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COST AND PERFORMANCE REPORT FOR A ZERO VALENT IRON (ZVI) TREATABILITY STUDY AT NAVAL AIR STATION NORTH ISLAND

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14. ABSTRACT
A zero-valent iron (ZVI) pilot treatability study was conducted for the treatment of chlorinated organics (primarily trichloroethylene) in groundwater at Operable Unit 20 at Naval Air Station North Island in 2006. From August 22, 2006 through September 7, 2006, Ferox^{sm} injection (pressurized injection of water and ZVI powder slurry) was implemented at five locations, between approximately 30 and 60 ft below ground surface. This report summarizes the cost and performance data from this treatability study.

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Cost and Performance Report for a Zero Valent Iron (ZVI) Treatability Study at Naval Air Station North Island

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EXECUTIVE SUMMARY

The objective of this cost and performance report is to summarize the results, review the performance, and draw lessons learned for future applications from the zero valent iron (ZVI) pilot test conducted at Operable Unit 20 (OU-20), Naval Air Station (NAS) North Island in San Diego, California.

NAS North Island is a 2,800 acre facility, just southwest of the City of San Diego. The ZVI injection treatability study was conducted at Operable Unit 20, which includes aircraft testing/maintenance shops and also chemical storage tanks and pipelines. The groundwater is contaminated with chlorinated volatile organic compounds (CVOCs) with trichloroethylene (TCE) as the main contaminant of concern at the site.

Geology at the site consists of silty sand and sandy silt mixtures with a deep clay aquitard layer, which limits downward migration of dense, non-aqueous phase liquid (DNAPL). Groundwater movement appears to be very slow, almost stationary. The groundwater plume is located from approximately 25 feet below ground surface (bgs) to 80 feet bgs.

At the site, ZVI injections were done at five locations between approximately 30 and 60 ft bgs, during the period of August 22, 2006 through September 7, 2006. At each injection location, Ferox^{sm} injection (pressurized injection of water and ZVI powder slurry) was conducted in nine discrete 3.5-foot intervals starting from the bottom of each borehole. One pound of ZVI powder was combined with approximately three gallons of potable water to make the suspended liquid ZVI slurry, which was introduced into the subsurface to react with and chemically reduce CVOCs. Injections were conducted from the corner soil boring locations to the center locations. The center point injections were conducted last. This particular injection design was intended to overlap and totally saturate the study area with the ZVI. The design dosage of ZVI powder for the entire treatability study area was determined to be 72,765 pounds, based on the mass ratios of iron to TCE and iron to soil.

Certain wells in the treatment area showed sharp declines in TCE, almost 90% reduction, as did dichloroethene (DCE). In the same wells, ethene gradually increased providing corroboration of complete dechlorination. In other parts of the treatment zone, the ZVI distribution may not have been as efficient. The monitoring well cluster that was the furthest away from the injection points showed lower treatment performance. The results show that ZVI was not evenly distributed, but in those locations where it did reach, it was effective in reducing CVOCs. Local aquifer heterogeneity could also have played a role in the lack of impact at the farther monitoring wells. The results also demonstrate a need for a smaller radius of injection and proper care for well development. The targeted radius of distribution of 20 ft or more at this site (assumed from the locations of the monitoring wells) may have been more ambitious than at previous sites. The well completion materials also may have affected ZVI injection performance at this site. Bentonite seals at four of the five new well clusters failed. This may have caused the persistent daylighting observed during the initial phase of the project, with the injected ZVI migrating preferentially towards the released pressure in the failed wells.

For the ZVI treatment at OU 20, the total cost of $607,386 was reported. For the 50-ft by 50-ft target treatment area (30-ft target depth), the unit cost of treatment is estimated at $164/cubic yard. This unit cost appears to be competitive with other in situ treatment technologies (e.g., in situ chemical oxidation), although unit cost comparisons can be misleading as several site-specific factors (e.g., degree of treatment achieved, level of contamination at the site, permeability of the soils, etc.) often are implicit in the unit cost.

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ACRONYMS AND ABBREVIATIONS

AST	aboveground storage tank
CL/ML	fine-grained clay/silt
CVOC	chlorinated volatile organic compound
DCE	dichloroethene
DNAPL	dense, nonaqueous phase liquid
EPA	U.S. Environmental Protection Agency
IDW	investigation-derived waste
ITSI	Innovative Technology Solutions, Inc.
NAS	Naval Air Station
ORP	oxidation-reduction potential
OU	operable unit
PCE	tetrachloroethene
PVC	polyvinyl chloride
SM	sandy/silt mixture
SP	poorly graded sands with little fines
TCE	trichloroethylene
VC	vinyl chloride
VOC	volatile organic compound
ZVI	zero valent iron

Section 1.0: INTRODUCTION AND SITE DESCRIPTION

This report evaluates the results of the zero-valent iron (ZVI) injection treatability study that was conducted at Operable Unit (OU) 20, Naval Air Station (NAS), North Island, California, and reported by Innovative Technology Solutions, Inc. (ITSI, 2007).

NAS North Island is a 2,800 acre facility, just southwest of the City of San Diego. It is bounded by the Pacific Ocean to its south and San Diego Bay to its northwest (Figure 1-1). OU 20 includes aircraft testing/maintenance shops and also chemical storage tanks and pipelines. The groundwater is contaminated with chlorinated compounds. The treatability study was conducted in a fairly developed portion of the site, which was occupied by large industrial and administrative buildings with adjoining concrete and asphalt paved parking lots and streets. The site contains minimal vegetation.

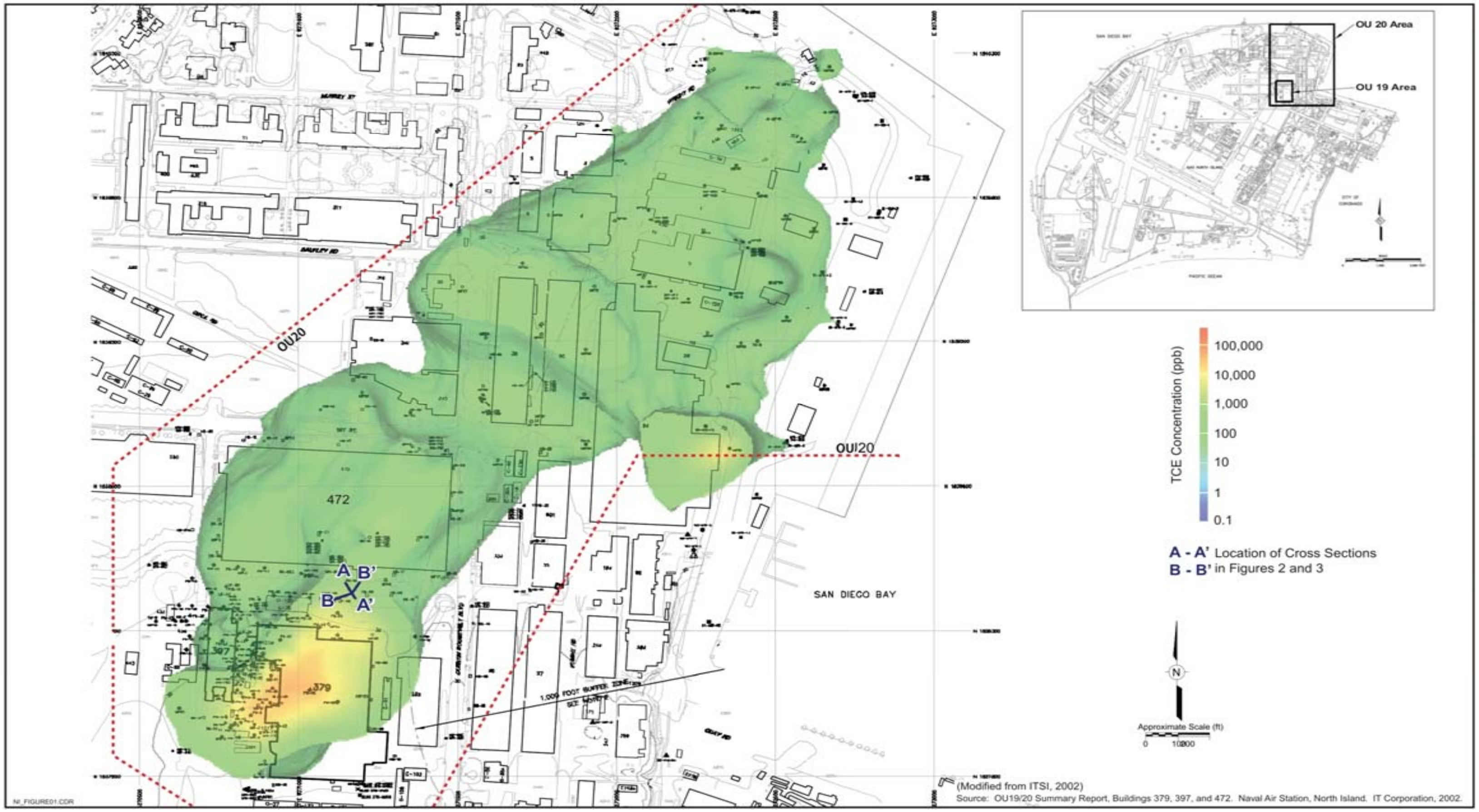

Figure 1-1. Site Location and Plume Extent Map of OU 20 NAS North Island (Source: ITSI, 2007)

Section 2.0: GEOLOGY AND HYDROGEOLOGY

Three geological units have been identified at NAS North Island. These units are (from the most recent to the oldest): artificial fill, Holocene beach deposits, and the Pleistocene Bay Point Formation. Artificial fill is mostly dredged material from San Diego Bay, placed in low-lying areas around the perimeter of the island. Holocene beach deposits consist of unconsolidated sand and silty sand of varying thickness deposited on the south-facing Pacific Ocean beach. The Bay Point Formation is the dominant stratigraphic unit on NAS North Island and consists mainly of thick marine, fossiliferous, loosely consolidated, fine- to medium-grained brown sand. In an easterly direction, toward the City of San Diego, the Bay Point Formation consists of non-marine, reddish, silty sands, gravel beds, and beach deposits. The deposition of the Bay Point Formation is consistent with a west dipping structural basin, resulting in thick marine deposits. Specifically, at OU 20, there are four distinct lithological units present. These include: (1) silty sand and sandy/silt mixtures (SM) up to a depth of 17 ft below ground surface (bgs), (2) poorly graded sands with little fines (SP) at a depth of 5 ft bgs to between 40 and 50 ft bgs, (3) silty sand and sandy/SM below poorly graded sands, and (4) a fine-grained clay/silt (CL/ML) unit at a depth of 60 ft bgs. The fine-grained clay/silt layer is the first real aquitard forming a barrier for downward migration of any dense, non-aqueous phase liquid (DNAPL). The last fine-grained clay/silt unit was not observed in the soil boring excavated for ITSIMW-2C. Calcareous shell fragments were found in the soil borings excavated at depths around 40 to 60 ft bgs. Figure 2-1 shows the location of two transects (A-A' and B-B') drawn across OU 20 to develop geological cross-sections of the site along two directions. Figure 2-2 and 2-3 are geological cross-sections along the northwest to southeast (A-A') and southwest to northeast (B-B') at the treatability study site. Water occurs at approximately 18 ft bgs.

There are three distinct groundwater zones (A, B, and C) identified at OU 20. Zone A lies between 18 to 28 ft bgs, Zone B lies between 40 to 45 ft bgs, and Zone C lies between 55 to 60 ft bgs. Figures 2-4 to 2-6 represent the groundwater elevations and direction of the groundwater in these zones. The gradients in all three zones are extremely low, so determining groundwater flow direction can be challenging. Groundwater in Zone A seems to be flowing north at a gradient of 0.0002 foot/foot (Figure 2-4). However, in Zones B and C the groundwater flow patterns seemed to change between August 2006 and February, 2007. The groundwater gradient in Zone B (Figure 2-5) was 0.0013 foot/foot and the groundwater ambiguously converged into a sink beneath the middle of the Second Street in August 2006; however, in February 2007 it was flowing north (Figure 2-6). In Zone C, groundwater moved in the northeast direction with a gradient of 0.002 foot/foot during the August 2006 sampling event; however, in February 2007 it was ambiguously converging into a sink in the middle of the Second Street. In general, groundwater movement appears to be very slow, almost stationary.

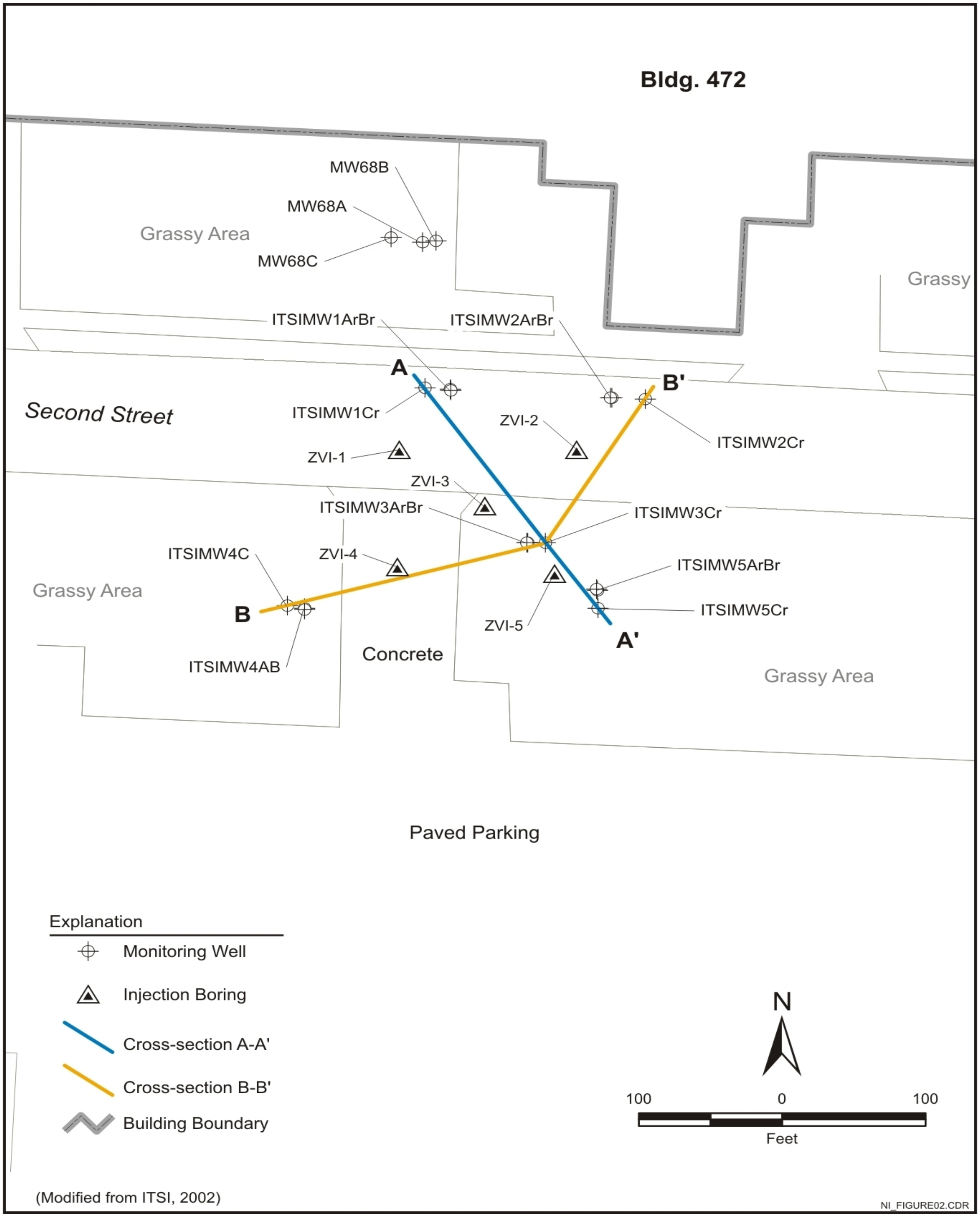

Figure 2-1. Location of Transects (A-A' and B-B') on OU 20 and ZVI Injection Points (Source: ITSI, 2007)

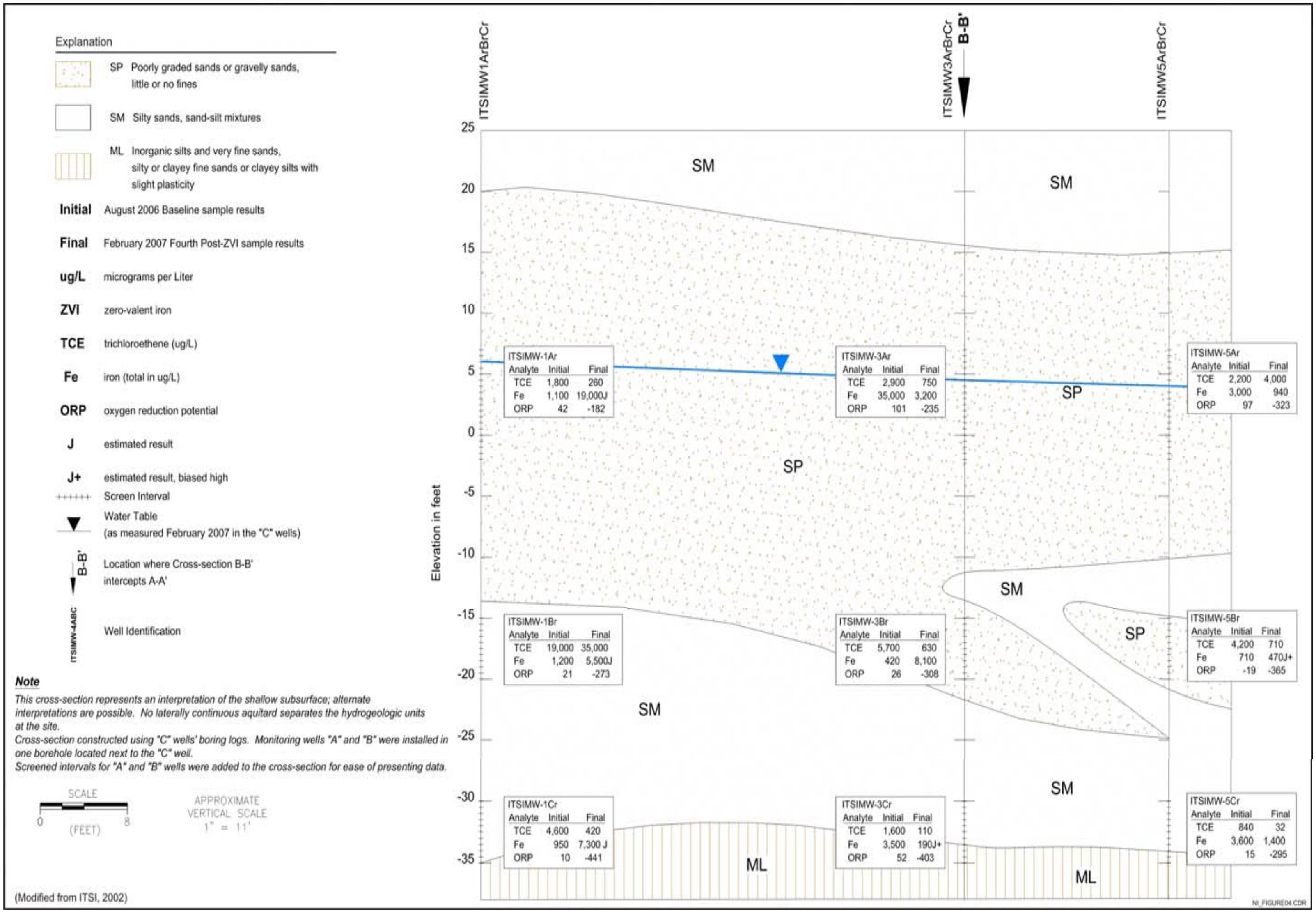

Figure 2-2. A-A' Geological Cross-section of OU 20 (Source: ITSI, 2007)

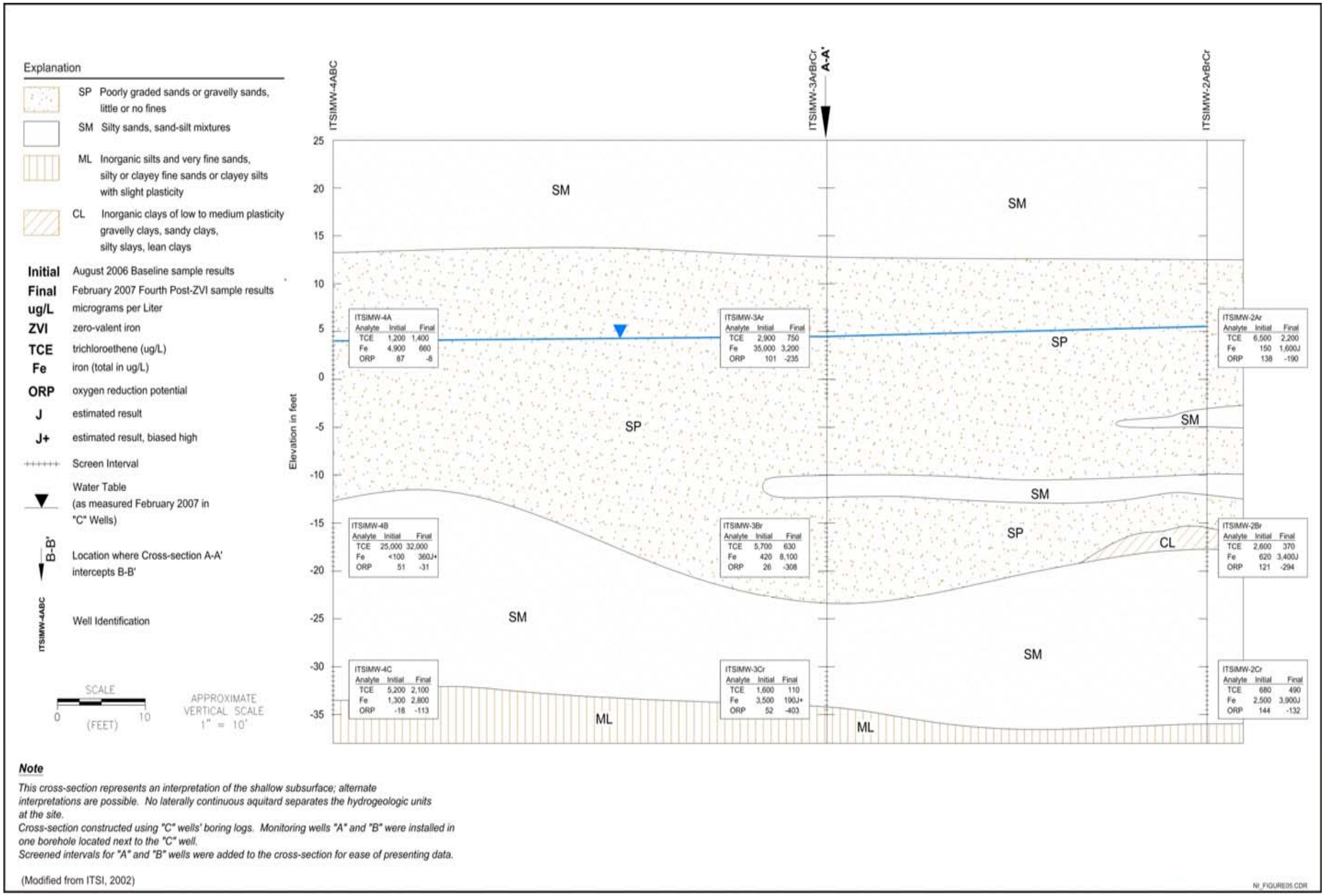

Figure 2-3. B-B' Geological Cross-section of OU 20 (Source: ITSI, 2007)

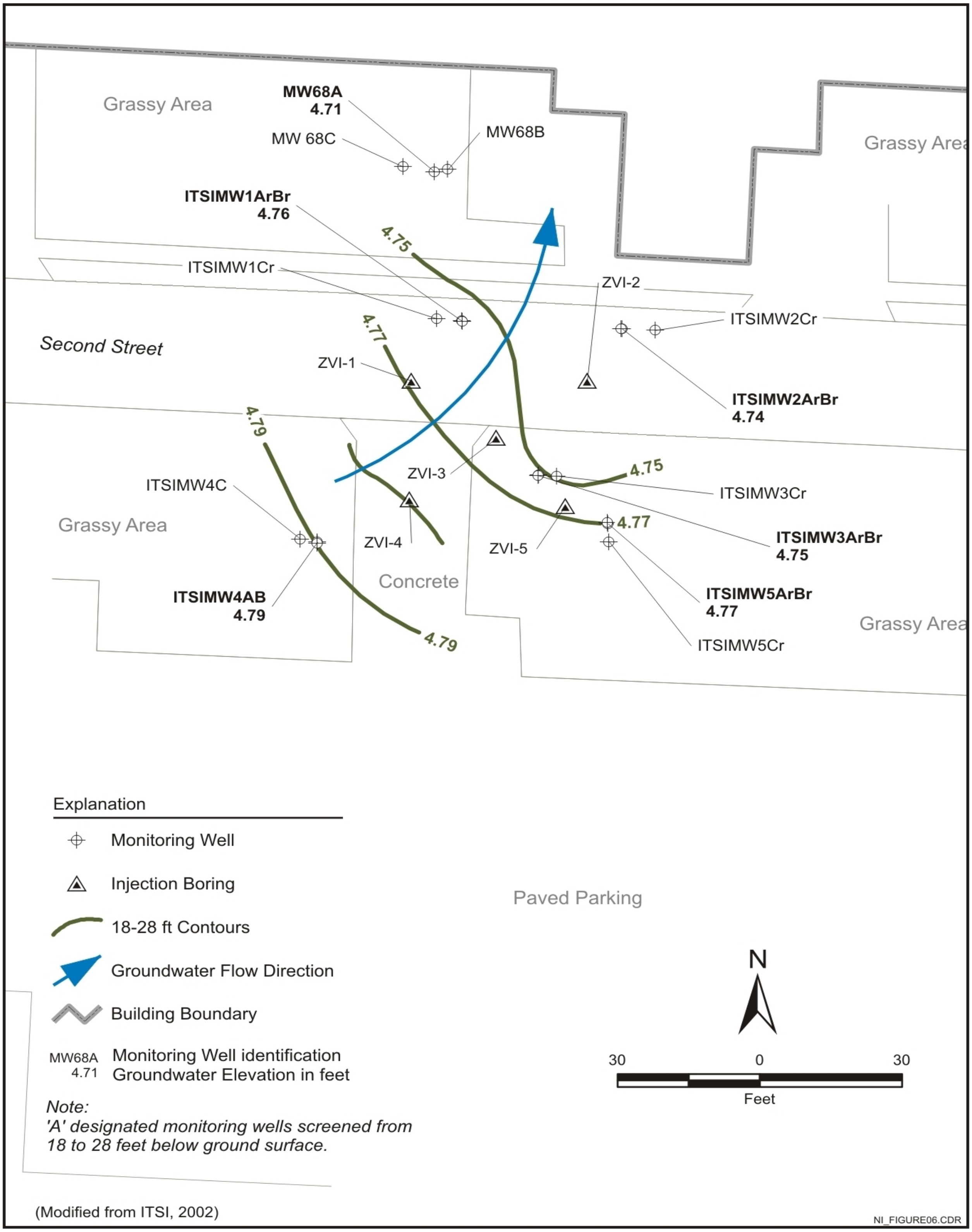

Figure 2-4. Groundwater Elevation and Direction Map for Zone A during August 06 Sampling Event (Source: ITSI, 2007)

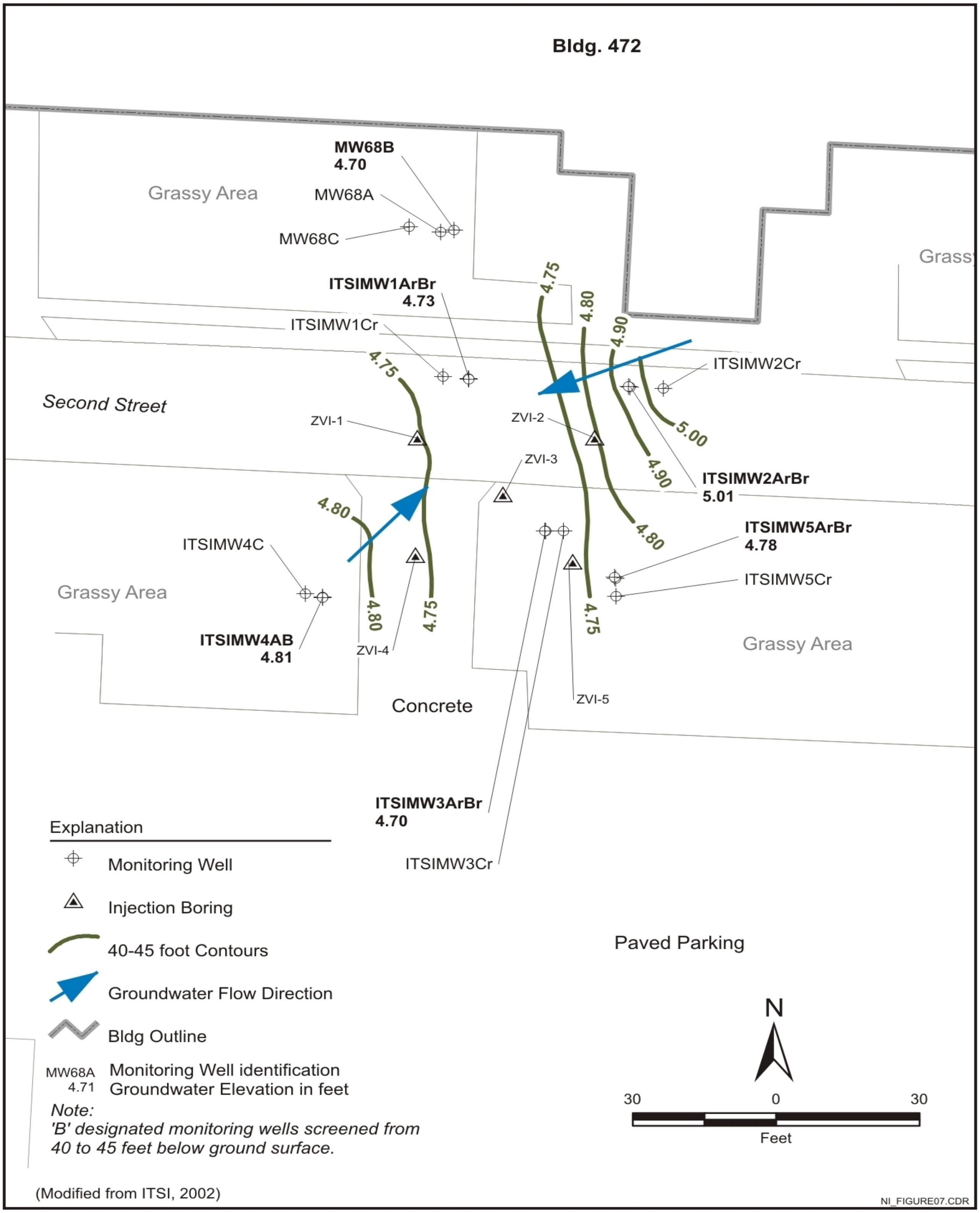

Figure 2-5. Groundwater Elevation and Direction Map for Zone B during August 06 Sampling Event (Source: ITSI, 2007)

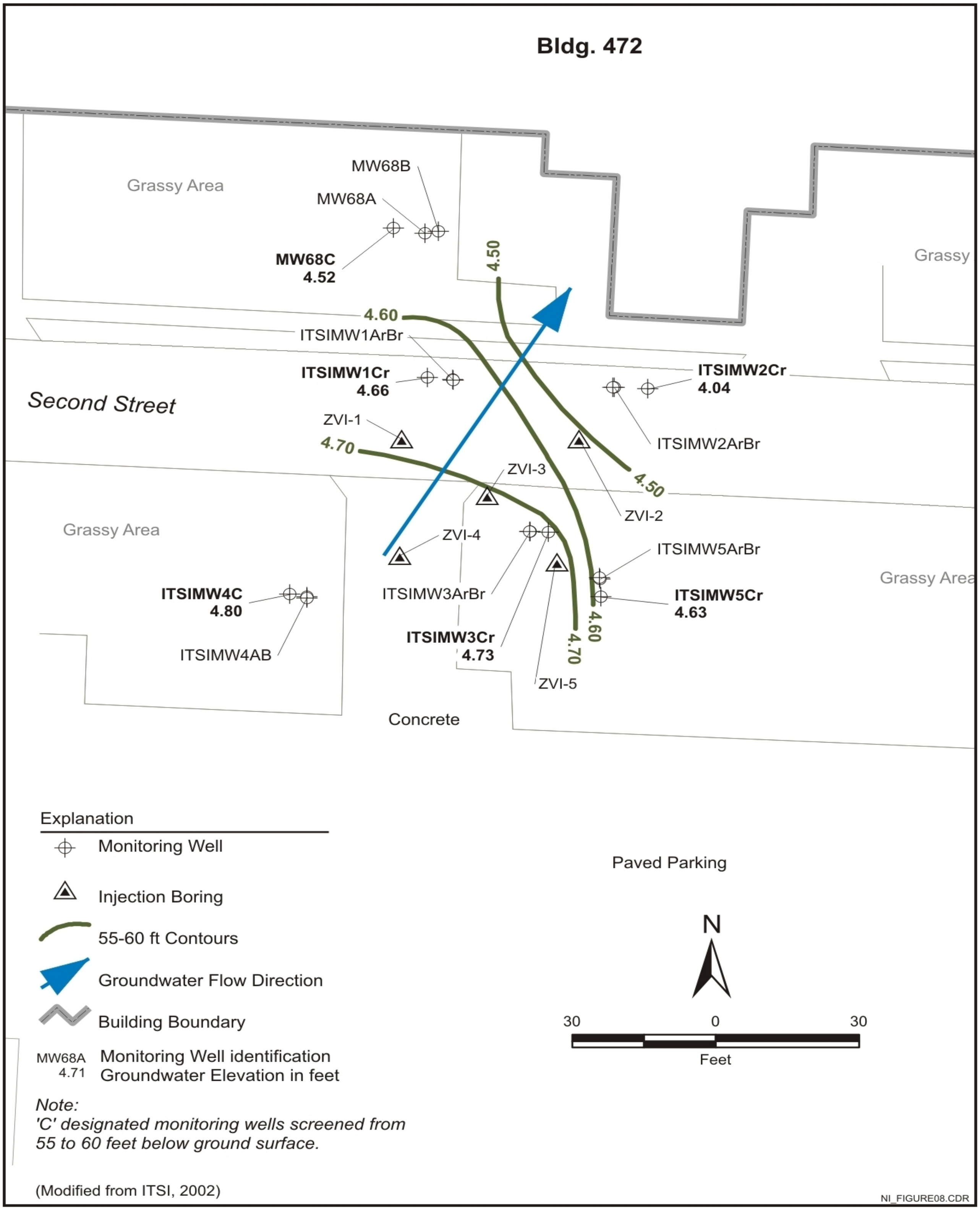

Figure 2-6. Groundwater Elevation and Direction Map for Zone C during August 06 Sampling Event (Source: ITSI, 2007)

Section 3.0: DISTRIBUTION OF CONTAMINANTS

The source of contamination in OU 20 is suspected to be located in the vicinity of Buildings 1 and 2 at the site (see Figure 1-1). The failure of an aboveground storage tank (AST) west of Building 379 was also considered responsible for the contaminant plume. The groundwater contaminant plume at OU 20 extends northeasterly downgradient from OU 19 into OU 20 and terminates on the east side of NAS North Island in the vicinity of the ship docks. Figure 1-1 shows the historical extent of the trichloroethylene (TCE)-impacted groundwater plume. The maximum concentration reported in the volatile organic compound (VOC) groundwater plume is 150 mg/L. Groundwater monitoring has demonstrated that the plume is located approximately 25 feet bgs to an approximate depth of 80 feet bgs. Investigations have shown that in the Treatability Study area, the plume is located between 30 and 60 ft bgs with maximum concentrations being at a depth of 50 ft bgs. The ZVI treatment was applied in this depth interval.

Section 4.0: TECHNOLOGY IMPLEMENTATION

At the site, ZVI injections were done at five locations between approximately 30 and 60 ft bgs, during the period of August 22, 2006 through September 7, 2006. At each injection location, Ferox^{sm} injection (pressurized injection of water and ZVI powder slurry) was conducted in nine discrete 3.5-foot intervals starting from the bottom of each borehole. Inflatable packers were installed in the borehole to isolate each 3-ft injection interval. The five injection locations, designated as soil borings ZVI-1 through ZVI-5, were located within the approximately 50-ft by 50-ft study area (Figure 2-1). One pound of ZVI powder was combined with approximately three gallons of potable water to make the suspended liquid ZVI slurry, which was introduced into the subsurface to react with and chemically reduce chlorinated VOCs. Injections were conducted from the corner soil boring locations to the center locations. The center point injections were conducted last. This particular injection design was intended to overlap and totally saturate the study area with the ZVI.

Prior to Ferox^{sm} injection, pneumatic fracturing was conducted at the site to increase formation porosity, connectivity of the pore spaces, and consequently to increase the permeability of the formation. This fracturing process lasts approximately 10 to 15 seconds and utilizes pressurized nitrogen gas to overcome the natural in situ stresses (e.g., formation overburden and cohesive forces) and create or open fractures radially from the borehole. Pneumatic fracturing can be particularly effective in low-permeability formations. The nitrogen gas acts as the carrier fluid to atomize the slurry and disperse it into the formation. Following the fracturing, the subsequent injection of atomized ZVI into the targeted zone utilizes the same assembly and packers to isolate discrete intervals. Injections, however, are performed at lower pressures (approximately 30 to 150 pounds per square inch [psi] at this site) than those needed for fracturing (up to 500 psi at this site). Although high to moderate permeability sands and silty sands make up much of the subsurface at OU 20, initial pneumatic fracturing was conducted by the vendor immediately prior to the ZVI injection at the deeper intervals in an attempt to maximize dispersal of the atomized ZVI slurry into the contaminated zone.

During the project operation, it was observed at four monitoring well locations (ITSIMW1 to 3 and ITSMW5) that ZVI slurry was coming up to the surface (or “daylighting”). Daylighting did not always occur at the nearest monitoring well. For example, on the first day of injections in ZVI-1, daylighting was experienced during the first injection interval (56.5 to 60 ft bgs) only at ITSIMW5AB. The well is located almost 75 ft away from the injection point. In this daylighting incident, surfaced ZVI slurry rose 4 ft into the air through the road box of ITSIMW5AB. ITSIMW4 was the only well cluster that did not encounter daylighting. The affected monitoring wells (ITSIMW1 to 3 and ITSMW5) were abandoned between August 23 to 30, 2006, prior to completion of the ZVI injection field activities. Abandonment consisted of overdrilling the affected wells, destroying or removing the polyvinyl chloride (PVC) screen and blank casing, and refilling with neat cement grout. After this well abandonment, daylighting was reduced, but did occur again at ITSIMW3 and 5, necessitating supplemental sealing with quick drying cement. The abandoned wells were reinstalled after completion of all ZVI injections.

The design dosage of ZVI powder for the entire treatability study area was determined to be 72,765 pounds, based on the mass ratios of iron to TCE and iron to soil. Due to daylighting of ZVI slurry, approximately 1,083 pounds of ZVI powder was recovered from the surface for disposal with other investigation-derived waste (IDW). The design for a typical 3.5-foot injection interval incorporated approximately 1,600 pounds of ZVI powder. After performing the injections, boreholes were abandoned by tremie backfilling with cement-bentonite grout. A total of 146 drums of solid waste and 73 drums of liquid waste were generated during the ZVI treatment field activities.

Section 5.0: PERFORMANCE ASSESSMENT METHODOLOGY

Five rounds of groundwater monitoring events were conducted as part of the ZVI Treatability Study. A baseline groundwater sampling event was conducted prior to injection activities and four subsequent Post-ZVI injection sampling events were conducted 2, 6, 12, and 24 weeks after completion of ZVI injection.

Groundwater samples were analyzed for the following:

- VOCs by U.S. Environmental Protection Agency (EPA) Method 8260B
- Total iron by EPA Method 6010B
- Dissolved iron, arsenic, and manganese by EPA Method 6010B
- Dissolved gases (ethene/ethane/methane) by RSK-175
- Alkalinity by EPA Method 310.1.

Between July 31 and August 4, 2006, five groundwater monitoring well groups designated as ITSIMW-1A, B and C through ITSIMW-5A, B and C were installed in the treatment area (see Figure 2-1 for well locations). Each monitoring well group consists of three monitoring wells, one screened at each of three depth intervals. Wells were installed using a hollow stem auger rig equipped with 10.5- and 8.5 inch diameter augers. “A” and “B” wells were installed within the same 10.5-inch borehole to depths of 30 feet and 45 feet, respectively. “C” wells were installed within the 8.5-inch boreholes to a depth of 60 feet. The “A” wells screened intervals were constructed with 10-foot lengths of 2-inch diameter 0.02-inch machine slotted PVC screen and the “B” and “C” wells screened intervals were constructed with 5-foot lengths of 0.02-inch machine slotted PVC screen. Number 3 sand was placed in the annular space to approximately 2 feet above the screen portion of the well casing. In the “A” well construction, an approximate 8-foot bentonite seal (from approximately 30 to 38 feet) was placed between the bottom of the “A” well and the top of the “B” well sand pack. The groundwater wells were surged to set the sand pack before placing a hydrated bentonite sanitary slurry seal to just below surface grade.

Pre-existing monitoring wells MW68-A, B, and C are present immediately downgradient of the treatment area and were monitored along with the treatment area wells.

Section 6.0: TECHNOLOGY PERFORMANCE

The Treatability Study Report (ITSI, 2007) provides a systematic description of the results of the baseline and post-injection sampling events. Technology performance has been discussed in a comprehensive manner in terms of chlorinated volatile organic compound (CVOC) concentrations (TCE, tetrachloroethene [PCE], etc.), potential byproducts of reductive dechlorination (dichloroethene [DCE], ethene, etc.), and indicator parameters (oxidation-reduction potential [ORP], pH, alkalinity, etc.).

Figures 6-1 and 6-2 illustrate the sharp TCE decline experienced in wells ITSMW1C and ITSIMW3C. TCE declined sharply (>90% reduction) in these wells, as did DCE. Ethene levels showed some increase in ITSIMWC, providing corroboration of complete dechlorination in this well. Figures 6-3 and 6-4 show corresponding declines in ORP and corresponding increases in pH in the wells. This provides confirmation that strongly reducing conditions were created in certain parts of the treatment zone, which led to dechlorination of CVOCs. No chloride data are presented in the report. Presumably, native chloride levels in the groundwater were expected to mask any increases due to dechlorination reactions. As Figures 6-5 and 6-6 show, the decline in alkalinity and increase in manganese levels also point to creation of reducing conditions, although the changes in these parameters were temporary in some cases.

In other parts of the treatment zone, the ZVI distribution may not have been as efficient. Figures 6-7 to 6-12 show the trends in the same parameters for ITSIMW4A and ITSIMW4B. These two wells showed any considerable changes in TCE or DCE. ORP did not show much decline and pH did not show much of an increase in these wells. Alkalinity levels did not change much, although manganese did show a noticeable increase, perhaps indicating mildly reducing conditions due to surrounding ZVI-rich zones.

The Treatability Study Report concludes that ZVI was not evenly distributed, but in those locations where it did reach, it was effective in reducing CVOCs. The report summarizes the performance data by groundwater zone (A, B, or C) and by distance from the nearest ZVI injection point, as reproduced in Table 6-1. Based on Table 6-1, the Treatability Study Report concludes that the success of ZVI distribution was driven by lithology and that the ZVI injection appears to have worked well in Zone C, but not very well in Zones A and B. The report (ITSI, 2007) points to the counterintuitive nature of this finding that the pneumatic fracturing and ZVI injection appears to have worked best in the finer sediments (silty sand and sandy silt) of Zone C, rather than in the poorly graded sands of Zones A and B.

However, it is possible that the ZVI injections performed better than what is first apparent in the data. Table 6-1 and many of the conclusions in the Treatability Study Report are based on spatial and temporal averaging of the data across several groups of wells and over multiple post-injection monitoring events. The averages may be suppressing trends that become more obvious when data for individual wells are compared event by event with the baseline. As indicated in previous ZVI application reviews (Battelle, 2005), adequate doses of ZVI tend to generate relatively more rapid reactions that may taper off over time. Temporal averaging may not capture important fluctuations in the data. Spatial averaging (i.e., across all wells less than 20 ft away from the nearest injection point) also may suppress the effects of any heterogeneity (in the aquifer or in the injection process itself).

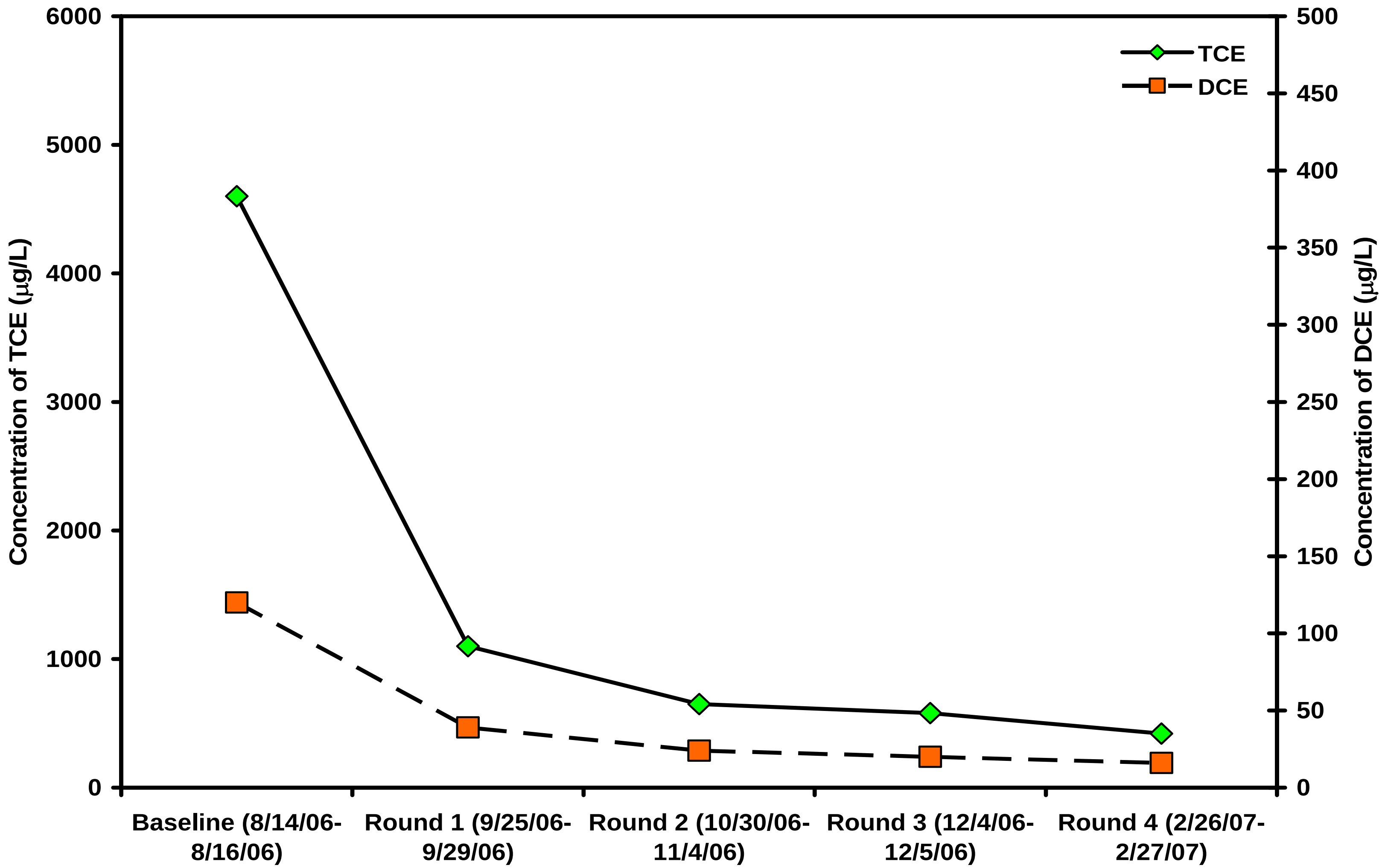

Figure 6-1. TCE and DCE Concentration Trends during Baseline and Post-injection Monitoring Events in ITSIMW 1C (Source: ITSI, 2007)

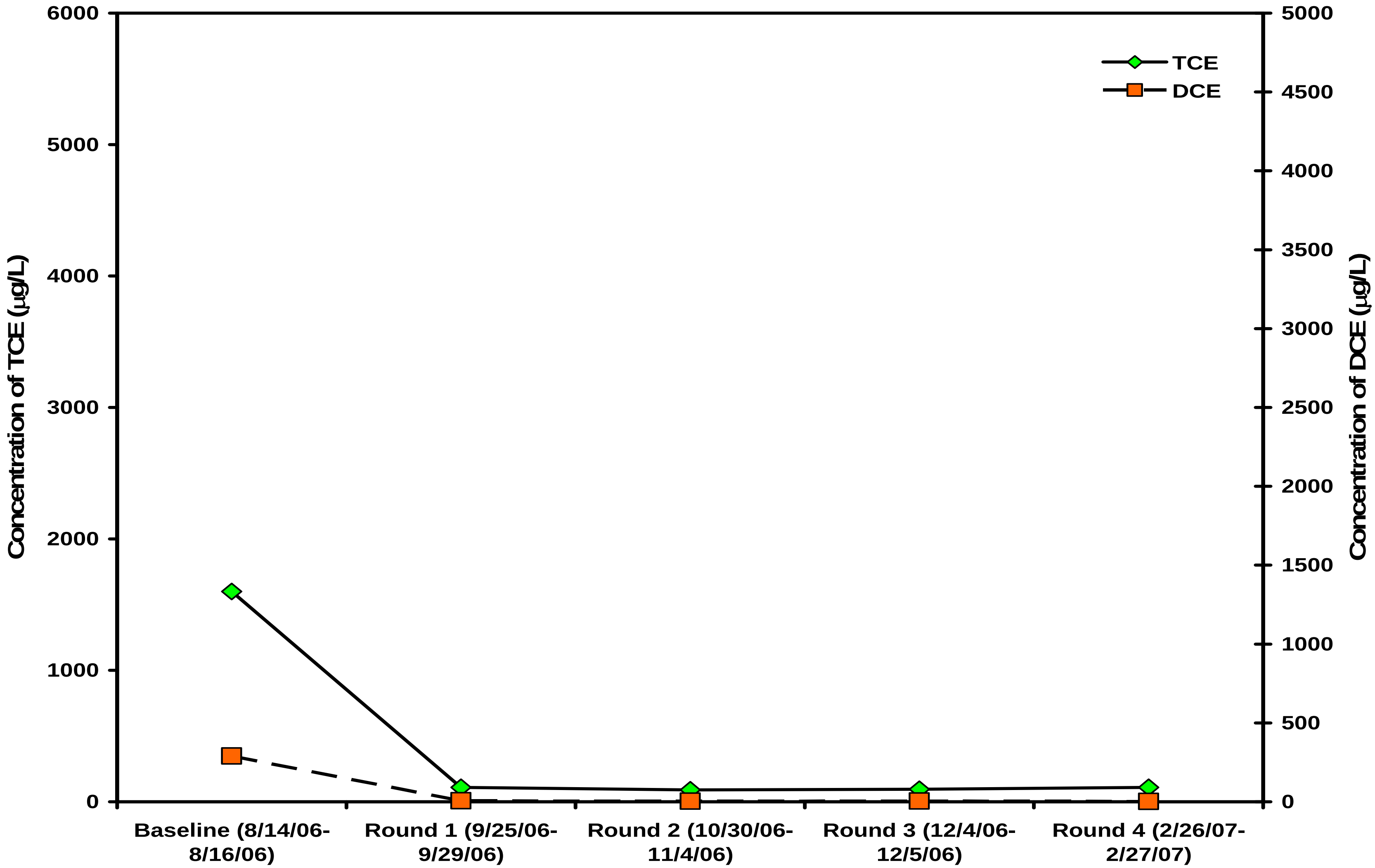

Figure 6-2. TCE and DCE Concentration Trends during Baseline and Post-injection Monitoring Events in ITSIMW 3C (Source: ITSI, 2007)

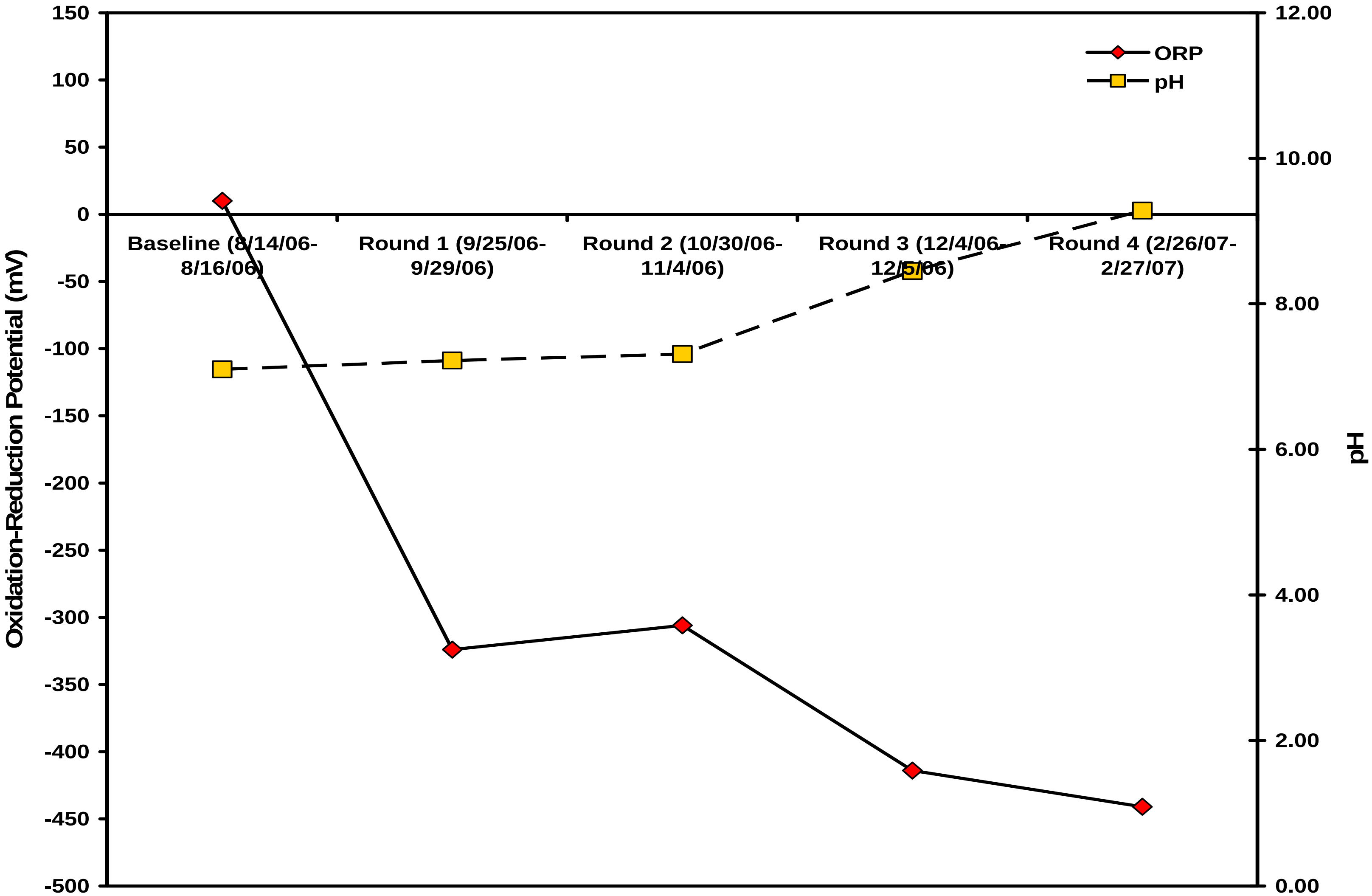

Figure 6-3. pH and ORP Trends during Baseline and Post-injection Monitoring Events in ITSIMW 1C (Source: ITSI, 2007)

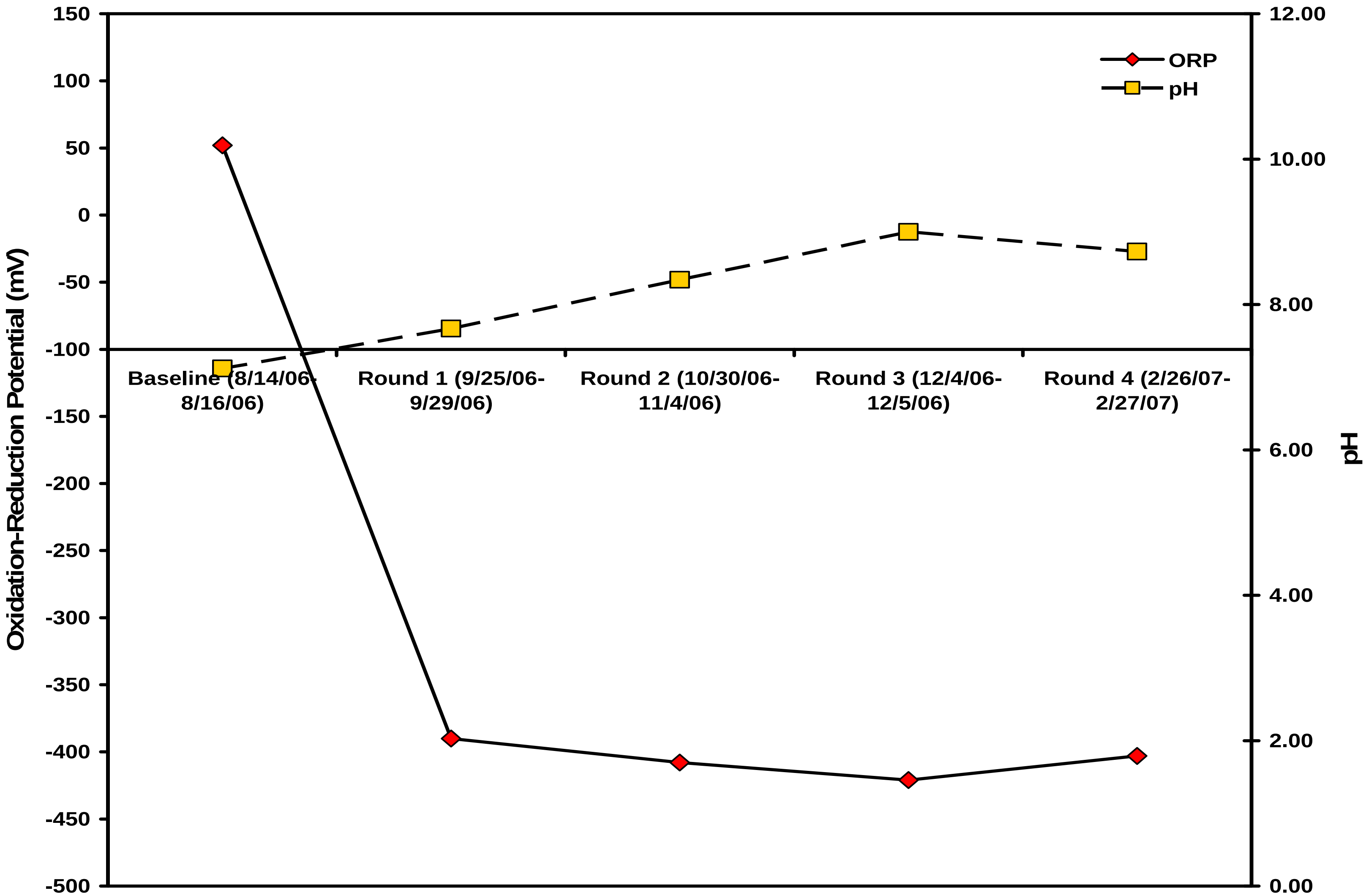

Figure 6-4. pH and ORP Trends during Baseline and Post-injection Monitoring Events in ITSIMW 3C (Source: ITSI, 2007)

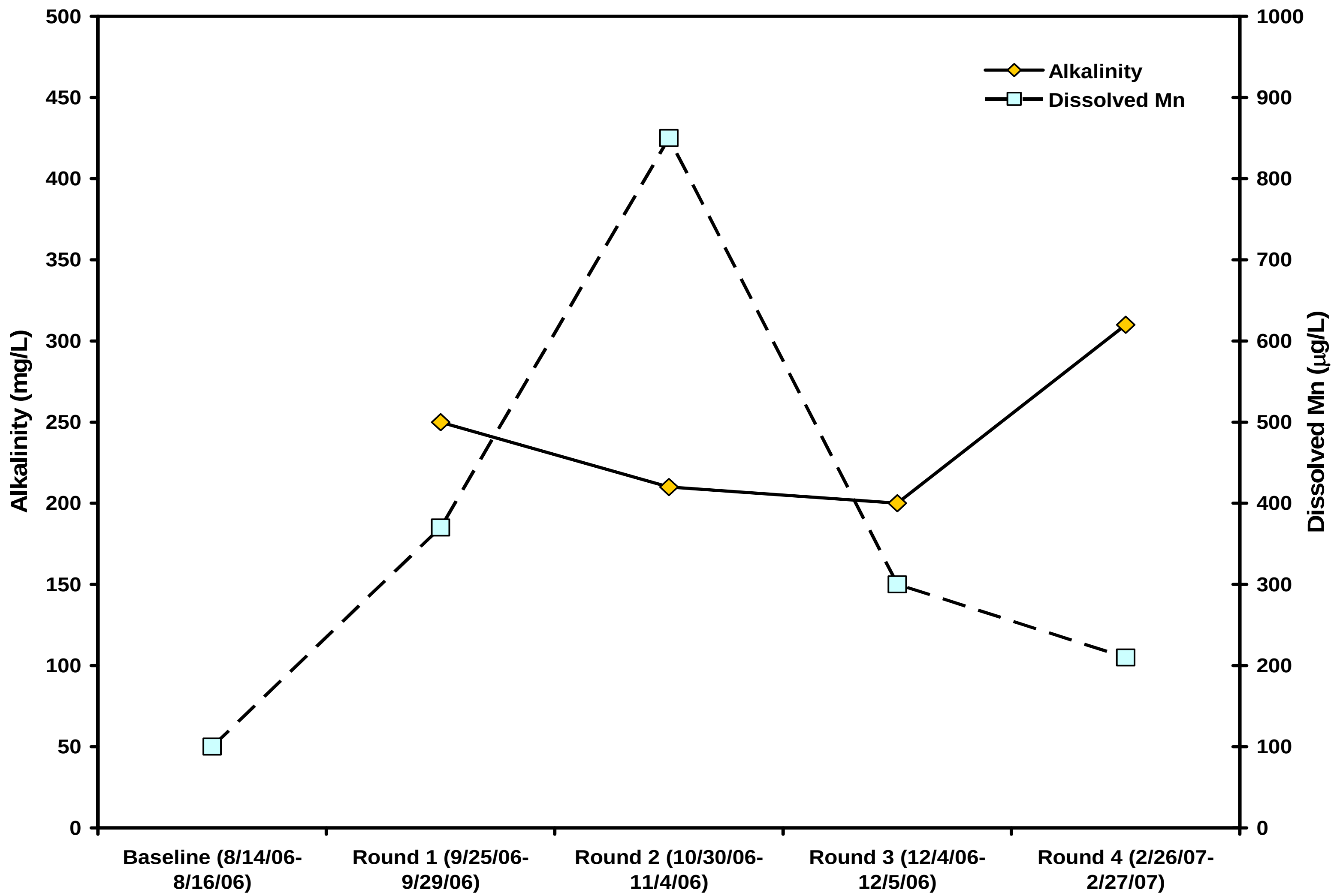

Figure 6-5. Alkalinity and Dissolved Mn Concentration Trends during Baseline and Post-injection Monitoring Events in ITSIMW 1C (Source: ITSI, 2007)

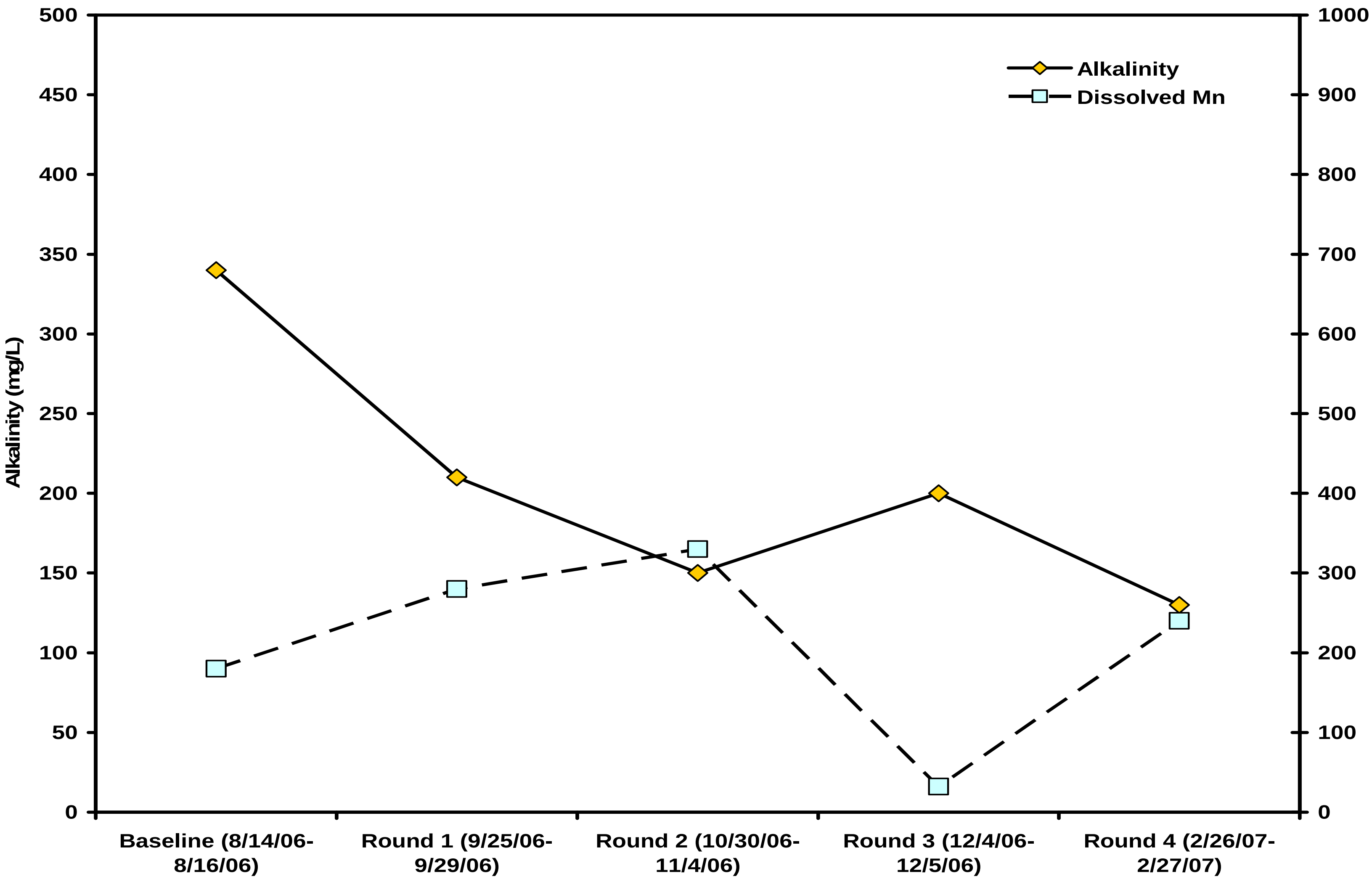

Figure 6-6. Alkalinity and Dissolved Mn Concentration Trends during Baseline and Post-injection Monitoring Events in ITSIMW 3C (Source: ITSI, 2007)

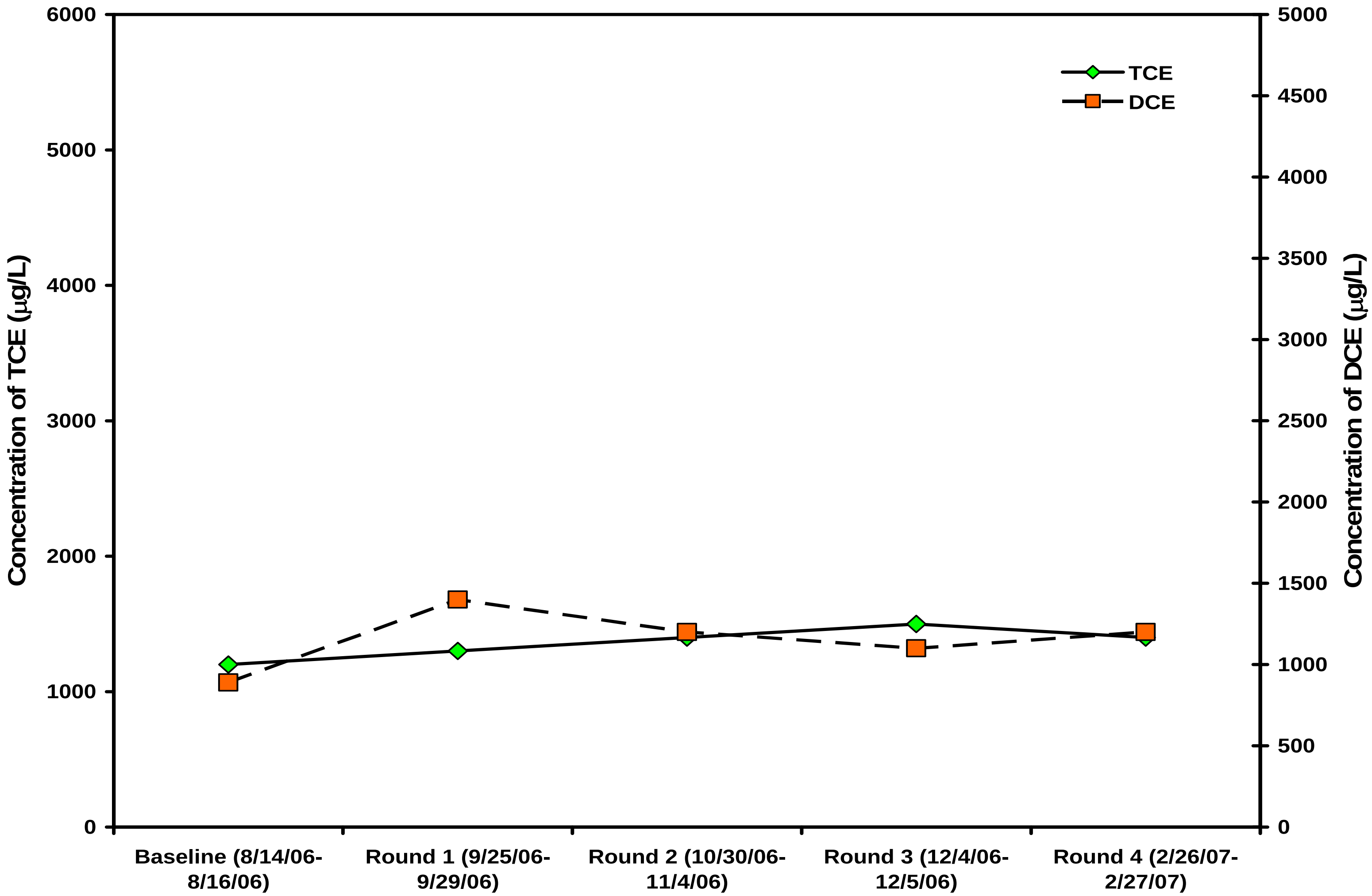

Figure 6-7. TCE and DCE Concentration Trends during Baseline and Post-injection Monitoring Events in ITSIMW 4A (Source: ITSI, 2007)

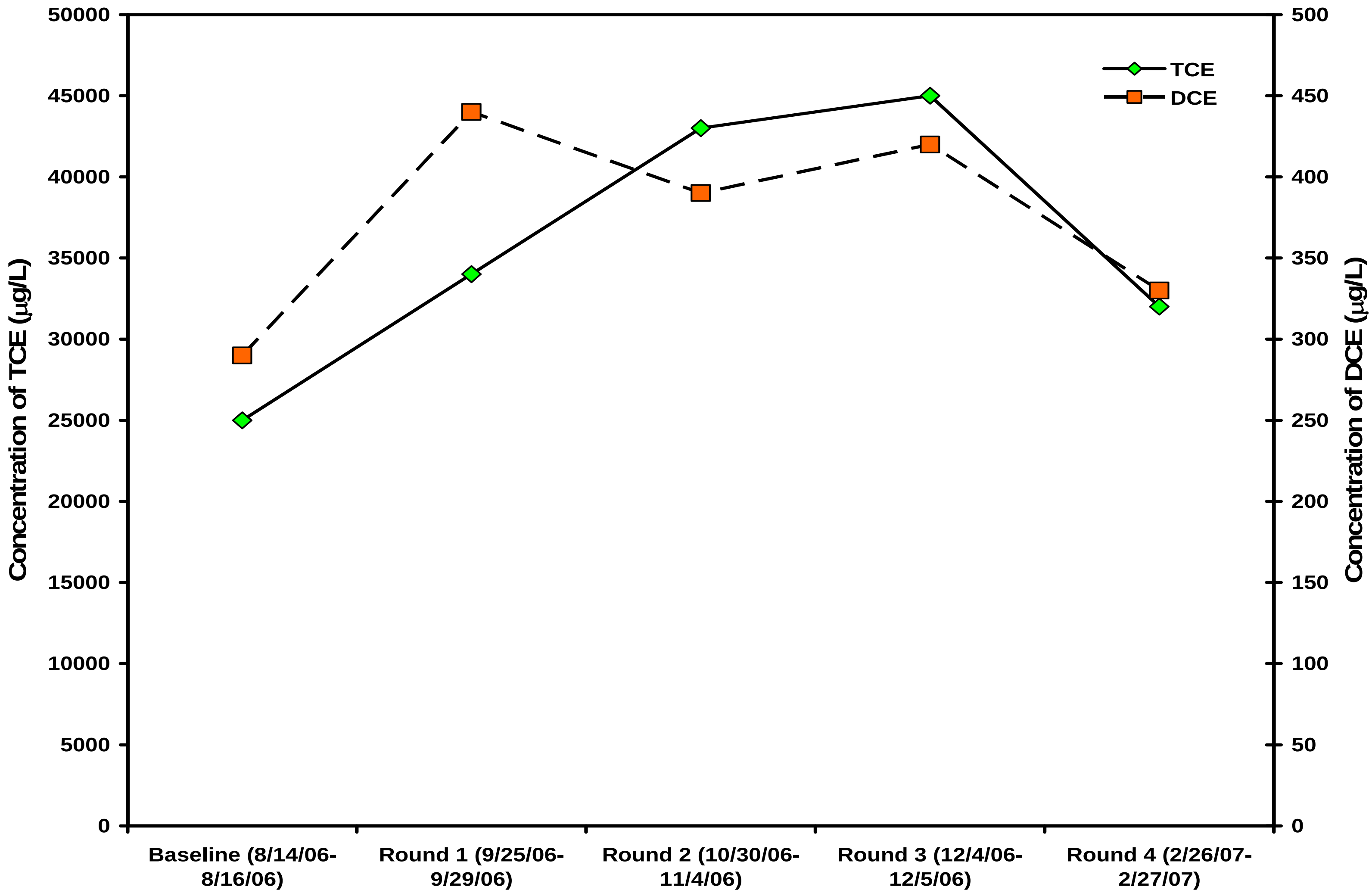

Figure 6-8. TCE and DCE Concentration Trends during Baseline and Post-injection Monitoring Events in ITSIMW 4B (Source: ITSI, 2007)

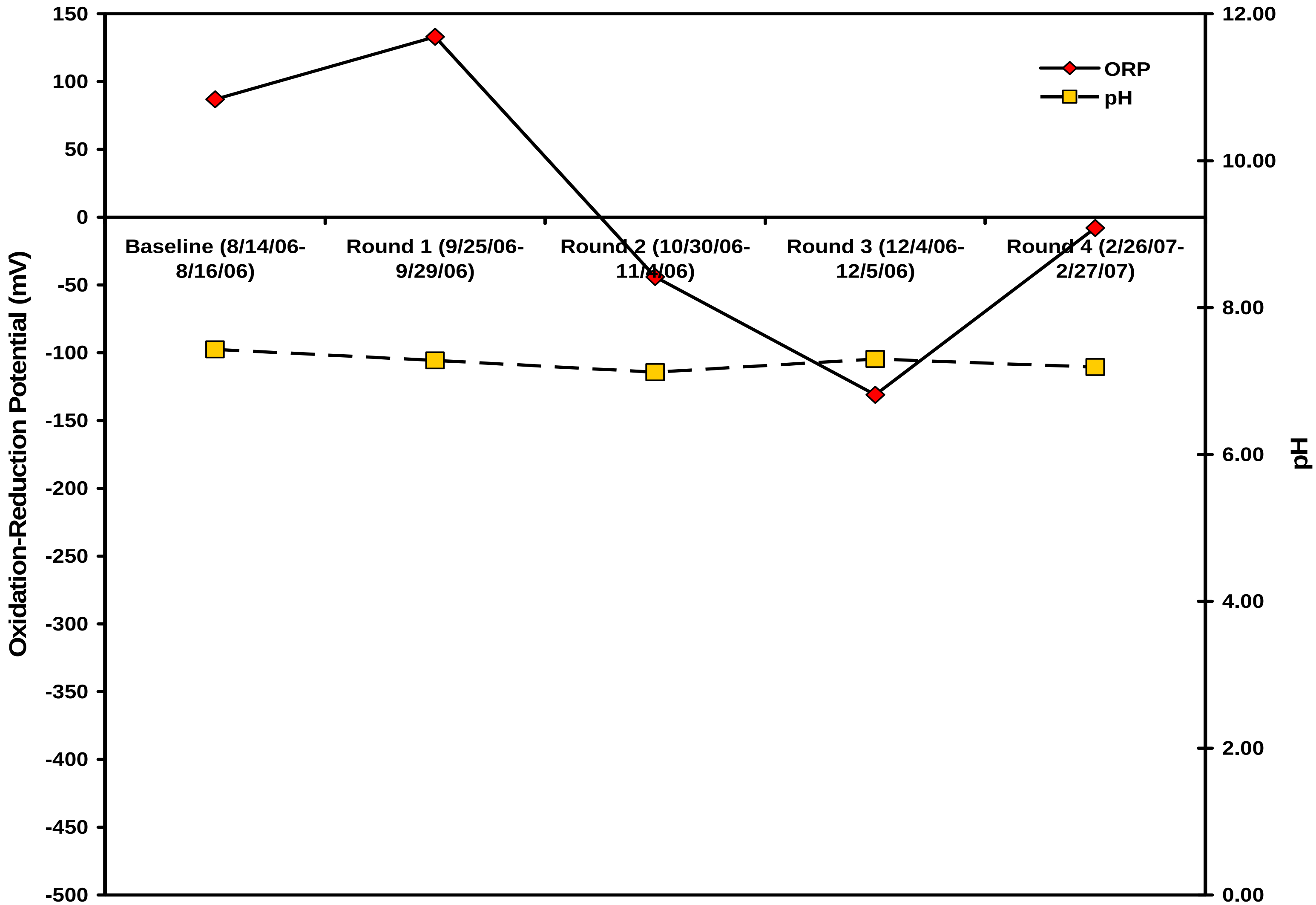

Figure 6-9. pH and ORP Trends during Baseline and Post-injection Monitoring Events in ITSIMW 4A (Source: ITSI, 2007)

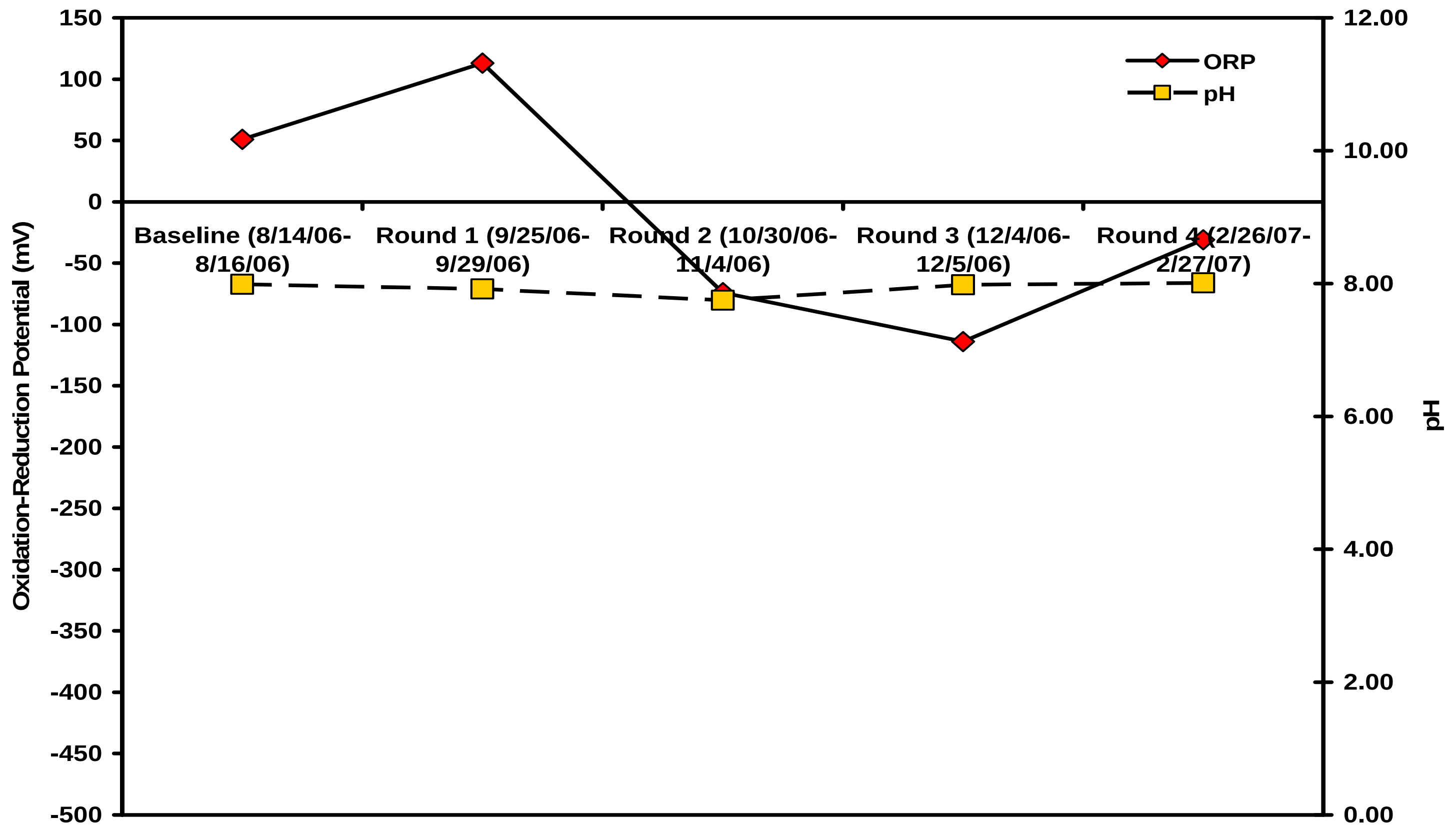

Figure 6-10. pH and ORP Trends during Baseline and Post-injection Monitoring Events in ITSIMW 4B (Source: ITSI, 2007)

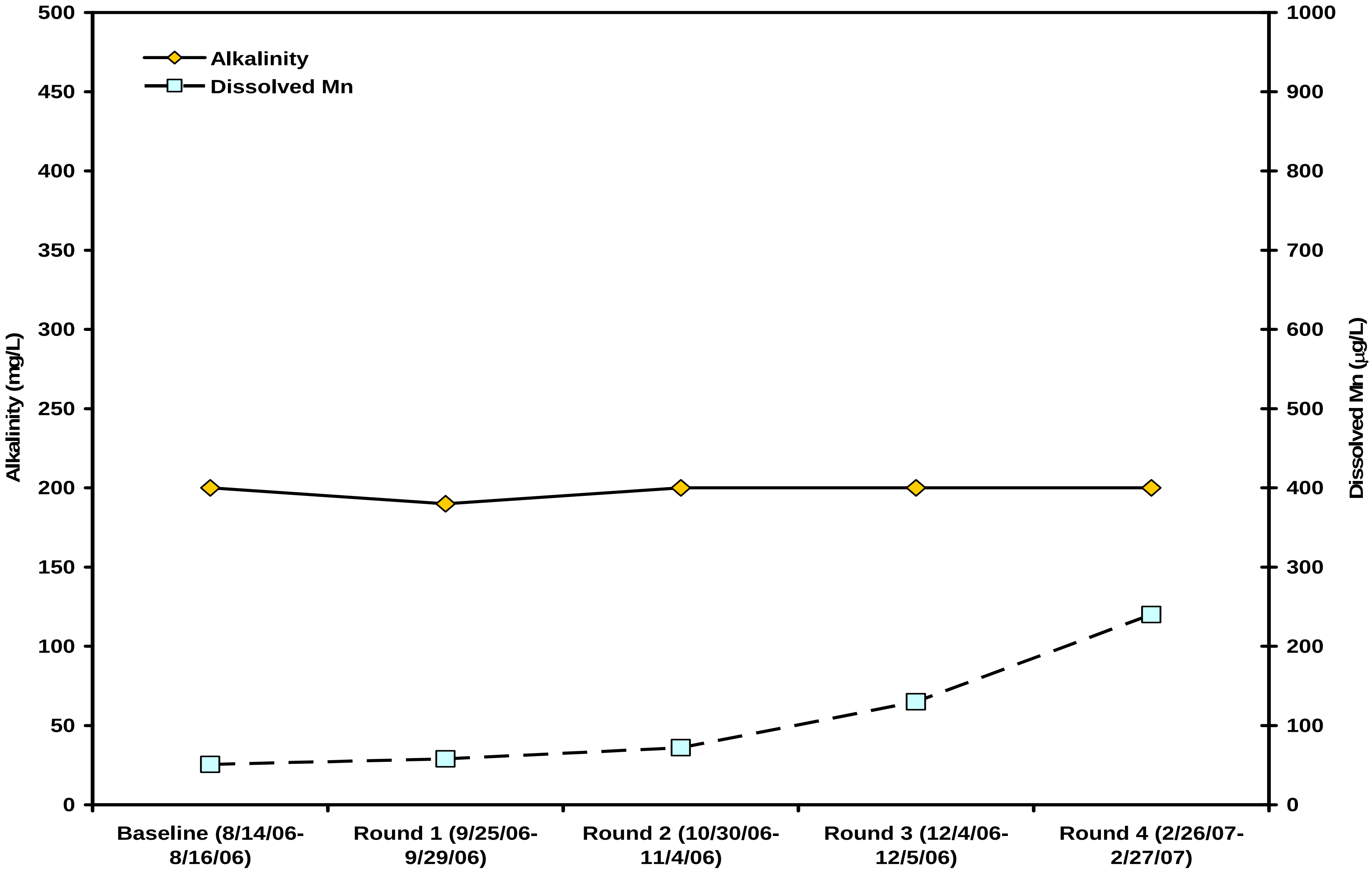

Figure 6-11. Alkalinity and Dissolved Mn Concentration Trends during Baseline and Post-injection Monitoring Events in ITSIMW 4A (Source: ITSI, 2007)

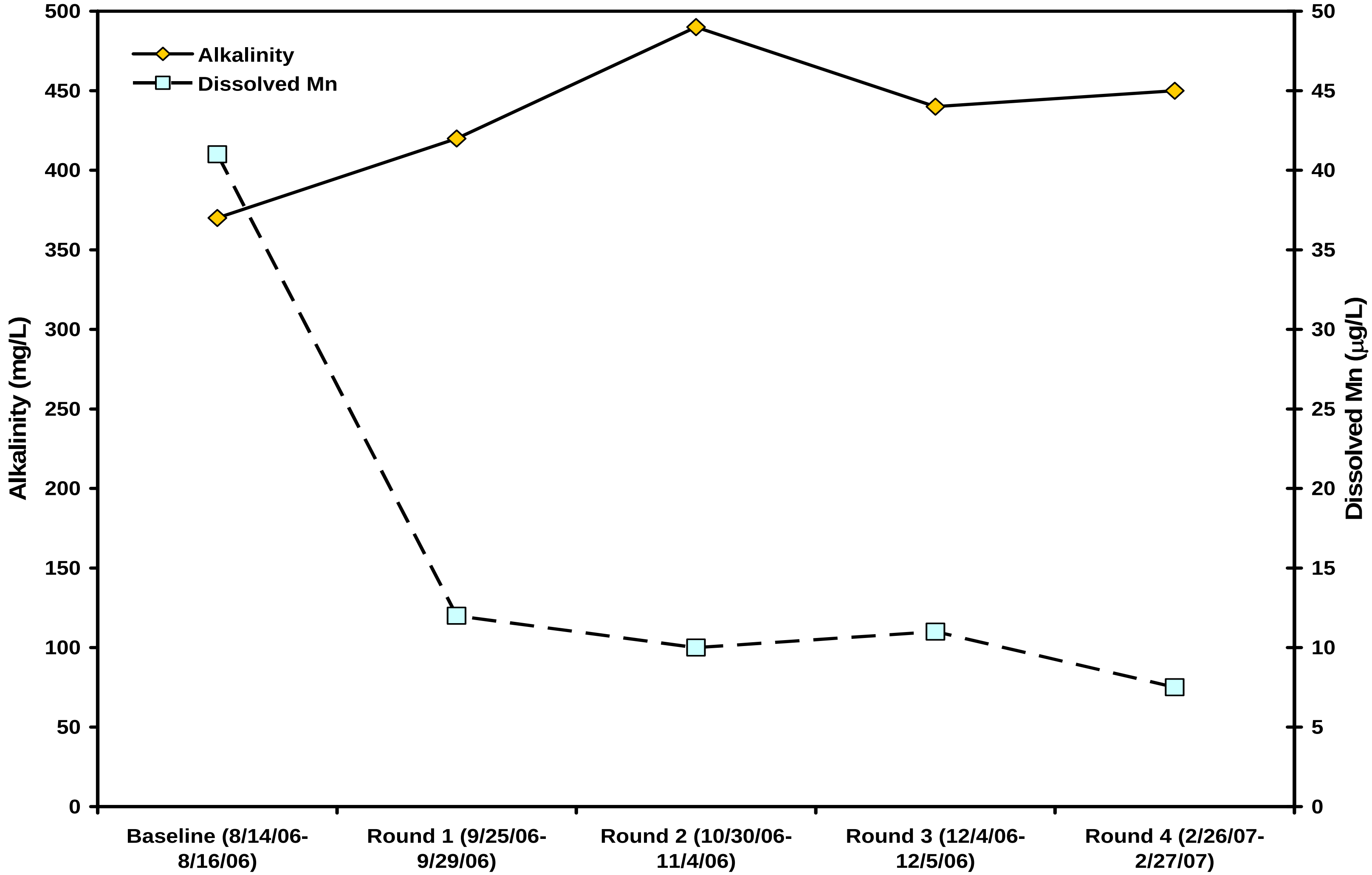

Figure 6-12. Alkalinity and Dissolved Mn Concentration Trends during Baseline and Post-injection Monitoring Events in ITSIMW 4B (Source: ITSI, 2007)

**Table 6-1. Performance Data by Groundwater Zone and Distance from Nearest ZVI injection*
(Source: ITSI, 2007)**

		Distance from closest ZVI injection location			
		<20 feet	**25 feet**	**50 feet**	**All Wells**
GW zone	**A**	71% decrease	23% increase	678% increase	35% decrease
	B	32% increase	12% increase	0	18% increase
	C	85% decrease	80% decrease	9% decrease	70% decrease
	All Zones	11% decrease	27% decrease	13% increase	11% decrease

*Percent (%) reduction and % increase were calculated using the average concentrations before treatment and from the fourth post-treatment monitoring event for the entire group of wells being analyzed. The "less than 20 feet" group includes monitoring well groups ITSIMW-1, ITSIMW-2, and ITSIMW-3. The 25-foot group adds monitoring well groups ITSIMW-4 and ITSIMW-5 to the "less than 20 feet" group, and the 50-foot group adds monitoring well group MW-68 to the previous well groups.

Table 6-2 is an attempt to evaluate the trends in key parameters as they relate to individual wells and individual events, while still keeping lithologic groups of wells together. The following 10 parameters and trends have been tracked in Table 6-2:

1. TCE > 90% reduction. Wells in which TCE declines by at least an order of magnitude at any time during the short 24-week period are probably indicative of faster abiotic reactions, which are more desirable than slower anaerobic biodegradation reactions.
2. TCE > 50% reduction. Any change of less than 50% in TCE levels could be attributed to natural fluctuations, but beyond this threshold, the reductions are probably treatment induced. Declines of between 50 to 90% in TCE may indicate slower biological reactions are at work, induced by the anaerobicity created by the ZVI.
3. DCE > 50% reduction. Strongly reducing conditions (indicative of a strong dose of ZVI) should abiotically reduce not just TCE, but DCE as well. Approximately 50% again may be looked upon as an arbitrary threshold indicative of a treatment induced trend, rather than natural fluctuation.
4. DCE > 50% increase. As encountered at other sites (Battelle, 2005), when the ZVI dose (ratio of ZVI mass to soil mass) is not high enough, the ZVI stimulates anaerobic biodegradation, rather than abiotic reduction. This may result in increase and accumulation of DCE byproduct. Abiotic beta-elimination reactions occurring under strongly reducing conditions often convert the majority of the TCE to ethene, without forming DCE and vinyl chloride (VC) intermediates. Therefore, a sharp increase in DCE may be indicative of biotic, rather than abiotic, reactions.
5. ORP < -350 mV. An ORP below -350 or -400 mV usually indicates that the ZVI mass is high enough to induce strongly reducing conditions leading to abiotic destruction of TCE, without the formation of considerable amounts of DCE.

Table 6-2. Trends in Key Geochemical Parameters for Evaluation of ZVI Injection Performance (Source: ITSI, 2007)

			< 20 ft		25 ft		50 ft
Depth	**PARAMETER**	**ITSIMW-1**	**ITSIMW-2**	**ITSIMW-3**	**ITSIMW-4**	**ITSIMW-5**	**MW-68**
A	TCE>90% reduction	Yes					
	TCE>50% reduction		Yes*	Yes *			
	TCE>50% increase					Yes *	Yes *
	DCE >50% reduction			Yes *			
	DCE >50% increase	Yes				Yes	Yes *
	ORP< -350 mV		Yes	Yes #		Yes #	
	ORP< -200 mV	Yes					
	pH >8.4			Yes *		Yes	
	Alkalinity > 50% reduction			Yes *			
	Mn > 100% increase	Yes *	Yes *		Yes *	Yes *	Yes *
	Ethene > 0.05 mg/L		Yes *	Yes *			
B	TCE>90% reduction			Yes			
	TCE>50% reduction		Yes *			Yes *	
	TCE>50% increase	Yes *			Yes		
	DCE >50% reduction	Yes *	Yes *	Yes *		Yes *	
	DCE >50% increase						Yes *
	ORP< -350 mV	Yes #	Yes #	Yes #		Yes *	
	ORP< -200 mV						
	pH >8.4	Yes *	Yes *	Yes *		Yes *	
	Alkalinity > 50% reduction			Yes *			
	Mn > 100% increase	Yes *	Yes	Yes *	Yes	Yes	
	Ethene > 0.05 mg/L	Yes *		Yes			
C	TCE>90% reduction	Yes *		Yes *		Yes *	
	TCE>50% reduction						
	TCE>50% increase						
	DCE >50% reduction	Yes *	Yes *	Yes *	Yes *	Yes *	
	DCE >50% increase						Yes *
	ORP< -350 mV	Yes *		Yes *			
	ORP< -200 mV		Yes			Yes *	
	pH >8.4	Yes *		Yes *			
	Alkalinity > 50% reduction			Yes *			
	Mn > 100% increase	Yes *		Yes *	Yes *	Yes *	Yes *
	Ethene > 0.05 mg/L						

6. ORP < -200 mV. At this level, the aquifer generally is reducing enough to stimulate anaerobic biodegradation, but not enough to stimulate abiotic reduction. Biodegradation is a desirable pathway, although not as preferable as abiotic reduction because of the slower timeframe and increased DCE generation potential.
7. pH > 8.4. A strong dose of ZVI is likely to increase the pH of an aquifer because of the formation of hydroxyl radicals. A threshold can be chosen by looking at the baseline pH, which ranges from 7 to 8. The natural buffering capacity of the aquifer would tend to keep the pH in this range. Once the pH increases beyond a pH of 8.4 (the pH of bicarbonate in water), the buffering capacity of the aquifer may be assumed to have been overcome by the strongly reducing conditions.
8. Alkalinity > 50% reduction. Strong reducing conditions typically cause alkalinity to decline, as carbonates of calcium and magnesium start precipitating out of the groundwater.
9. Manganese > 100% increase. An increase in dissolved manganese (Mn^{2+}) is a general indicator of reducing conditions, although not strong enough for abiotic reduction (or perhaps even anaerobic biodegradation). May indicate that at least some ZVI has reached this location and is having an impact.
10. Ethene > 0.05 mg/L. Again a somewhat arbitrary threshold of 10 times the detection limit of ethene may indicate strong ethene formation and complete dechlorination of TCE, rather than incomplete dechlorination to DCE or VC. May also indicate reduction of DCE and VC, the more recalcitrant byproducts of TCE.

A “Yes” in one of the cells indicates that the data follow (at one time or another during the post-injection monitoring) the desired trend in the parameter. An asterisk indicates that the trend continued through the last (24-week) monitoring event in the series. A ‘#” sign indicates that the trend continued at a weaker, but still desirable, pace through the final (24-week) monitoring event. For example, if ORP did decline below -350 mV and stayed below this level through the 24-week event, then the ‘Yes’ merits an asterisk. This is the most desirable outcome. If the ORP declines to -350 mV during one or more monitoring events, then rebounds a bit, but still remains below the -200 mV threshold for stimulating biodegradation, then the ‘Yes’ merits a ‘#’. The most desirable cells (outcomes) are shaded in green, the somewhat desirable cells are shaded in yellow, and the less desirable cells are shaded in red. A green box (border) around all 10 parameters for a well indicates that the overall outcome for the well is most favorable. The yellow box indicates that the overall outcome for the well is somewhat favorable.

Table 6-2 shows that the ZVI distribution and, consequently the treatment efficiency, are much better in all three groundwater zones than expected from Table 6-1. The best performing wells were ITSIMW1C, ITSIMW3C, and ITSIMW5B. ORP declined to less than -350 mV in these wells, indicating strongly reducing conditions conducive to faster abiotic reactions (e.g., beta-elimination) that progress without formation of undesirable intermediates, such as DCE. DCE itself declined sharply in these wells, thus confirming the ORP indicator. Also, supporting strong ZVI dosage in these three wells is pH (>8.4). All three indicators remained at these desired levels through the final monitoring event (24 weeks), indicating that the ZVI remained strongly reactive. In ITSIMW3C, alkalinity declined noticeably, thus providing another confirming indicator. TCE itself showed an order-of-magnitude decline in all three wells and this level of decline was sustained through the final monitoring event in wells ITSIMW1C and ITSIMW3C.

Also performing well were monitoring wells ITSIMW1B, 2B, 3A, and 5B. Although the TCE decline in 5B was not as sharp as in some of the other wells, ORP, pH, and DCE all indicate strongly reducing conditions that were sustained through the final event. In ITSIMW1B, 2B, and 3A, ORP declined below -350 mV at some point in time, then rebounded a bit, eventually remaining below -200 mV in the final event. This indicates that these locations received relatively strong ZVI doses. Subsequently, the reactivity of the ZVI weakened, but redox conditions in the final monitoring event were still anaerobic enough to induce biodegradation. All of the wells in this group, except ITSIMW1B, showed sustainable TCE declines of 50% or more and sustainable declines in DCE. In ITSIMW1B, TCE levels actually increased, although all other trends are favorable. This may show that any decline in TCE was offset by TCE redistributing from surrounding locations, all other indicators of ZVI dosing are favorable.

Wells ITSIMW1A, 2A, 2C, 5A, and 5C performed reasonably well. All of these wells showed some favorable trends indicative of a noticeable ZVI impact, although not as strong as in some other wells. Well ITSIMW2A, for example, showed a sharp ORP decline (<-350 mV) at some point in time, a sharp increase in ethene production, and a moderate decline in TCE level. DCE levels, pH, and alkalinity in this well did not show any noticeable impact. In ITSIMW1A, TCE showed a sharp decline, but DCE levels increased, as ORP declined only moderately to below -250 mV. All of the wells in this group show (in one way or another) mildly reducing conditions, strong enough to stimulate biodegradation, but not abiotic reduction. TCE levels rose in 5A, despite all other indicators showing anaerobic biological activity; this indicates that any biodegradation of TCE may have been offset by redistribution of TCE from the surrounding aquifer, due to the injections. Even the distant well cluster MW68 shows some impact from the ZVI, resulting in mildly reducing conditions.

This leaves only the ITSIMW-4 cluster (A, B, and C) that showed very little impact from the ZVI (some impact is discernible from the rise in manganese level, probably the weakest of the 10 indicators). Although the Treatability Study Report groups ITSIMW4 and MW5 together as being 25 ft away from the nearest injection point, ITSIMW4 appears to be several feet further away from injection point ZVI4 than ITSIMW5 is from ZVI5 (although not as distant as the "distant well" MW68). The greater distance coupled with natural aquifer heterogeneity may have played a role in reducing the impact of the ZVI injection on ITSIMW4. However, this lack of impact is consistent in all three groundwater zones (A, B, and C) at this location. Therefore, lithology does not appear to be the cause of poor ZVI distribution at some locations. Neither does depth, if it were expected that the shallower A interval is ubiquitously more prone to daylighting and hence poor ZVI distribution. The other four wells in Zone A appear to have received moderate to high doses of ZVI. In fact, MW4 is the only well cluster in the treatment zone that survived the effect of pneumatic fracturing and was not damaged. Distance from the injection point and natural local heterogeneity in the aquifer are probable contributors to the poor ZVI distribution at the ITSIMW4 cluster. In previous field applications (Battelle, 2005), ZVI impact has tended to lessen beyond a radius of 10 or 15 ft beyond the injection point. The noticeable impact of ZVI in monitoring wells that are up to 20 ft away from the injection point at this site may be an improvement over previous applications.

When contacted, the pneumatic fracturing and ZVI injection vendor attributed the daylighting to the absence of a bentonite-cement seal in the original monitoring wells. The original wells (ITSIMW1 to 5) were completed with Volclay or bentonite. When pneumatic fracturing was initiated and pressure was applied to the surface, the bentonite seals on some of the wells (ITSIMW1, 2, 3 and 5) failed and the injected slurry migrated preferentially to these wells. Once these wells were abandoned and backfilled with cement grout, the daylighting was largely mitigated. In the first phase of the ZVI injection, before the abandonment of the monitoring wells, the vendor estimated that approximately half the design mass of ZVI was injected and much of it probably took preferential pathways towards the failed wells. After the affected wells were abandoned, the remaining ZVI mass was injected. Much of the ZVI injection in ZVI4 (the well closest to ITSIMW4) was done before the affected wells were abandoned and this could have led to preferential migration of ZVI in the direction of the failed wells (and away from ITSIMW4).

Section 7.0: COST

The objective of the cost template in Table 7-1 is to compare costs for different technologies on an equivalent basis. Therefore, costs that are site-specific or situation-specific, such as work plan preparation, design, planning, permitting, monitoring, etc. have been excluded. The focus is on the cost that is required to mobilize to the site, conduct the treatment, and demobilize. A total treatment cost for the project is estimated by adding the capital investment and operating cost. Next, a unit cost of treatment is estimated based on the volume of aquifer targeted for treatment. This is based on two assumptions driven by past experience with such projects. One is that most, if not all, treatments seek to create conditions conducive to the removal of contamination in a given volume of aquifer and that this volume is a bigger driver of the treatment cost than, say, the contaminant mass (which can be subject to poor initial estimates, different degrees of post-treatment residuals, etc.). Second, the assumption is that the volume targeted for treatment is more relevant than the volume actually claimed to be treated. Often, the reagent injected may migrate beyond the boundaries of the target treatment zone, but this extra volume is not included. Finally, the maximum depth of treatment and geology of the site are qualitative/semi-quantitative measures that drive degree of difficulty and treatment costs need to be calibrated against these measures.

Table 7-1. Cost Template

No.	Item	Units	Unit Cost	Cost
	CAPITAL INVESTMENT (Fixed Cost)			
1	Site preparation (e.g., ZVI injection boreholes drilling subcontractor, utility lines, concrete pad, etc.)			
5	Other (please specify)			
			TOTAL CAPITAL	$
	OPERATING COST (Variable Cost)			
6	Equipment leasing (e.g., storage tanks, etc. not provided by vendor)			
7	Chemicals/reagents (ZVI)	71,944lbs		
8	Other consumables (not included in vendor's cost)			
9	Power	kW-hrs		
10	Other utilities			
11	Waste disposal - 146 drums solid waste - 73 drums liquid waste			
12	ZVI vendor's cost (for mobilizing and operating the system)			
13	Other (please specify)			
			TOTAL OPERATING COST	$
			TOTAL TREATMENT COST FOR PROJECT	$607,386
	VOLUME OF AQUIFER TARGETED FOR TREATMENT		Cu yd	3,704
	UNIT COST OF TREATMENT		$/Cu yd	164
	MAX. DEPTH OF TREATMENT		ft	60
	GEOLOGY OF SITE (e.g., high-permeability versus low-permeability)			Moderate permeability, low gradient

For the ZVI treatment at OU 20, the total cost of $607,386 reported under Scenario 1 of the Treatability Study comes closest to the total cost number sought in Table 7-1. This reported total cost does include some items, such as health and safety and administrative oversight, which may best be left out of a comparison-driven table, such as Table 7-1, but most of the other components do apply. Much of the treatment cost probably is captured in the vendor's cost, including items such as the ZVI material, tanks and injection equipment, and the associated mobilization/ demobilization and operation. An itemized breakdown of these cost elements was not available at the time of this review, but placeholders are presented in Table 7-1 to highlight some of these elements. The oversight contractor's costs included in this total probably include installation of the injection boreholes, field oversight (labor), and waste disposal. For the 50-ft by 50-ft target treatment area (30-ft target depth), the unit cost of treatment works out to be $164/yd^3. This unit cost appears to be competitive with other in situ treatment technologies (e.g., in situ chemical oxidation), although unit cost comparisons can be misleading, as several site-specific factors (e.g., degree of treatment achieved, level of contamination at the site, permeability of the soils, etc.) often are implicit in the unit cost.

Section 8.0: CONCLUSION

In general, except for the instances of daylighting, the ZVI injection at OU 20 appears to have worked relatively well. Seven of the 15 wells showed strong ZVI impact (conditions conducive to faster abiotic reduction) and five more wells showed moderate impact (conditions conducive to anaerobic biodegradation) on TCE treatment. Only three wells, all in the same cluster (MW4), showed a lack of any noticeable impact. This well cluster is the furthest away from the nearest injection point (as compared to the other well clusters) and this distance may have contributed to the lower performance. Local aquifer heterogeneity too may have played a role in the lack of impact at this well cluster.

The targeted radius of distribution of 20 ft or more at this site (assumed from the locations of the monitoring wells) may have been more ambitious than at previous sites. Targeting a higher radius of influence of the injected ZVI may have caused the vendor to operate at higher injection pressures, leading to daylighting at some intervals. Targeting a shorter radius of influence may be desirable if it allows the vendor to operate at lower injection pressures, and if it helps control daylighting.

The well completion materials also may have affected ZVI injection performance at this site. Bentonite seals at four of the five new well clusters failed. This may have caused the persistent daylighting observed during the initial phase of the project, with the injected ZVI migrating preferentially towards the released pressure in the failed wells. Daylighting would have considerably reduced the efficiency of the ZVI distribution by biasing the ZVI migration towards certain points in the treatment zone. Bentonite-cement seals on monitoring wells typically are desirable at pneumatic fracturing sites. Once the wells with the failed seals were abandoned and backfilled with cement grout, daylighting was largely mitigated and ZVI distribution probably progressed more evenly beyond this point.

Section 9.0: REFERENCES

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Innovative Technology Solutions, Inc. (ITSI). 2007. *Zero Valent Iron Injection Treatability Study Report, Operable Unit 20, Naval Air Station, North Island, San Diego, California*. Prepared for NAVFAC Southwest, San Diego, California. Prepared by ITSI, Walnut Creek, CA. May.