

OBSERVED ENHANCED REDUCTIVE DECHLORINATION AFTER IN SITU CHEMICAL OXIDATION PILOT TEST

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ABSTRACT: A patented in situ chemical oxidation (chemox) technology (U.S. Patent No. 6,019,548) using sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and potassium permanganate (KMnO_4) was pilot tested at an active facility (site) to remediate residual dense non-aqueous phase liquid (DNAPL) and dissolved chlorinated volatile organic compounds [VOCs with trichloroethene (TCE) as the major identified constituent]. The technology uses persulfate to satisfy a majority of the non-target oxidant demand [e.g., soil oxidant demand (SOD)], and permanganate to mineralize target VOCs. During the pilot test, a total of 8,200 kg of $\text{Na}_2\text{S}_2\text{O}_8$ was injected over a period of 64 days followed by 45,000 kg of KMnO_4 injected over a period of 172 days in the semi-confined, sand and gravel aquifer at the site. An unanticipated observed benefit of the oxidant injection was enhanced reductive dechlorination of the chlorinated VOCs in and downgradient of the injection area during post-injection monitoring at the site. The interpretation of the post-injection VOC data (including reductive dechlorination daughter product to parent compound ratios) and chloride mass balance calculations provided strong evidence of enhanced reductive dechlorination at the site. Additional data collection and analyses (including hydrogen, sulfate, dissolved iron and phospho-lipid fatty acid sampling results) indicated that sulfate-reducing bacterial activity was the primary mechanism of reductive dechlorination at the site. The observed enhancement of reductive dechlorination after the oxidant injection may be due to one or more of the following mechanisms: 1) $\text{Na}_2\text{S}_2\text{O}_8$ injection directly enhancing sulfate-reducing bacterial growth by supplying sulfate (an electron acceptor for the bacterial activity, which is a dissociation product of $\text{Na}_2\text{S}_2\text{O}_8$); 2) oxidant injection providing simpler organic carbon for the bacteria (a food source) by degrading naturally occurring complex organic carbon in the aquifer; 3) oxidant injection making VOCs more bioavailable by breaking down the sorption sites (e.g., naturally occurring complex organic carbon).

INTRODUCTION

The remediation technology in situ chemical oxidation treats a target contaminated area by adding oxidants (e.g., KMnO_4) to mineralize the target contaminants into innocuous end products (e.g., TCE mineralization to carbon dioxide and chloride). Oxidant demands in a contaminated subsurface include the oxidant demand by target contaminants and the non-target oxidant demand (e.g., SOD). Permanganate, one of the popular oxidants, is a strong oxidant capable of mineralizing a wide range of contaminants. However, one of the shortcomings of permanganate addition is MnO_2 precipitation (the end product of permanganate use), which, in excessive amount, has a potential of clogging the aquifer. United Technologies

Corporation (UTC) in conjunction with the University of Connecticut's Environmental Research Institute (ERI) has developed and patented (U.S. Patent No. 6,019,548) a novel in situ chemical oxidation process to mineralize VOCs using persulfate (e.g., Na₂S₂O₈) and permanganate (e.g., KMnO₄) either sequentially or simultaneously. The primary purpose of persulfate addition is to satisfy a majority of the non-target oxidant demand. The claimed benefits of the patented chemox process are primarily to: (a) minimize MnO₂ precipitation by satisfying the non-target oxidant demand by persulfate injection prior to permanganate injection; (b) reduce the total amount of oxidant required for mineralization of target VOCs.

Based on the results of the laboratory treatability studies and a three-dimensional high-resolution site characterization, a large field-scale pilot test was conducted at the site by XDD (a licensee of the technology) from November 1998 through August 1999. The target test area at the site is a 10-ft (3-m) thick semi-confined, sand and gravel aquifer [hydraulic conductivity of 0.29 cm/sec and groundwater velocity of 5 ft/day (1.5 m/day)] with residual DNAPL and VOCs (major constituent = TCE).

FIELD-SCALE PILOT TEST

The primary purpose of the pilot test was to understand the behavior of the reaction under field conditions between the oxidants and the target VOCs, and between the oxidants and the native soil minerals. The target test area comprised of two treatment zones, each sized approximately 160-ft (49-m) long, 175-ft (53-m) wide and 10-ft (3-m) thick. The oxidant injection was performed through two rows of injection wells with 6 injection locations in each row (see Figure 1 for well locations). The monitoring was performed via a total of 80 discrete monitoring points at 36 locations, distributed in three rows downgradient of injection row 1 and five rows downgradient of injection row 2. The pilot test consisted of Na₂S₂O₈ injection followed by KMnO₄ injection (refer to Table 1 for injection summary).

TABLE 1. Pilot test operational overview.

INJECTION	Na₂S₂O₈ Injection	KMnO₄ Injection
Injection duration, days	64	172
Monitoring duration, days	During injection + 6 quarterly events	
Oxidant quantity, Kg	8,200	45,000
Volume of water, L	4,300,000	4,400,000
Injection flow rate/location, Lpm	4.33	1.57, 1.89 and 3.78
Injection concentration, g/L	2	5 and 10
Geochemistry monitoring	pH, oxidation reduction potential, conductivity and temperature	
Chemical parameter monitoring	VOCs, chloride, residual Na ₂ S ₂ O ₈ , residual KMnO ₄ , sodium, sulfate, potassium and manganese	

POST-INJECTION MONITORING

A total of seven post-injection monitoring events were conducted after the pilot test conclusion at the site [i.e., six quarterly monitoring events beginning at the end of injection (August and December 1999 and March, June, September and December 2000)

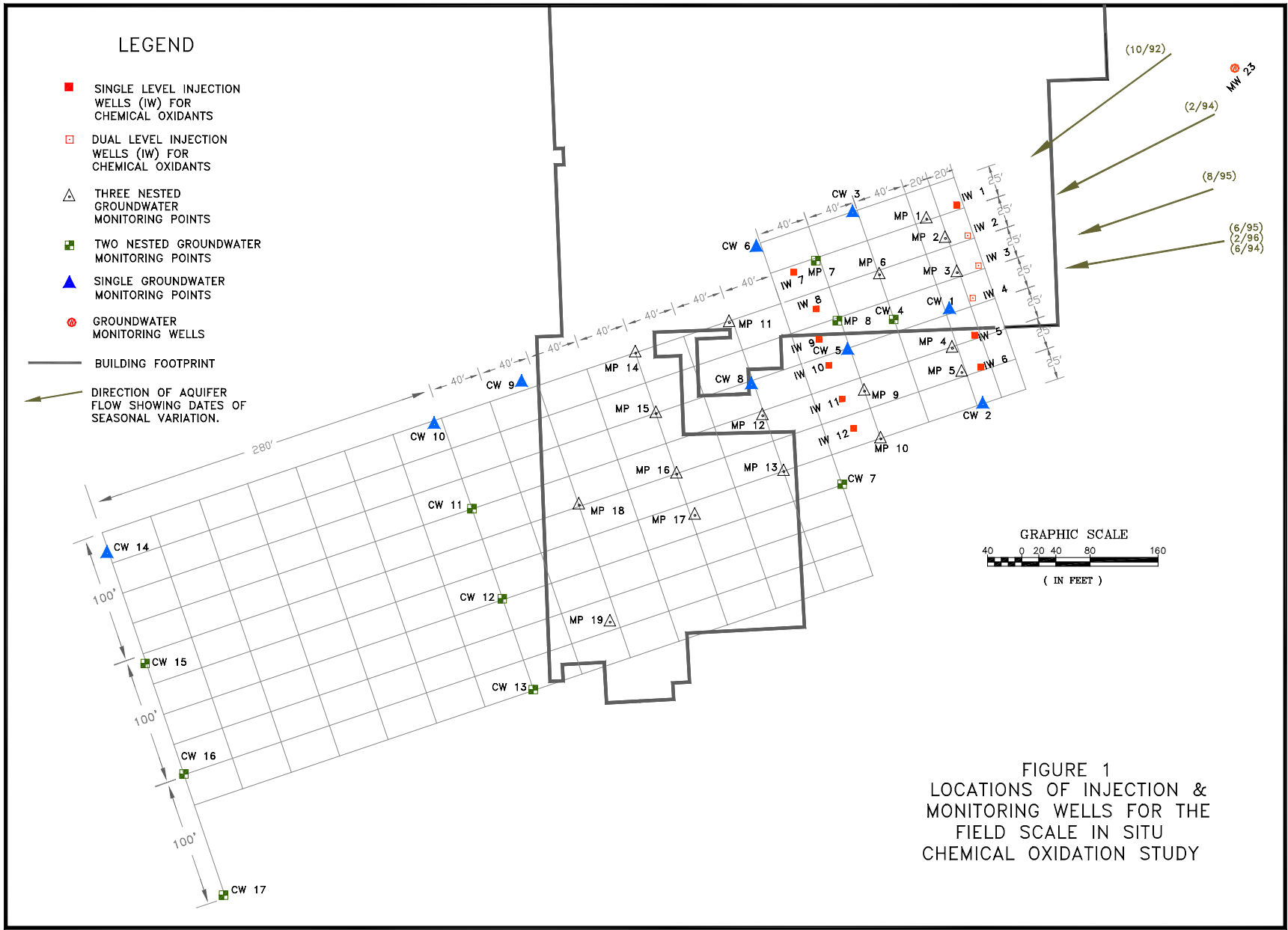


FIGURE 1
 LOCATIONS OF INJECTION &
 MONITORING WELLS FOR THE
 FIELD SCALE IN SITU
 CHEMICAL OXIDATION STUDY

and an additional monitoring event in June 2001]. The post-injection monitoring data collected through March 2000 showed evidence of ongoing reductive dechlorination processes at the site. Therefore, additional sampling was conducted in May 2000 [consisting of hydrogen (H₂), sulfate (SO₄²⁻), field dissolved iron (Fe²⁺) and phospholipid fatty acid (PLFA) analyses] to evaluate reductive dechlorination as an enhanced TCE removal mechanism at the site.

The evaluation of the post-injection VOC data, the chloride mass balance calculations and additional investigation results provided evidence of sulfate-reducing bacterial activity as the primary mechanism of reductive dechlorination potentially enhanced by the oxidant injection.

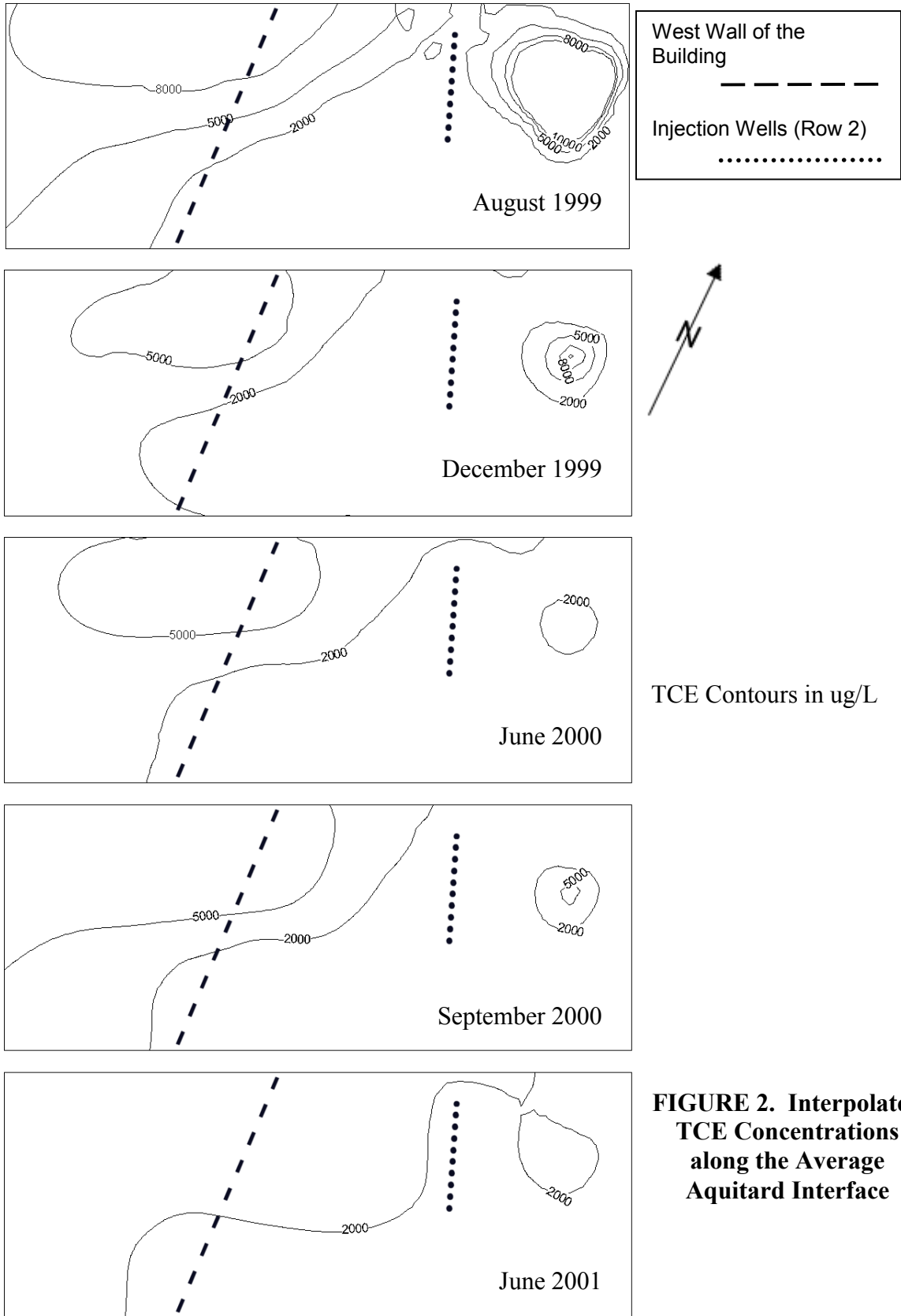
VOC Data Interpretation. TCE, its reductive dechlorination daughter products cis-1,2-dichloroethene (cis-DCE) and vinyl chloride (VC) and degradation product chloride concentration data were collected at the 80 monitoring points located in the target test area during all seven post-injection monitoring events. A 735-ft (224-m) long by 288-ft (88-m) wide modeling grid encompassing the target test area was created using GMS[®] software for the data interpolation. The average interpolated concentrations for the modeled zone were computed using a three-dimensional data kriging process in the GMS[®] software. Table 2 presents the GMS[®]-calculated average interpolated concentrations within the modeled zone for six post-injection monitoring rounds (the December 2000 data was not modeled since it was an incomplete monitoring event).

TABLE 2. Average interpolated concentrations.

	TCE (ug/L)	cis-DCE (ug/L)	VC (ug/L)	Chloride (mg/L)
August 1999	3,538	9,715	1,012	38
December 1999	2,297	6,886	1,107	36
March 2000	1,640	3,582	662	99
June 2000	1,965	5,745	1,122	38
September 2000	2,111	5,878	1,119	40
June 2001	1,688	4,684	1,077	41

As shown in Table 2, the average TCE and cis-DCE concentrations have decreased significantly over the post-injection monitoring period from August 1999 through June 2001. The average TCE concentration decreased from 3,538 ug/L in August 1999 to 1,688 ug/L in June 2001, similarly, the average cis-DCE concentration decreased from 9,715 ug/L in August 1999 to 4,684 ug/L in June 2001. The March 2000 monitoring event showed anomalously low VOC concentrations and high chloride concentrations. The average VC concentration was relatively stable through the post-injection period indicating relatively equivalent rates of VC production (from cis-DCE degradation) and degradation (into ethane or ethane). The average concentration of chloride, a chlorinated VOC end-product, has remained elevated, ranging from 36 to 41 mg/L (excluding the March 2000 data of 99 mg/L), during the post-injection monitoring period compared to the pre-injection average concentration of 17 mg/L.

Figure 2 presents GMS[®] interpolated TCE concentration isopleths of five post-injection monitoring events (excluding the March 2000 and December 2000 data) in a plan view at the average bottom of the aquifer. The dotted line on the figures indicates



location of injection row 2, and the dashed line represents the west wall of the facility building. Injection row 1 is located immediately to the right of the modeling grid (i.e., northeast) and is not shown in the figure. Visual interpretation of the TCE isopleths suggests that TCE concentrations within the modeled zone have generally decreased from August 1999 through June 2001. Generally, the highest TCE concentrations are observed along the aquitard interface (i.e., bottom of the aquifer) extending from the property boundary to the downgradient end of the modeled zone.

Reductive dechlorination daughter product to parent compound ratios (cis-DCE to TCE and VC to cis-DCE) for each monitoring round are primary evidence of the enhancement of the ongoing reductive dechlorination process at the site. The daughter product to parent compound ratios were calculated using the average interpolated concentrations computed using GMS[®] software. The ratio data (refer to Table 3) show increased ratios of reductive dechlorination daughter products to parent compounds (cis-DCE:TCE and VC:cis-DCE) in the post-injection period compared to the pre-injection monitoring event. Cis-DCE:TCE ratio increased from 2.18 in November 1998 to as high as 3.96 in June 2000 (approximately 80% increase) and VC:cis-DCE ratio increased from 0.21 in November 1998 to as high as 0.36 in June 2001 (approximately 70% increase).

TABLE 3. Reductive dechlorination daughter product to parent compound ratios.

	cis-DCE : TCE molar ratio	VC : cis-DCE molar ratio
November 1998 (background)	2.18	0.21
August 1999 (end of injection)	3.72	0.16
December 1999	3.89	0.26
March 2000	2.96	0.29
June 2000	3.96	0.30
September 2000	3.78	0.30
June 2001	3.76	0.36

Chloride Mass Balance. To estimate an equivalent VOC mass reduction during the post-injection monitoring period, a chloride mass balance was performed since chloride is a non-sorbing (travels with groundwater) chlorinated VOC degradation end-product. The chloride mass balance was calculated by comparing the chloride masses of two subsequent quarterly events (calculated from the average interpolated chloride concentrations) and adjusting for the chloride influx [calculated from the average interpolated chloride concentrations and groundwater flow along the upgradient (right) boundary of the modeled area] and outflux [calculated from the average interpolated chloride concentrations and groundwater flow along the downgradient (left) boundary of the modeled area]. The calculated estimate of chloride mass produced during each quarter was then converted into an equivalent mass of TCE destructed between each quarter of monitoring (i.e., 3 moles of chloride are produced from each mole of complete TCE destruction). The chloride mass balance calculations were performed through September 2000. During the post-injection monitoring period through September 2000, a net increase of approximately 1,669 Kg in chloride mass was observed, equating to approximately 2,060 Kg of equivalent TCE destruction. Due to an anomalously high

average chloride concentration in March 2000, the March-00 to June-00 quarter showed a net decrease of 86 Kg of chloride and therefore was assumed zero.

TABLE 4. Post-injection chloride mass balance.

Duration	Chloride produced (Kg)	Equivalent TCE (Kg)
Aug-99 to Dec-99	217	267
Dec-99 to Mar-00	903	1,115
Mar-00 to Jun-00	0	0
Jun-00 to Sept-00	549	678
TOTAL	1669	2060

Additional Investigation Results. Based on the quarterly monitoring data collected through March 2000, enhanced reductive dechlorination through sulfate reduction was hypothesized to be responsible for the TCE destruction ongoing at the site. To determine the role of sulfate reduction in the ongoing reductive dechlorination process, additional analyses for H₂, SO₄²⁻, field Fe²⁺ and PLFA sampling was performed in May 2000 at locations CW13, CW15 and CW16 (fourth and fifth row of monitoring points, downgradient of the second row of injection points- refer to Figure 1). These locations showed high concentrations of TCE and its reductive daughter products during the previous quarterly monitoring event (March 2000), and were assumed to be likely locations where TCE reduction was ongoing. Refer to Table 5 for the sampling results.

TABLE 5. Additional investigation results.

Location	H ₂ (nM/L)	SO ₄ ²⁻ (mg/L)	Field Fe ²⁺ (mg/L)
CW13	1.55	430	1.4
CW15	1.36	156	0.3
CW16	1.69	277	1.2

H₂ sampling was performed to determine the dominant terminal electron-accepting process in the aquifer. The hydrogen sampling at these locations yielded concentrations ranging from 1.36 to 1.69 nM (nano-moles/liter). Hydrogen concentrations ranging from 1 to 4 nM support sulfate reduction as the dominant terminal electron accepting process (Wiedemeier et al.1, 1996). The hydrogen data support the conclusion that reductive dechlorination of TCE and its daughter products (dominated by sulfate reduction) is occurring in the treatment zone. Sulfate concentrations at these locations were in the range of 43.3 to 430 mg/L in the May 2000 field-sampling event. Ample sulfate concentrations in the groundwater support the proliferation of sulfate-reducing bacteria in the aquifer. At concentrations higher than 20 mg/L sulfate ions may compete with the chlorinated VOCs for reduction by sulfate-reducing bacteria (Wiedemeier et al.2, 1996). Although, based on the data analysis above, this does not appear to be a significant limitation at the site. The dissolved Fe concentrations were low (ranging from 0.3 to 1.4 mg/L) similar to previously measured total Fe concentrations at the site, indicating the depletion of more preferential electron acceptors relative to sulfate (i.e., oxygen, nitrate, manganese and iron).

PLFA are found within the membranes of all living cells but decompose quickly upon cell death. Thus, measuring PLFA content provides a quantitative measure of the

viable microbial biomass present. To relate the complex mixture of PLFA to the organisms present, structural group interpretation and biomarkers are employed. The 'branched monoenoic' structural type of PLFAs is commonly found in the cell membranes of obligate anaerobes such as sulfate- or iron-reducing bacteria. 'Mid-chain branched' PLFAs are indicative of the presence of sulfate-reducing bacteria. Additionally, the sulfate-reducing bacteria are part of the Gram Negative bacterial community. The PLFA results indicated the presence of Gram Negative type of bacteria (including sulfate-reducing bacteria) at CW13 and CW15 (31.7 and 24.9% of the total PLFA moles, respectively). Additionally, the bio-indicator for the sulfate-reducing bacteria was detected in CW13 and CW16 at 7.6 and 8.5% of the total PLFA, respectively. Furthermore, the Gram Negative communities in any of these samples did not contain detectable biomarkers for a bacterial response to environmental stress. The data provide an evidence of sulfate-reducing bacterial activity dominated reductive dechlorination contributing to TCE removal at the site.

SUMMARY

The post-injection monitoring site data provides supporting evidences of ongoing sulfate-reducing bacterial activity at the site. While the quantification of the amount of sulfate-reducing bacterial activity for the overall TCE degradation is difficult, the data does indicate that reductive dechlorination of TCE was enhanced after the conclusion of the oxidant injection pilot test. The reductive dechlorination enhancement may be explained by one or more of the following mechanisms: 1) $\text{Na}_2\text{S}_2\text{O}_8$ injection directly enhancing sulfate-reducing bacterial growth by supplying sulfate (an electron acceptor for the bacterial activity, which is a dissociation product of $\text{Na}_2\text{S}_2\text{O}_8$); 2) oxidant injection providing simpler organic carbon for the bacteria (a food source) by degrading naturally occurring complex organic carbon in the aquifer; 3) oxidant injection making VOCs more bioavailable by breaking down the sorption sites (e.g., naturally occurring complex organic carbon).

In summary, the groundwater VOC concentration data at the pilot-tested site provide evidence of TCE reductive dechlorination enhancement following the oxidant (i.e., $\text{Na}_2\text{S}_2\text{O}_8$ and KMnO_4) injection.

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