

INJECTION OF ZERO-VALENT IRON INTO A BEDROCK FORMATION FOR THE REDUCTION OF TCE

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ABSTRACT: An innovative approach to emplace zero-valent iron (ZVI) for the treatment of trichloroethene (TCE) in a weathered bedrock aquifer was implemented at a former industrial site in central New Jersey. A dual-phase extraction system (DPE) consisting of an SVE system in conjunction with a pump-and-treat groundwater remediation system had previously achieved significant mass reduction in the shallow weathered bedrock formation within the former source area. The TCE concentrations were once as high as 170,000 µg/L. Three years into the DPE operation, the level stabilized at approximately 300 µg/L to 3,000 µg/L. A field program was devised to assess the effectiveness of ZVI in further reducing TCE concentrations in the former source zone to levels that may achieve site closure or pave the way for Remediation by Natural Attenuation. A proprietary ZVI powder, roughly 70 µm in size, was emplaced in the bedrock aquifer via three injection points in the former source area of the plume by an innovative injection technique in which a ZVI-water slurry was driven into the formation by a nitrogen gas stream acting as a carrier fluid. Results of the groundwater sampling program showed an immediate reduction in TCE concentrations by more than 99%. Seven months after the injection, TCE concentrations remain depressed and the reaction is still occurring. A corresponding increase in *cis*-1,2-DCE concentrations and the appearance of trace levels of vinyl chloride and ethene signified reductive dechlorination of the TCE by the ZVI.

INTRODUCTION

Site Background. The site occupies approximately 10 acres of land in central New Jersey and is located in a mixed industrial-commercial-residential area. The original facility was constructed in the early 1900s as a manufacturing plant for electrical equipment (Figure 1). In 1984, operations were discontinued at the facility triggering an investigation under New Jersey's Environmental Cleanup Responsibility Act (now known as the Industrial Site Recovery Act). This facility has since remained vacant. Most of the former structures have been decontaminated and demolished except for their concrete slab foundations. Numerous investigations and remediation efforts were conducted onsite targeting the shallow bedrock aquifer, which extends to a depth of approximately 28 feet below ground surface in the source area. As part of these environmental investigations, more than 70 monitoring wells had been installed on and off the property. Groundwater elevation and quality data have been collected since 1986. TCE was identified as the primary contaminant of concern in the shallow bedrock aquifer with concentrations as high as 170,000 µg/L within the former source area and as high as 2,000 µg/L downgradient of the former source area.

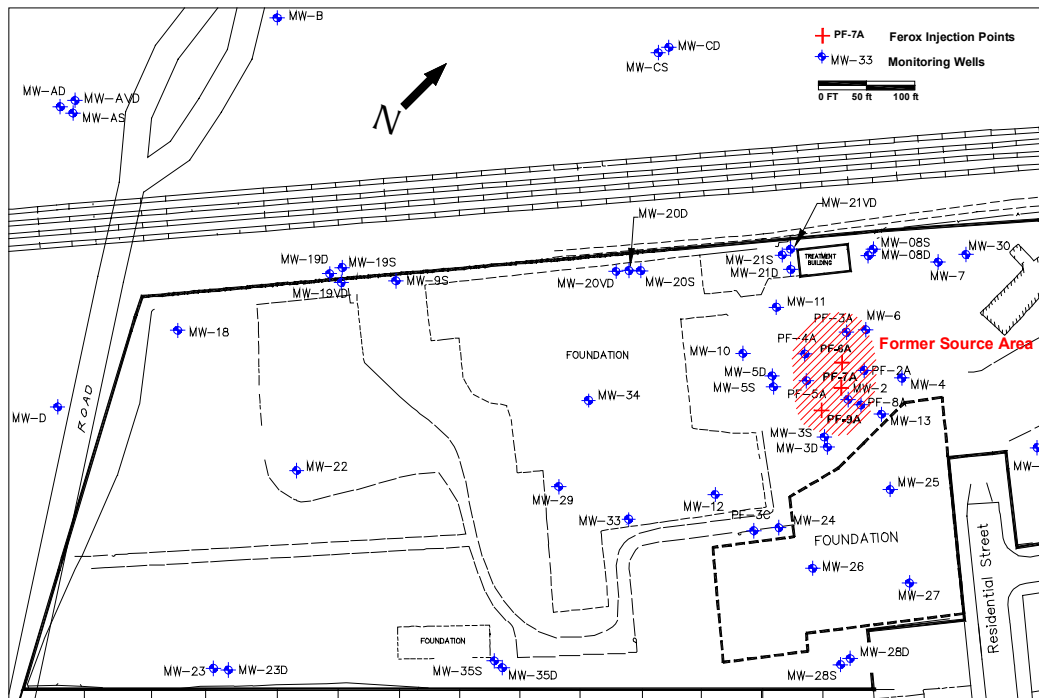


FIGURE 1. Site Map Showing The Former Source Area and Locations of FeroxSM Injection Points

In the mid-1990s, an enhanced DPE system was installed in the former source area. The efficiency of the system was greatly enhanced with the application of Pneumatic Fracturing within the treatment area that greatly increased the hydraulic conductivity within the targeted zone, thus allowing for the effective and efficient removal of the free-phase TCE.

The DPE system was successful in achieving a quick mass removal during the first few years of its operation and thereby reducing TCE concentrations in the source area from upwards of 170,000 µg/liter to levels generally less than 3,000 µg/liter in the late 1990s. For the first 2 years of its operation, the system removed approximately 145 pounds (lbs) of TCE per year. In contrast, the system removed 4.6 lbs during the last year of its service. The reduction and “leveling off” in the mass removal rate of the system suggested that the recovery had reached an asymptotic level. Several attempts to enhance recovery including system pulsing and re-application of Pneumatic Fracturing did not increase mass removal rates. It has been theorized that the former presence of TCE in DNAPL phase may have lead to the diffusion of the compound into the rock matrix of the weathered shale, which is relatively porous. After the removal of the free product, the absorbed TCE slowly leaches out of the rock fragments and reached a partitioning equilibrium with the groundwater in establishing relatively constant dissolved concentrations that show a certain fluctuation due to hydraulic variations.

Local Hydrogeology. The site is located at the eastern terminus of the Piedmont Province of the Appalachian Highlands and is underlain by a low-permeability fractured bedrock aquifer. The formation consists of low-permeability reddish-brown to brownish-purple siltstone and shale that is thinly bedded and fissiled within the area of the site. A

thin layer of unconsolidated soils overlays the bedrock formation and is approximately 5 to 8 feet in thickness in the treatment area.

Hydraulic conductivity in the fractured rock formation varies, but was generally found to be approximately 5×10^{-5} cm/sec. Groundwater flow is strongly influenced by the secondary (fracture) porosity along the regional bedding planes which dips approximately 7 degrees to the north-northwest. The predominance of nearly horizontal bedding fractures results in highly anisotropic conditions, with horizontal conductivities approximately two orders of magnitude greater than the vertical hydraulic conductivities.

Objectives. A field program to inject ZVI powder using a gas-based process (FeroxSM Technology) was proposed and conducted to achieve two objectives. The first objective was to demonstrate that injected ZVI within the former source area was capable of achieving greater TCE reduction than the existing DPE system, which had reached its limit of effectiveness. The second objective was to assess the extent of the TCE reduction with the goal of achieving concentrations that will allow for the regulatory agency's approval of remediation by Natural Attenuation.

TECHNOLOGY BACKGROUND

The insitu reduction of dissolved chlorinated volatile organic compounds (CVOCs) utilizing zero-valent iron (ZVI) has been accepted as an effective means of insitu chemical reduction. To date, ZVI technology has been applied at numerous sites either as a passive barrier-type of remediation system or injected and dispersed into granular medium formations. Directly addressing CVOC contamination in a fractured bedrock formation remained a challenge, mostly from an emplacement or delivery aspect. The development and advancement of the ZVI injection technology was seen as a breakthrough in overcoming this hurdle and thereby expanding the application of the ZVI technology to bedrock formations as well as other low-permeability geologic materials. This newly developed technology, FeroxSM, was based on a patented insitu chemical reduction process (US Patent No. 5,975,798), in which high-reactivity fine-grained ZVI particles are injected into the subsurface using an innovative injection process.

Feroxsm Technology. The technology involves the injection of a highly reactive ZVI powder, delivered as an iron-water slurry using nitrogen gas as the carrier fluid using an atomized multi-phase injection technique. This allows the delivery of the ZVI iron into the targeted saturated or unsaturated contamination zone. In lower permeability formations, such as weathered bedrock or clayey soils, FeroxSM is integrated with the Pneumatic Fracturing technology to enhance the effective permeability and connective porosity of the treatment zone for emplacement of the ZVI. Figure 2 shows a general schematic of the injection process. The injection assembly consists of the injection nozzle located between two or more straddled pneumatic packers. Injections are typically done in discrete 2.5-ft (0.76-m) to 3.5-ft (1.07-m) intervals isolated by the packers. This ensures a more even vertical distribution of the materials throughout the treatment zone. Following each injection, the injection assembly is lowered or raised to the next interval to repeat the process.

Nitrogen is the preferred carrier fluid as it facilitates the anoxic condition of the treatment zone. Typically, nitrogen is supplied to the site in bulk trailers. A pneumatic

injection module regulates and controls the pressure and flow of the nitrogen from the bulk trailer as it is delivered to the injection nozzle. A separate injection trailer mixes the iron-water slurry and pumps it into the gas stream. The high volume flow rate and velocity of the nitrogen gas “atomize” the slurry into a fine mist (much akin to an aerosol) and disperse it into the formation. The key advantage of this injection process over a conventional hydraulic pumping method is that the compressibility of the nitrogen allows for a sudden yet controlled expansion of the gas thus converting the potential energy stored under high pressure to kinetic energy expressed as injection velocity and volume.

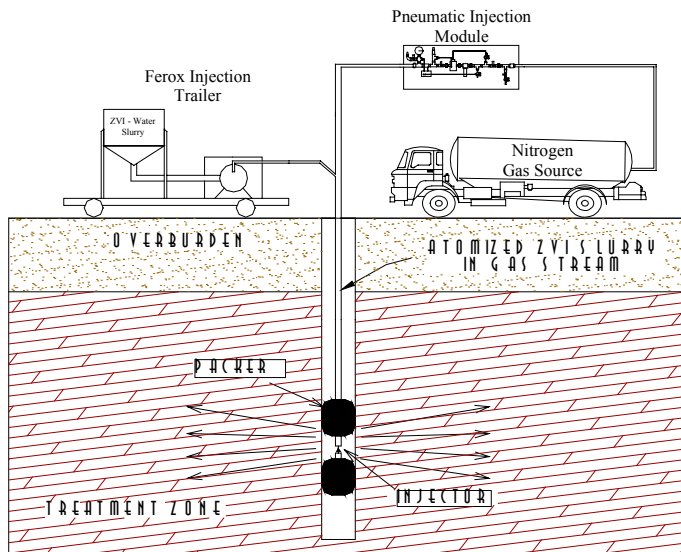


FIGURE 2. FeroxSM Injection Schematic

Once the powder is emplaced, the reaction mechanism begins with the corrosion of the ZVI powder as it comes into contact with water molecules. The products of corrosion are ferrous iron (Fe^{+2}), hydrogen gas (H_2), and a hydroxyl ion (OH^-). The hydrogen gas then combines with the halogenated organic compound (e.g., TCE) on the surface of a catalyst (iron powder, naturally occurring electron mediator, or unidentified constituent in the soil organic matter) whereby the contaminant is dehalogenated. In addition to the dehalogenated compound, a proton (H^+) and chloride ion (Cl^-) are also produced. The proton then combines with the hydroxyl ion formed during the corrosion reaction to reform a water molecule. Accordingly, the end products of this reaction are ferrous iron, chloride ions and the dehalogenated compound.

Pneumatic Fracturing Technology. Pneumatic Fracturing (PF) is a patented (US Patent No. 5,032,042), innovative technology developed by the New Jersey Institute of Technology (NJIT). Application of PF serves to enhance effective permeability by creating fractures within the subsurface and to reduce geologic heterogeneities within the treatment zone, thereby increasing the bulk permeability of the formation. The process may generally be described as the injection of a gas into the subsurface at a pressure that exceeds the natural insitu stresses, and at flow volumes exceeding the natural permeability of the formation. The result is the creation or dilation of interconnected fractures or soil pore spaces.

Fracturing was performed on the site in 1995 for the application of the DPE system. Prior to the injection of the FeroxSM slurry, PF was applied again at the injection points. The re-application was intended to dilate and clear out the existing fractures that were created during the initial fracturing event. The application of the PF technology resulted in an increased injection radius and facilitated a more effective dispersion of the iron powder during the FeroxSM application.

FIELD PROGRAM APPROACH AND PROCEDURE

The general layout of the injection area is presented in Figure 3. Three existing DPE wells (PF-6A, PF-7A and PF-9A) were selected as the injection wells. The locations of these three wells transect the middle of the former source area. These three wells were constructed as open boreholes from approximately 8 ft (2.44 m) to 28 ft (8.53 m) bgs with a solid steel casing through the overburden to the surface. They were installed as extraction wells during the operation of the DPE system and, as such, were previously pneumatically fractured as part of the permeability enhancement in 1995.

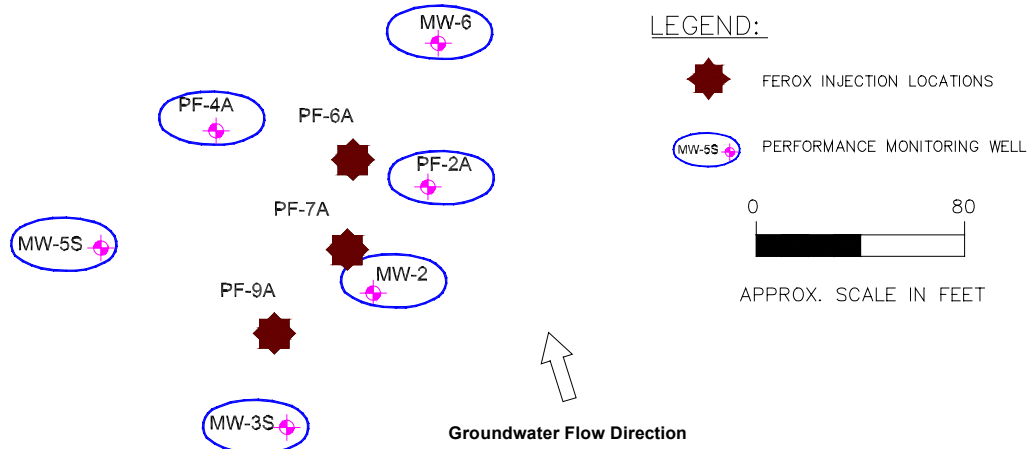


FIGURE 3. Layout of FeroxSM Injection Pilot Test

With the approval from the regulatory agency, the DPE system was shut off one month prior to the commencement of the injections to allow the groundwater to equilibrate to an unstressed state and to allow field personnel to make the necessary modifications to the existing extraction wells for the planned injection and monitoring.

Injection Procedure. The design entailed the emplacement of 5,000 lbs (2,275 kg) of ZVI into the treatment zone via the three selected injection points. This amount was estimated based on an approximated mass of TCE within the test area. Within each injection point, pneumatic fracturing was performed preceding the injection of the ZVI slurry to re-dilate existing fractures and possibly induce new fractures in the weathered shale formation in order to provide effective emplacement of the iron powder. Injection at each of the three points started from the bottom of the hole. While injecting at base of the borehole, only a single packer was used to provide an upper seal to the injection. This resulted in the lowest injection interval of approximately 2.5 ft (0.76 m) in length. When the straddle packer assembly was used in subsequent shallower injections, the fracture intervals were approximately 3.5 to 4 ft (1.07 to 1.22 m).

During each fracturing and injection event, surface heave was monitored using a surveying level in conjunction with heave rods. This data serve as a secondary parameter to quantify fracture propagation. Two heave rods were placed at distances of approximately 1 to 2 ft (0.31 to 0.62 m) and 6 to 10 ft (1.83 to 3.05 m) from the injection borehole, respectively. During each pneumatic injection, the rods were monitored with a

surveying level to determine the maximum amount of surface displacement that occurred during the injections.

Injection pressure was recorded using a built-in pressure transducer and data-logging device in the pneumatic injection module. The characteristics of the pressure history curve during the fracturing and injection provide insights to the nature of the gas propagation into the formation from the injection point.

The pressure influence in nearby monitoring wells and boreholes was also monitored during the injection. These data are used to interpret the direction of fracture propagation, distance of propagation, as well as connectivity throughout the treatment zone. These measurements were made using pressure gauges equipped with maximum drag arm indicators mounted on the center rods of pneumatic packers used to seal off an adjacent wells or boreholes.

Groundwater Sampling Plan. Six monitoring wells (MW-2, MW-3S, MW-5S, MW-6, PF-2A and PF-4A) within the vicinity of the injection area were designated as performance verification monitoring wells. One of the three injection wells, PF-7A, was also monitored for groundwater quality. Two baseline and five post-injection sampling events were conducted to evaluate the effectiveness of the Feroxsm technology. Samples were analyzed by certified laboratories for VOCs following EPA Method 8260B as well as other pertinent parameters including anions alkalinity, ethene, total organic carbon and total/dissolved iron. During groundwater sampling, a flow-through-cell was used to monitor field geochemical parameters such as pH, dissolved oxygen (DO), oxidation reduction potential (ORP) and conductivity. These parameters allow field personnel to determine the representativeness of the purged water to the formation groundwater. They are also important indicators of the aquifer geochemical conditions in response to the injected ZVI.

Two baseline sampling events were performed 2 weeks and 1 day prior to the injection activities. PF-7A was not sampled during the first baseline sampling event. Five post-injection sampling events were conducted at intervals of 1 week, 4 weeks, 8 weeks, 13 weeks, and 30 weeks after the injection.

FIELD PROGRAM RESULTS

Injection Operation and Observations. The field injection activities took place over a period of 3 days. Within each target interval, approximately 125 to 300 kg of iron powder suspended in potable water were injected into the formation. Also included in this slurry was sodium bromide, which was used as a qualitative tracer in subsequent groundwater monitoring. A total of 5,005 lbs (2,275 kg) of iron powder was injected within the target zone through 3 boreholes from approximately 12 to 28 feet bgs. A detailed record of iron and sodium bromide injection volumes was kept as the injection progressed.

Minimal heave was observed during the injection events. In most instances heave was only observed during injections at the shallower intervals, and was limited to less than 1.5 cm. The lack of heave during deeper intervals is typical of the fracturing process due to the overlying weight of the overburden. No residual heave was measured during the fracturing events.

In all instances, pressure response was measured at multiple monitoring points, and at radial distances varying from 10 ft (3.05 m) to 60 ft (18.29 m). The pressure response recorded during the injection events provides additional assurance that the iron slurry was being emplaced within the target zone.

The injection pressure data with respect to time at the injection points suggest that the dilation of pre-existing fractures was successful. A quasi-steady injection flow was established at pressures significantly lower than that needed during the initial fracturing program during the mid-1990s.

Groundwater Sampling Results. Table 1 presents the results of the groundwater sampling and field geochemical parameters. Note that *trans*-1,2-DCE were mostly non-detect with occasional detections at single-digit µg/L levels. Over all, TCE concentrations in the injection area were drastically reduced subsequent to the emplacement of the ZVI, which had also promoted a much more reducing and anaerobic environment within the affected aquifer, creating conditions favorable to natural attenuation.

The most significant TCE reductions were seen in PF-7A, MW-2 and PF-2A, wells closest to the injection points. The corresponding increase in pH and decrease in ORP and DO demonstrated the reduction was attributed to the ZVI. In PF-7A and MW-2, where the reduction kinetics were the highest, *cis*-1,2-DCE concentrations showed an initial decreasing trend followed by a slight rebound or accumulation, likely due to the reduction of TCE to *cis*-1,2-DCE that is subsequently reduced, but at a slower rate. TCE in PF-2A, slightly sidegradient and upgradient to the injection points, showed a significant initial decrease followed by a gradual recovery as time progressed. The amount of ZVI reaching the well was likely insufficient to overcome the influx of TCE-laden groundwater. Ethene was detected occasionally at trace levels in all three wells. The resultant concentrations of ethene due to the dechlorination of the low levels of VC to ethene on a molar basis appeared to be below the analytical detection level on a weight by volume basis.

The other sidegradient well, MW-5S, is farther removed from the injection points than the other wells. CVOC concentrations at MW-5 did not show an impact by the ZVI injection. However, pH, DO and ORP measurements indicate that the ZVI has influenced the geochemistry of the groundwater at this point.

Downgradient wells MW-6 and PF-4A also showed clear indications of TCE reduction by the ZVI. However there appears to be a rebounding trend in TCE at PF-4A, though its concentration remained lower than the baseline by a factor of three. The geochemical parameters continue to indicate an induced reducing environment conducive to reductive dechlorination of the CVOCs. As the treated water moves out of the injection area, it may be re-contaminated with residual TCE near PF-4A. A particular characteristic of samples from PF-4A is the increase in *cis*-1,2-DCE concentrations to levels significantly above baseline. Correspondingly, there were frequent detections of VC, which has been seldom detected historically. This may be explained by the position of PF-4A, which sits directly downgradient of the center of the injection area, where sufficient *cis*-1,2-DCE and VC may be generated and accumulated.

Analysis for chloride ion was part of the sampling program; however, due to the high background concentrations of chloride in the groundwater (>30 mg/L), it was not feasible as an indicator of dechlorination.

TABLE 1. FEROX Performance Verification Sampling Results

Monitoring Wells	Sampling Events	Time Line	TCE (ug/liter)	cis-1,2-DCE (ug/liter)	VC (ug/liter)	Ethene (ug/liter)	pH (s.u.)	DO (mg/L)	ORP (mv)
PF-2A	Baseline I	- 2 weeks	1100	110	U	U	7.22	7.08	156
	Baseline II	- 1 days	730	44	U	U	6.87	5.29	192
	Post-Inj. I	+ 1 week	27	7	U	U	7.55	1.61	-162
	Post-Inj. II	+ 4 weeks	U	25	U	0.0036	7.68	0	-362
	Post-Inj. III	+ 8 weeks	42	42	1.96	U	7.54	0	-215
	Post-Inj. IV	+ 13 weeks	99	170	U	0.005	7.38	0	-211
	Post-Inj. V	+30 weeks	210	280	U	0.0015	7.52	0	-144
PF-4A	Baseline I	- 2 weeks	2800	380	U	U	7.57	1.08	120
	Baseline II	- 1 days	980	300	U	U	7.25	0.22	136
	Post-Inj. I	+ 1 week	200	69	U	U	9.25	0	-659
	Post-Inj. II	+ 4 weeks	360	250	24	0.015	9.08	0	-533
	Post-Inj. III	+ 8 weeks	49	61	10.53	U	9	0	-535
	Post-Inj. IV.a	+ 13 weeks	830	800	71	0.025	9.16	0	-335
	Post-Inj. IV.b	+ 15 weeks	290	480	42	NA	9.31	0	-269
	Post-Inj. V	+30 weeks	330	600	18	0.003	7.45	0	-190
PF-7A	Baseline I	- 2 weeks	NS	NS	NS	NS	NS	NS	NS
	Baseline II	- 1 days	770	180	U	U	6.62	4.56	178
	Post-Inj. I	+ 1 week	10	23	U	U	9.22	0	-580
	Post-Inj. II	+ 4 weeks	3	3	U	0.0006	8.2	0	-537
	Post-Inj. III	+ 8 weeks	9	9	U	NA	7	0	-449
	Post-Inj. IV	+ 13 weeks	47	39	U	NA	8.91	2.23	-483
	Post-Inj. V	+30 weeks	13	58	2	0.006	9.12	0	-359
MW-2	Baseline I	- 2 weeks	3700	68	U	U	7.42	6.42	125
	Baseline II	- 1 days	610	65	U	U	7.46	5.35	128
	Post-Inj. I	+ 1 week	8	17	U	U	9.56	0	-542
	Post-Inj. II	+ 4 weeks	2	2	U	0.001	8.6	0	-496
	Post-Inj. III	+ 8 weeks	5	7	U	U	9	0	-403
	Post-Inj. IV	+ 13 weeks	6	5	U	0.0064	10.03	1.76	-715
	Post-Inj. V	+30 weeks	3	15	U	0.0015	9.22	0	-314
MW-3S	Baseline I	- 2 weeks	140	3	U	U	7.83	0.56	268
	Baseline II	- 1 days	130	U	U	U	7.68	1.36	109
	Post-Inj. I	+ 1 week	53	2	U	U	8.05	0.28	165
	Post-Inj. II	+ 4 weeks	74	4	U	U	7.69	0	5
	Post-Inj. III	+ 8 weeks	37	1.7J	U	U	8	0	65
	Post-Inj. IV	+ 13 weeks	16	1.7J	U	U	7.77	2.23	-62
	Post-Inj. V	+30 weeks	5	2	U	U	7.85	0	80
MW-5S	Baseline I	- 2 weeks	990	160	U	U	7.57	0	248
	Baseline II	- 1 days	1200	210	U	U	7.5	0.96	108
	Post-Inj. I	+ 1 week	900	130	U	U	7.77	0	-257
	Post-Inj. II	+ 4 weeks	930	190	U	U	7.9	0	-26
	Post-Inj. III	+ 8 weeks	879	142	U	U	8	0	49
	Post-Inj. IV	+ 13 weeks	1000	170	U	U	7.87	0	-66
	Post-Inj. V	+30 weeks	530	150	U	0.001	7.6	0	-78
MW-6	Baseline I	- 2 weeks	560	300	0.7	U	8.15	10.49	280
	Baseline II	- 1 days	930	360	U	U	8.06	8.56	116
	Post-Inj. I	+ 1 week	130	71	U	U	8.18	1.2	-126
	Post-Inj. II	+ 4 weeks	26	10	U	0.0042	8.22	0	114
	Post-Inj. III	+ 8 weeks	32	13	U	U	8	0	103
	Post-Inj. IV	+ 13 weeks	41	28	U	U	8.1	0	6
	Post-Inj. V	+30 weeks	72	49	U	U	8.02	0.71	71

Notes: U - compound not detected at method detection limit, NS - not sampled

The site is currently under a quarterly groundwater monitoring program, which encompasses the entire site and includes several offsite downgradient wells. Two quarterly monitoring events have taken place since the pilot testing of the ZVI injection. No significant changes to the contaminant concentrations have been seen outside of the test area. However, there are indications that the injected ZVI have modified the redox condition of the aquifer as well as decreased the DO content.