fees (related to pneumatic fracturing technique patented by the New Jersey Institute of Technology), field documentation reports, regulatory agency and technical support, and project management.

Information was not provided about the unit cost for treatment of SA-2 in terms of either cost per cubic yard of media treated or cost per pound of contaminant destroyed. Instead, NASA reported the unit cost based on the mass of ZVI injected. They reported that the cost to implement the pilot test was \$27 per pound of ZVI injected, based on the cost of \$299,800 for ARS services and the 11,000 pounds of ZVI injected. The actual field demonstration portion of the test was approximately 70 percent of the total costs (\$209,900), corresponding to about \$19 per pound of ZVI injected.

Operation and maintenance (O&M) costs for the pilot test are related mainly to groundwater monitoring. Seven post-injection monitoring events were performed between September 1999 and March 2002. Table 2 shows the estimated aggregate O&M costs for this period were \$70,400.

Observations and Lessons Learned [1, 4, 5, 6, 7]

During the period from July 2000 to March 2002, the ZVI chemical reduction pilot test in SA-2 reduced the concentrations of TCE in two source area monitoring wells by 52 and 90%, respectively. TCE concentrations were reduced during the first 13 months after injection and then began to show increases, possibly indicating rebound. MSFC plans to continue groundwater monitoring on a quarterly basis to evaluate the potential for rebound.

As of March 2002, TCE degradation products, including DCE, VC, and chloride, were identified in the groundwater, and the redox potential for the groundwater changed to highly reducing conditions, providing support that the chemical reduction process was affecting groundwater quality.

NASA's contractor reported that the following types of additional information are needed at the site. Continued groundwater monitoring should provide data about the performance of the downgradient reactive zone as well as sustained trends in the source areas. Some supplemental groundwater monitoring points would provide data to better understand groundwater movement and interpret water quality results. Monitoring for end products such as methane, ethene and ethane should be conducted more frequently. Use of carbon isotope ratios in groundwater may be useful in understanding the magnitude of biological degradation that may be contributing to contaminant degradation. Before termination of the pilot test, *in situ* and monitoring well groundwater samples should be collected to estimate the remaining amount of contaminant mass.

NASA's contractor also reported that several key "unknowns" about site conditions and the technology exist and may not be resolved. The available site characterization data indicated that the mass occurs largely in the dissolved groundwater phase, but that some soil-partitioned contamination may be present beneath areas of the site. The distribution of the ZVI within the target zones has only been qualitatively defined; surface techniques to fully delineate the distribution have not yet been successful. As with conventional permeable reactive barriers, the long-term duration of the ZVI effectiveness may remain unknown.

NASA's contractor stated that creating a slurry-based ZVI reactive zone using injection technology (as opposed to forming a reactive wall of granular ZVI using conventional trenching techniques) presented unique design considerations.

The injections can be impacted by geologic heterogeneities that affect the ZVI placement in the subsurface. This increases uncertainty with respect to the amount of ZVI available versus the required retention time for groundwater treatment within the reactive zone.

EPA expressed the following concerns about the pilot test results provided for SA-2:

- The radius of influence of the ZVI injections should not be considered the same as the radius of influence of the pneumatic fracturing/FeroxSM delivery system, as observed through pressure measurements, daylighting/geysers/heave, and evaluation of soil cores for iron distribution
- The amount of ZVI needed to maintain long-term effectiveness of the technology in SA-2 has not yet been established
- There may be a concern with the bedrock portion of the aquifer (the pilot study evaluated only the rubble zone) in that there may be a downward migration of groundwater from the rubble zone to the bedrock in the area of highest concentration of groundwater contamination, and the injection of 11,000 lbs of ZVI into the rubble zone may have also affected the bedrock (further investigation is planned for the bedrock aquifer).

EPA also expressed concerns with the potential for on-going sourcing of TCE to the SA-2 plume from the MSFC-005 surface impoundment subsurface soils. EPA suggested that the potential for current and future migration of TCE from subsurface soils to groundwater is a significant uncertainty, and that the relationship of this uncertainty to the observed “rebound” effect should be explored.

NASA reported that the subsurface residuum was directly sampled between depths of 10 and 28 feet below land surface, at four separate locations outside the SA-2 pond and within the indicated groundwater “hot spots”, and that no significant amounts of contaminants were observed within the unsaturated intervals. These and other results indicated to NASA that the available information supports the conceptual site model that current and future migration of TCE from subsurface soils to groundwater is not a significant uncertainty at SA-2. However, NASA reported that it is planning to conduct supplemental investigations at SA-2 that would include a task to re-confirm the extent of contaminated subsurface media, based on using a MIP technique.

At another source area at MSFC, SA-12, injection of ZVI was found to not reduce the concentration of TCE. This was due to the presence of some separate phase DNAPL that was unexpectedly encountered in this area, with concentrations

(residuum and groundwater media) of TCE on the order of 500,000 µg/L. Further testing was planned for this area.

Table 2 – Actual Project Costs [5]

Cost Category/Element	Cost (2002\$ Basis)
1. Capital Cost for Technology	
Technology mobilization, setup, and demobilization	\$6,000
Planning and preparation	\$82,900
Site work - preparation/restoration	\$215,300
Equipment and appurtenances	\$70,150
Startup and testing	\$10,050
Other	\$44,400
<i>TOTAL CAPITAL COSTS</i>	\$428,800
2. O&M for Technology	
Labor	\$33,500
Materials	\$9,700
Utilities and fuel	---
Equipment ownership, rental, or lease	---
Performance testing and analysis	\$21,000
Other (includes nonprocess equipment overhead and health and safety)	\$6,200
<i>TOTAL OPERATION AND MAINTENANCE COSTS</i>	\$70,400
3. Other Technology-Specific Costs	
Compliance testing and analysis	---
Soil, sludge, and debris excavation, collection, and control	---
Disposal of residues	---
4. Other Project Costs	
Total cost	\$428,800
Total cost for calculating unit cost	---
Quantity treated	Not provided
Calculated unit cost	Not calculated
Basis for quantity treated	---

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Acknowledgments

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