In-Situ Remediation of Chlorinated Solvent Source Zone using ZVI-Clay Treatment Technology

Detailed site assessment work at a manufacturing facility in South Carolina indicated that a former French drain was acting as a continuing source of chlorinated solvents to ground water. The former drain structure was used historically for the disposal of various laboratory wastes (including chloroform [TCM], 1,1,2,2-tetrachloroethane [TCA], carbon tetrachloride [CT], and aromatic solvents) and was later closed by backfilling with soil. Source remediation was needed at the Site to improve the quality of down-gradient groundwater for compliance with state regulations. Zero-valent iron (ZVI) and clay soil mixing source-treatment technology was selected as the best option for source remediation at the site. The source-area treatment was completed in December 2007. A total of 42.9 tons of ZVI and 82.5 tons of bentonite clay were mixed into the subsurface to treat 883 cubic meters of source-zone soil was blended into the soil by Redox Tech. The blending was completed with Redox Tech's proprietary rotary soil blending equipment. The results of post-treatment sampling activities confirm that the ZVI-clay source-area treatment significantly reduced contaminant mass in the source zone and suggest that the treatment has had a positive impact on groundwater quality in the area. The soil mixing equipment and field implementation methodology used in this project were selected to address the specific needs of a site with a small, shallow source area.

INTRODUCTION

A manufacturing facility in South Carolina has a former French drain that was used from 1960 to 1972 for disposal of various laboratory wastes (including chloroform [TCM], 1,1,2,2-tetrachloroethane [TCA], carbon tetrachloride [CT], and aromatic solvents). The drain structure was closed by backfilling with soil. Numerous groundwater and soil investigations at the site indicated that the former drain was acting as a continuing source of chlorinated solvents and other volatile organic compounds (VOCs) to groundwater.

SITE DESCRIPTION

Soils underlying the manufacturing facility are typically comprised of clay loams that are nearly level, deep and moderately well drained. Shallow sediments underlying the former French drain consist of interbedded silty sand and clay. These sediments are underlain by a continuous dark gray to black, very stiff, clay approximately 22 to 25 feet below ground surface (bgs). This clay unit ranges in thickness from 3 to 10 feet. The clay overlies and defines the top of a locally confined unit of relatively clean, fine to medium grained sand. Shallow groundwater occurs under water table conditions and was encountered in the area of the former French drain at approximately twelve to fifteen feet bgs.

The delineated surface footprint of the former French drain source area was approximately 6.1 m by 6.1 m, and the contaminated soil depth extended to approximately 7.6 m below grade. The

source-area volume was estimated to be approximately 280 cubic meters with maximum observed source zone concentrations of TCM, TCA, and xylenes in the subsurface as high as 13,000 ppm, 4,400 ppm, and 3,000 ppm, respectively. Lower concentrations of CT and ethylbenzene were also found.

Vertical soil profiles within the shallow aquifer zone indicate that the highest historical source-area constituent concentrations were detected in the upper portion of the surficial aquifer in the immediate vicinity of the former French drain. Analytical results from groundwater monitoring wells installed approximately 300 feet down-gradient of the area indicated groundwater constituent concentrations that were several orders of magnitude lower than concentrations in the source area. Source-area constituents down-gradient of the source zone in monitoring wells screened below the confining clay layer in the deeper aquifer were below detection levels.

SOURCE-AREA TREATMENT SELECTION

Groundwater at this site is not used as a potable source and eventually discharges to an adjacent river. However, source remediation was needed to improve the quality of down-gradient ground water for compliance with state regulations. Both a traditional feasibility study and an environmental sustainability assessment were conducted to evaluate potential remedy options. Based on these assessments, ZVI-Clay source treatment technology, combined with down-gradient natural attenuation, was selected as the best option for source remediation at the site.

In-situ shallow soil mixing with ZVI-clay has been shown to be an effective treatment for chlorinated solvent contamination with a relatively fast treatment time.   This technology calls for the mechanical mixing of ZVI and a clay stabilizing agent (bentonite clay) directly into the contaminated soil, thereby creating a homogenous mixture of soil, clay, iron, and the target contaminants. The mixture becomes a reaction zone with low permeability, minimizing contaminant mass flux. Implementation of this technology at previous sites involved the use of large, expensive drilling equipment.   However, the soil mixing equipment and field implementation methodology used in this project were selected specifically to minimize mobilization costs and to address the particular needs of a site with a small, shallow source area.

The ZVI-clay treatment approach has several benefits. First, the source-area constituent mass is reduced via chemical reduction with ZVI reactive media. ZVI has the demonstrated ability to degrade halogenated organic compounds to both partially and fully dechlorinated hydrocarbon compounds and inorganic chloride ion using anaerobic iron corrosion processes to drive these reactions. Next, the clay promotes uniform distribution of the iron during the mixing process and significantly decreases constituent mobility and mass flux from the source area by reducing the permeability of the treated area. Finally, operation and maintenance requirements are minimal, thus making the technology sustainable.

During previous site investigation activities, soil cores were collected and submitted for laboratory studies to characterize the potential of the ZVI-Clay technology to treat the Site target compounds.   The studies indicated that the Site target compounds (carbon tetrachloride, chloroform, and 1,1,2,2-tetrachlorethane) can be readily degraded using the ZVI-Clay treatment technology. Treatment of the carbon tetrachloride was shown to yield some methylene chloride degradation products; however this compound is expected to biodegrade in the downgradient

aquifer region if not fully treated by the ZVI. These results provided a basis for development of the treatment implementation methodology.

MATERIALS AND METHODS

The source-area treatment was completed at the Site in December 2007. Prior to the start of the soil mixing activities, the top five feet of uncontaminated soil in the treatment area was removed to account for the anticipated volume increase due to "fluff" of soil resulting from the mixing and addition of the ZVI and clay and to allow for deeper vertical mixing in the treated area. The removed soil was stockpiled on-site to be reused for site grading and restoration following the soil mixing activities.

As in-situ blending is limited by the reach of the mixing tool (approximately 20 to 25 feet), the treatment area was designed to resemble a bowl, as shown in Figure 1. This design allowed for the maximum mixing depth to be achieved in the center of the source zone (in the area with the highest VOC concentrations). The 40-foot by 60-foot treatment area was divided into 23 cells (Figure 1).   At the entry and exit points of the mixing area, the extent of mixing curved upwards where the equipment entered/exited the area.
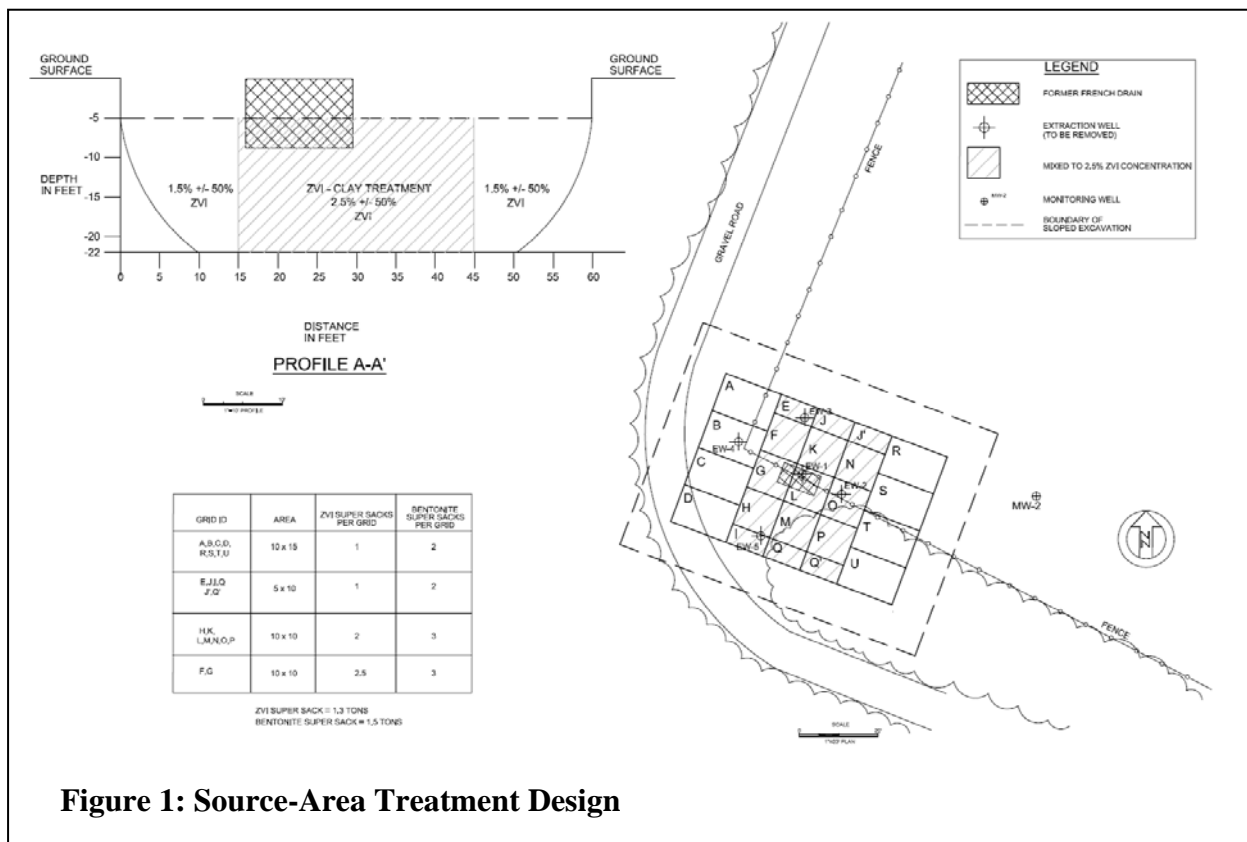

Figure 1: Source-Area Treatment Design

The implementation of the ZVI-clay soil mixing technology at previous sites involved the use of a crane-mounted caisson drilling rig. However, the relatively small size of the source area, as well as the prohibitive cost of the crane-mounted equipment, precluded the use of this type of machinery for this project. Therefore, Redox Tech's smaller and more cost-effective, soil mixing equipment was selected for use at the site.

After the ZVI and clay had been appropriately distributed among the cells, a conventional excavator with two-foot long ripper teeth was used to roughly mix the ZVI, bentonite clay, and soil. During this step, water was added to each cell to hydrate the bentonite and assist in the mixing process. The volume of water was monitored with an in-line water meter. In addition, a field technician sprayed water from the side of the excavation using a pump in a 500-gallon plastic water storage tank to further assist in the mixing process and to control dust. Approximately 53 gallons of water per cubic yard of soil (a total of approximately 61,000 gallons) was mixed into the treatment area. To prevent the excavator from moving or sliding while mixing in the final row of cells, the excavator was secured to a bulldozer.

Following the initial mixing of the ZVI, clay, and water using the conventional excavator, an *in-situ* blender was used to more thoroughly distribute the material throughout the source-area. The *in-situ* blender was a 28-inch diameter mixing drum with specially designed teeth (Figure 2) that rotated at speeds up to 100 revolutions per minute (rpm) with torque of 20,300 pounds per foot. The blender was mounted on a large excavator (Figure 3) with a modified diesel engine and hydraulic power system capable of hydraulic pressures of 5,000 pounds per square inch (psi).

Figure 2: *In-situ* Blender with Specially Designed Teeth

Figure 3: *In-situ* Blender Mounted on Excavator during Soil Mixing Activities

Soil mixing began at southeastern cell and progressed northwest, with two to five cells within a row mixed at a time. Peerless[TM] ZVI was mixed to a concentration of 2.5% by weight in the most contaminated subsurface soils, as shown by the hatched area in Figure 1. Peerless[TM] ZVI was mixed to a concentration of 1.5% by weight on the northwest and southeast ends of the treatment area, where the *in- situ* blending tool entered and exited. The remaining treatment area was mixed to a Peerless ZVI concentration of 1.5%. All soil within the treatment area was mixed to a bentonite clay concentration of 4%.

The low permeability clay unit was encountered at 22 feet bgs where the conventional excavator was unable to advance further. Soil mixing was not advanced beyond this clay unit. The rate of soil mixing ranged from 94 cubic yards per day to 252 cubic yards per day, with an average of 144 cubic yards per day. Over a period of eight days, a total of 42.9 tons of ZVI and 82.5 tons of bentonite clay were mixed into the subsurface to treat 1,155 cubic yards (883 cubic meters) of source-zone soil.

In order to evaluate the success of the *in-situ* mixing, initial soil sampling and iron content testing was conducted during the field activities. The iron content of discrete samples collected each day from the newly-treated areas was analyzed by magnetic separation and water content testing. All quality control tests indicated that adequate mixing was accomplished across the treatment area and that the required ZVI concentrations were achieved.

Following the completion of the soil mixing, the sloped portion of the excavation on each side of the treatment area was backfilled, creating a berm around the mixed soil. The treatment area was then covered with a woven geotextile fabric to assist in stabilizing the material and to prevent separation. The 110-foot by 75-foot fabric was sewn at the manufacturing facility and delivered to the site as a single panel. The fabric was secured by placing stockpiled soil on the edges. Upon completion of installation of the geotextile fabric, the stockpiled soil from the excavation, estimated to be approximately 645 cubic yards, was spread across the treatment area to cover the

mixed material and assist in consolidation of the treatment matrix. The soil was placed in concentric circles from the outer edges to the center of the treatment area and compacted. Approximately 100 tons of imported topsoil was then placed over the treatment area (to a thickness of approximately six inches). The area was graded and vegetated with seed (a fescue and ryegrass mix) distributed evenly across the area to ensure permanent grass cover. Silt fences were also erected around the treated area for erosion prevention control.

POST TREATMENT MONITORING

A soil and groundwater monitoring program was implemented to determine the impact of the source area remedy on constituent concentrations at the Site. To evaluate the effectiveness of the ZVI-clay treatment on the degradation of source zone contaminants, soil borings were collected one year after the completion of the soil mixing treatment. The soil borings were advanced within the treatment area adjacent to 2004 pretreatment baseline borings. Soil samples were collected at similar vertical sampling depths as the 2004 baseline samples and were analyzed for VOCs. Data from the post-treatment sampling events was then compared to the baseline data to evaluate source treatment effectiveness. In addition, a groundwater sampling program was developed to demonstrate that the proposed ZVI-clay treatment has positively impacted groundwater concentrations (i.e., decreased constituent concentrations) downgradient of the source area. Results of the post-treatment soil and groundwater sampling are presented below.

RESULTS AND DISCUSSION

The source area soil mixing ZVI-clay treatment was designed both to treat contaminants through contact with ZVI and to reduce contaminant mobility by reducing source-area aquifer permeability. The expected source treatment results include dechlorination of the chlorinated organic compounds, e.g. carbon tetrachloride, chloroform, and 1,1,2,2-TCA (Matheson and Tratnyek, 1994). Compounds that react very slowly with the ZVI (i.e. methylene chloride) or are not degraded by the ZVI (i.e., xylene) will remain bound within the reduced permeability treatment zone. The reduced mass flux of these compounds from the treated area to the aquifer will allow for longer treatment time in the source zone and will facilitate natural attenuation and biodegradation downgradient of the treated source area.

POST-TREATMENT SOIL SAMPLING

Post-treatment soil samples were collected from the source area in December 2008, approximately one year after completion of the treatment (Figure 4). One background sample (RP-01/PT-01) was collected northwest of the treated source area. Additional post-treatment samples were collected adjacent to the three 2004 pre-treatment boring locations that exhibited the highest VOC concentrations during the 2004 investigation. A total of four post-treatment soil samples were collected from varying depths in each of the three source-area soil borings (from approximately the same sample elevation ranges as the pre-treatment samples). The post-treatment soil samples were submitted to the laboratory for VOC analysis.

Figure 4: Post-treatment Soil Sample Locations

VOC concentrations detected in the post-treatment source-area soil have shown a significant decrease (up to three orders of magnitude for some compounds) from pre-treatment baseline concentrations. Figure 5 illustrates the changes in soil concentration from pre-treatment to post-treatment of carbon tetrachloride, chloroform, and 1,1,2,2-tetrachloroethane at one sample depth from location RP-05/PT-05 (collected within the former source area). At this location, concentrations of these compounds were reduced to below detection levels after the source-area treatment. The samples collected from the other source-zone locations/depths showed similar results; carbon tetrachloride, chloroform, and 1,1,2,2-tetrachloroethane concentrations were also below detection levels in all other post-treatment source area samples. These results indicate that the ZVI treatment is degrading source-area chlorinated organic compounds.

Figure 5: Concentrations in Soil at Location RP-05/PT-05 (Depth of 87 to 88 ft MSL)
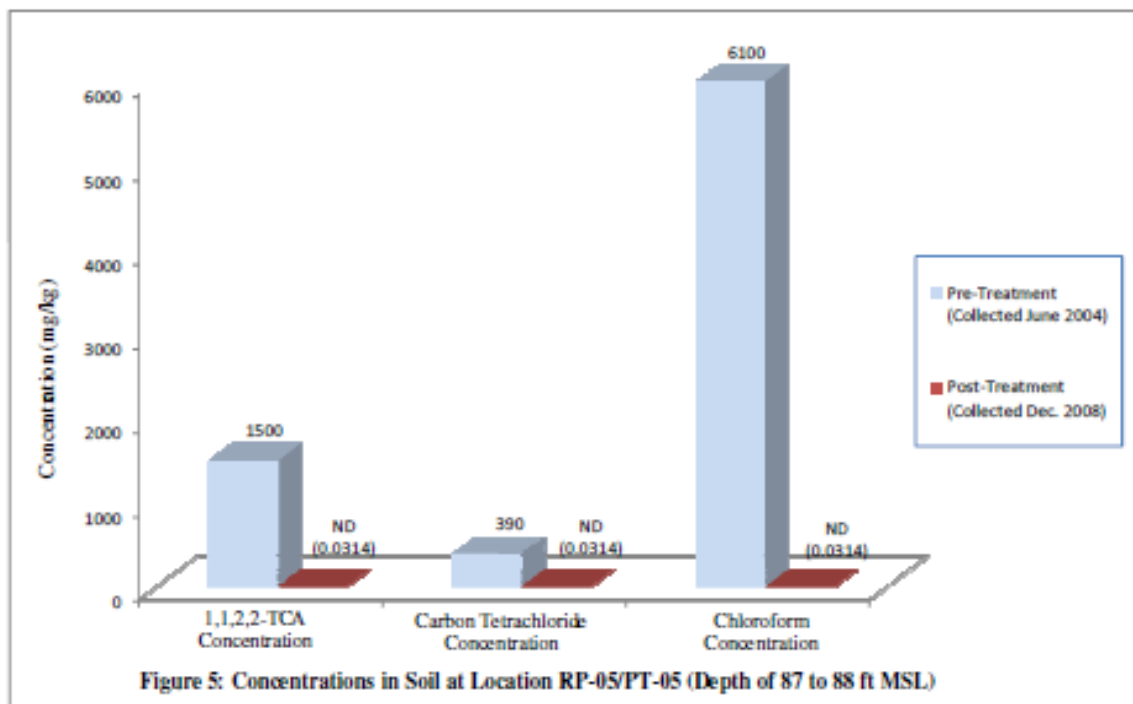
The carbon tetrachloride and chloroform reduction reactions are expected to generate some methylene chloride as a reaction by-product (Matheson and Tratnyek, 1994). Methylene chloride is degraded by the ZVI, although the reaction rate (e.g. half-life) is very slow. Low levels of methylene chloride were detected in the post-treatment soils, supporting reductive dechlorination of the parent compounds. The increased residence time in the source area, due to reduced permeability in the treated matrix, is expected lead to greater dechlorination of methylene chloride in the future.

Xylenes and other substituted benzene compounds (i.e., toluene, ethylbenzene, etc.) were not expected to be degraded by the ZVI but are immobilized in the low permeability treatment zone, and, therefore, have reduced diffusion out of the matrix. Furthermore, the source area was oxygen depleted prior to the soil mixing activities, which limited biodegradation. The soil mixing process introduced oxygen into the source area and enhanced aerobic degradation of these compounds. This enhanced aerobic degradation is evidenced by decreases in concentrations observed in the post-treatment samples. Subsequent release of these compounds to the aquifer system will be controlled by diffusive mass transfer processes. The diffusion flux should be low enough for the aquifer assimilative capacity to naturally attenuate these compounds via aerobic degradation processes

POST-TREATMENT GROUNDWATER MONITORING

Groundwater flow within the region of the former French drain source area trends in a northeastern direction, and the area has a relatively low gradient (calculated as 0.015 ft/ft from May 2009 measurements and 0.011 ft/ft from October 2009 measurements). Groundwater velocities in this area are likewise low, and as such, it would take several years before a definitive impact from the remediation activities would be apparent in any of the monitoring

8

wells down gradient of the immediate source area. However, the monitoring well immediately adjacent to the source area (MW-2) appears to be showing indications of treatment reactions.

Xylenes, carbon tetrachloride, chloroform, and 1,1,2,2-tetrachloroethane have historically exhibited the highest detected concentrations at the site and have been identified as good indicator parameters for groundwater impact from the source area. In well MW-2 (Figure 1), the 2009 post-treatment results indicate decreasing trends for 1,1,2,2-tetrachloroethane, carbon tetrachloride, and chloroform when compared to the last several years of monitoring (Figure 6). Initially, a slight increase in methylene chloride concentration (Figure 7) was observed post-treatment in MW-2. This well is at the edge of the treated matrix, where travel distance and available residence times for dechlorination reactions is shorter, and therefore, some methylene chloride diffused into the aquifer system prior to reacting with the ZVI. As a longer residence time was achieved, the methylene chloride concentration in MW-2 began to decrease.

Figure 6: MW-2 Post-Treatment Groundwater Monitoring Results (Indicator Parameters)
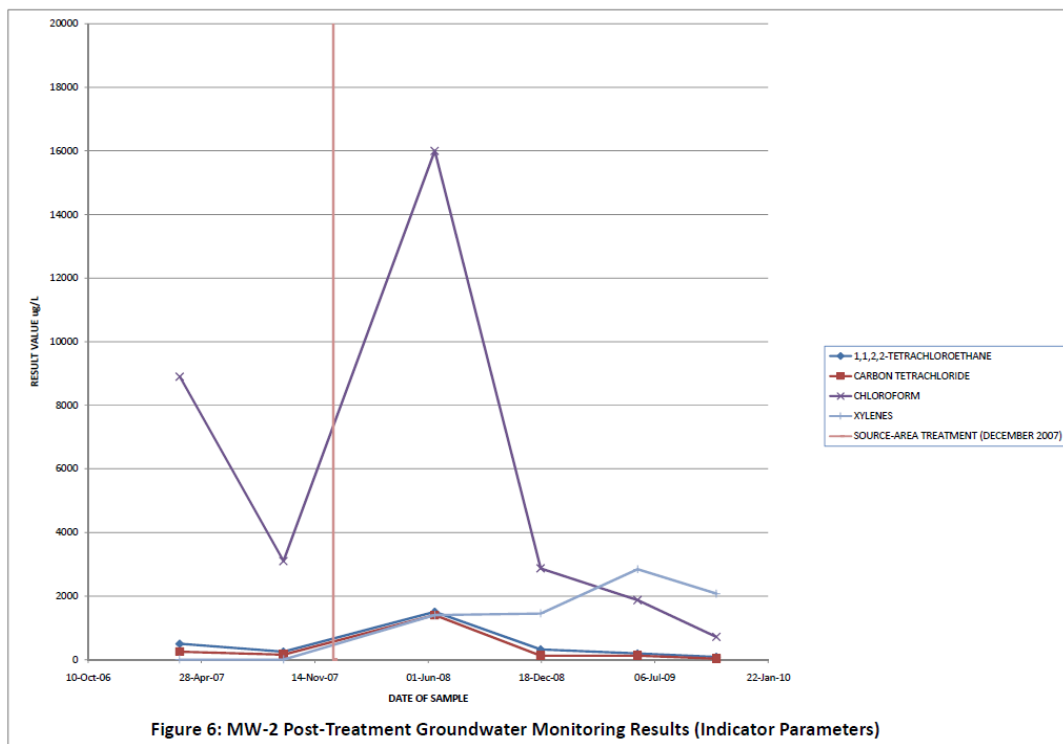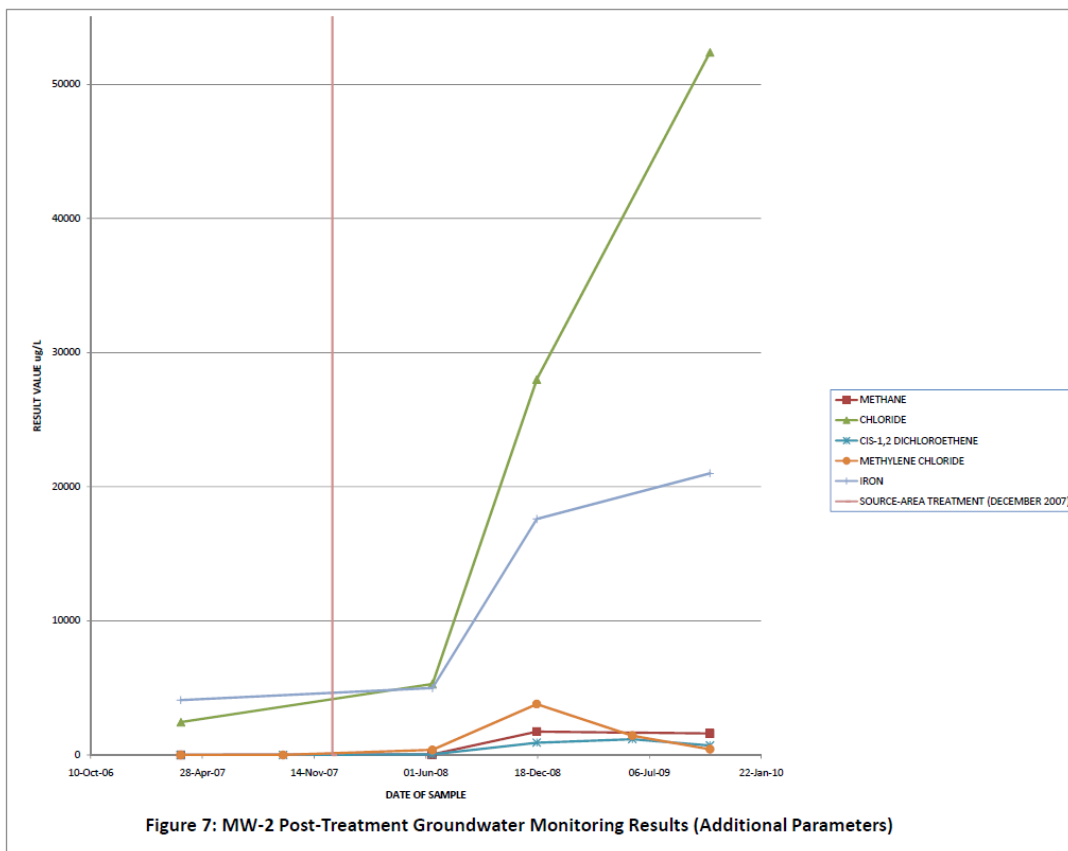
Figure 7: MW-2 Post-Treatment Groundwater Monitoring Results (Additional Parameters)

Chloride concentrations in MW-2 continue to rise, as would be expected from the treatment of carbon tetrachloride and/or chloroform by ZVI (Figure 7). Post-treatment increases in iron and methane also indicate that conditions in well MW-02 are strongly reducing and are likely conducive to further degradation of source-area contaminants. Impact of the source-area treatment on the remaining down-gradient wells remains uncertain thus far.

CONCLUSIONS

Post-treatment soil samples collected from the source area show a significant decrease in constituent concentrations when compared to pre-treatment soil sampling results. In addition, although only preliminary post-treatment groundwater trends can be discerned at this time (due to the low gradient and low groundwater velocities in the source area), the monitoring well immediately adjacent to the source area (MW-2) appears to be showing evidence of treatment reactions.

Overall, the results of the post-treatment sampling activities confirm that the ZVI-clay soil mixing source-area treatment has significantly reduced contaminant mass in the source zone and suggest that the treatment has had a positive impact on groundwater quality in the area. Furthermore, the results illustrate the success of implementing ZVI-clay soil mixing technology with smaller, more cost-effective, soil mixing equipment to address the specific needs of a site with a small, shallow source area.

REFERENCES

Matheson, L. J. and P. G. Tratnyek. 1994. "Reductive Dehalogenation of Chlorinated Methanes by Iron Metal." *Environ. Sci. Technol.*, 28: 2045-2053.