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Port Hueneme, California 93043-4370

**TECHNICAL REPORT
TR-2308-ENV**

**ADDENDUM TO COST AND PERFORMANCE REPORT OF
ELECTRICAL RESISTANCE HEATING (ERH) FOR SOURCE
TREATMENT**

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14. ABSTRACT Electrical Resistance Heating (ERH) was applied at Site 1 located at the U.S. Naval Station Annapolis from January to June 2006. ERH was applied to treat soils and groundwater at depths up to 66 ft below ground surface and contaminated primarily with 1,1,2,2-tetrachloroethane (TeCA), trichloroethylene (TCE), and 1,1,2-trichloroethane (TCA) at the site. This report summarizes the cost and performance data from this ERH application.					
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Addendum to
Cost and Performance Report of
Electrical Resistance Heating (ERH) for Source Treatment

Contract Number: N62473-07-D-4013
Task Order: 007

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EXECUTIVE SUMMARY

The objective of this addendum is to supplement the final report titled “Cost and Performance Review of Electrical Resistance Heating (ERH) for Source Treatment” with a review of information obtained from the ERH application at Site 1, U.S. Naval Station, Annapolis (USNA), Maryland.

ERH was applied at Site 1 on the north shore of the Severn River, directly across from the U.S. Naval Academy in Annapolis, Maryland. Site 1 was used as a refuse disposal site and is bordered by private property to the west; Woolchurch Cove, Naval Station Lagoon, and the Severn River to the south; and Naval Support Facility Annapolis facilities to the east and north. The geology of the site is mostly sand interbedded with thin layers of silt and limonite or siderite cemented sandstone. The groundwater table at the site is located approximately 60 feet below ground surface (bgs) and the direction of the groundwater is southwest towards the river. None of the groundwater aquifers are used for domestic water supply within the one mile radius of the site.

ERH was applied to treat soils and groundwater contaminated primarily with 1, 1, 2, 2-tetrachloroethane (TeCA), trichloroethylene (TCE), and 1, 1, 2- trichloroethane (TCA) at the site. The chlorinated volatile organic carbon (CVOC) source area was located in the northwestern portion of Site 1. The highest baseline soil concentration of CVOCs encountered (169 mg/kg) was at 66 ft bgs and in groundwater it was around 45,000 µg/L of TeCA in the same vicinity. The ERH system consisted both of surface and subsurface components. Only the top 15 ft or so of the saturated zone was targeted for ERH treatment. The chronology below lists all of the important dates in the ERH application at the site.

- | | |
|---|--|
| • Mobilization and site setup | November 7 to 14, 2005 |
| • Drilling program for ERH system | November 15, 2005 through January 17, 2006 |
| • Installation of subsurface ERH system | December 16, 2005 through January 25, 2006 |
| • ERH system fully operational | January 28, 2006 |
| • Discontinued ERH electrode operation | May 31, 2006 |
| • Shut down VR blower and steam condenser | June 10, 2006 |

Groundwater and soil monitoring was conducted during and after the treatment. An organic vapor analyzer-flame ionization detector (OVA-FID) and Summa canisters were used to monitor CVOC concentrations at the inlet to the vapor-phase granular activated carbon (GAC) vessels. Thermocouples were used to measure temperature in the subsurface.

When the vapor extraction system first began on January 28, 2006 (when the subsurface was at ambient temperature), the daily recorded level of CVOCs in the extracted vapor was already relatively high at 1,000 parts per million by volume (ppmv) in the Summa canisters. Total CVOC concentrations in the vapor fluctuated around the same order of magnitude level throughout the heating, increasing to about 4,000 ppmv around mid-March (average ground temperature at 90°C) and decreasing to about 20 ppmv in mid-April (with average ground temperatures approaching 99°C). The estimated CVOC mass recovered in the extracted vapor was 1,880 lbs or more than twice the estimated pre-treatment mass.

By the time the ERH application was discontinued on May 31, 2006, most of the thermocouples below 35 ft bgs were showing temperatures greater than 99 or 100°C. MW-16 is the closest downgradient well and is screened near the water table. This is also the well that showed the maximum impact of the adjacent ERH treatment in terms of a rise in water temperature from 15 to 50°C (with a time lag after the end of ERH treatment, as the heated water from the ERH zone moved downgradient). In June 2006, after the ERH system was shutdown and the average subsurface temperature in the ERH zone was 99°C, the

temperature in MW-16 was 35°C and TeCA levels had dropped from 45,000 to ~5,000 µg/L. During the same time (January-June 2006), TCE levels increased substantially from ~3,000 µg/L to ~25,000 µg/L, indicating that TCE was produced from the abiotic degradation of TeCA.

There were uncertainties relating to type of degradation (abiotic or biotic), amount of residual dense, non-aqueous phase liquid (DNAPL) mass post ERH-treatment, and residual contaminant distribution unaddressed at the site. As with most DNAPL sites, there are some uncertainties that are a consequence of the limitations inherent in performance monitoring at DNAPL source sites. However, additional soil gas sampling within and around the treatment zone and installation of monitoring wells screened at shorter intervals within and below the treatment zone may help to address some of these uncertainties. A microbial evaluation with polymerase chain reaction (PCR) analysis for presence of microbial communities involved in CVOC dehalogenation would also be desirable. Overall, the ERH application was well executed and has contributed towards considerable improvement of the soil and groundwater quality at this site.

CONTENTS

EXECUTIVE SUMMARY	ii
TABLES	iv
FIGURES.....	v
ACRONYMS AND ABBREVIATIONS	vi
Section 1.0: INTRODUCTION	1
Section 2.0: GEOLOGY AND HYDROGEOLOGY	2
Section 3.0: CONTAMINANT DISTRIBUTION.....	7
Section 4.0: TECHNOLOGY IMPLEMENTATION.....	8
Section 5.0: PERFORMANCE EVALUATION APPROACH.....	13
Section 6.0: TECHNOLOGY PERFORMANCE.....	14
Section 7.0: COST	29
Section 8.0: DISCUSSION	39
Section 9.0: REFERENCES	40

TABLES

Table 1. Generalized Lithologic and Hydrogeologic Units in Vicinity of Site 1, Annapolis, Maryland.....	4
Table 2. Maximum CVOC Concentration for Each Boring	7
Table 3. Subsurface Temperatures on 03/07/06 (°C).....	18
Table 4. Subsurface Temperatures on 05/31/2006 (°C).....	18
Table 5. Vapor Stream Concentration.....	26
Table 6. Vapor Stream Mass Removal Rate	26
Table 7. Vapor Stream Cumulative Mass Removal Estimate.....	27

FIGURES

Figure 1. ERH Treatment Area in Site 1, U.S. Naval Academy Annapolis, MD	3
Figure 2. Groundwater Flow at Site 1.....	5
Figure 3. Conceptual Site Model	6
Figure 4. Conceptual Site Model with TeCA Plume Emanating from the Source	6
Figure 5. CVOC Contamination in Baseline Soil Borings	9
Figure 6a. Soil Boring Locations	10
Figure 6b. Monitoring Wells Locations.....	11
Figure 7. Horizontal Layout of Electrodes.....	15
Figure 8. Vertical Heating Intervals of Various Electrodes.....	16
Figure 9. Daily Average Subsurface Temperature.....	17
Figure 10. Total CVOC Concentrations in Recovered Vapor	19
Figure 11. Concentration of CVOC Constituents in Recovered Vapor	20
Figure 12. Cumulative CVOC Mass Recovered.....	20
Figure 13. Site 1 – SB40: TeCA in Pre- and Post-ERH Soils.....	21
Figure 14. Site 1 – SB40: TCE in Pre- and Post-ERH Soils.....	22
Figure 15. Site 1 – SB36: TeCA in Pre- and Post-ERH Soils.....	23
Figure 16. Site 1 – SB36: TCE in Pre- and Post-ERH Soils.....	24
Figure 17. Degradation Pathway of TeCA (Source: Lorah and Olsen, 1999)	25
Figure 18. MW-02 VOC Trend Graph.....	30
Figure 19. MW-03 VOC Trend Graph.....	31
Figure 20. MW-09 VOC Trend Graph.....	32
Figure 21. MW-10 VOC Trend Graph.....	33
Figure 22. MW-14 VOC Trend Graph.....	34
Figure 23. MW-15 VOC Trend Graph.....	35
Figure 24. MW-16 VOC Trend Graph.....	36
Figure 25. MW-17 VOC Trend Graph.....	37
Figure 26. Groundwater Temperatures for Annapolis, MD.....	38

ACRONYMS AND ABBREVIATIONS

bgs	below ground surface
CVOC	chlorinated volatile organic carbon
DNAPL	dense, non-aqueous phase liquid
ERH	electrical resistance heating
FID	flame ionization detector
GAC	granular activated carbon
OVA-FID	organic vapor analyzer-flame ionization detector
PCR	polymerase chain reaction
PCU	power control unit
ppmv	parts per million by volume
TCA	trichloroethane
TCE	trichloroethene
TeCA	1,1,2,2-tetrachloroethane
TMP	temperature monitoring point
U.S. EPA	U.S. Environmental Protection Agency
USNA	U.S. Naval Station Annapolis

Section 1.0: INTRODUCTION

The objective of this addendum is to supplement the final report titled “Cost and Performance Review of Electrical Resistance Heating (ERH) for Source Treatment” (Gavaskar et al., 2007) with a review of information obtained from the ERH application at Site 1, U.S. Naval Station, Annapolis (USNA), Maryland (Shaw, 2006; Tetra Tech, 2005; Tetra Tech 2007a; Tetra Tech 2007b).

ERH application was done at Site 1 to treat contaminated soils and groundwater. The site is located within USNA (Figure 1) on the north shore of the Severn River, directly across from the U.S. Naval Academy in Annapolis, Maryland. Site 1 is bordered by private property to the west; Woolchurch Cove, Naval Station Lagoon, and the Severn River to the south; and Naval Support Facility Annapolis facilities to the east and north. A deep ravine and wooded area separate Site 1 from the residential property on the west side. The Navy Commissary and Exchange building and associated parking areas currently occupy the northwestern portion of the site. Several areas at the site were used for burning refuse and the site was generally used as a refuse disposal site.

Section 2.0: GEOLOGY AND HYDROGEOLOGY

Table 1 lists the different geological units together with the hydrogeological units found at the site. The uppermost formation at Site 1 is called Aquia Formation, which is approximately 60 to 130 feet thick and is mainly comprised of medium to coarse grained, glauconitic quartz sand, interbedded with thin layers of silt and limonite or siderite cemented sandstone. Underlying the Aquia is the Brightseat Formation, which is described as an olive-gray to black glauconitic silt and clay. The Upper Cretaceous Severn, Matawan, and Magothy Formations underlie the Brightseat Formation.

The groundwater table at the site is located around 60 feet below ground surface (bgs) and the direction of the groundwater is southwest towards the river (see Figure 2). As listed in Table 1, the aquifers include, in descending order, the Aquia, the Monmouth, the Magothy, the Upper and Lower Patapsco and the Patuxent. The confining units (aquitards or aquicludes), in descending order, are the Brightseat, the Matawan, the Upper and Lower Patapsco, and the Arundel Clay. Reported hydraulic conductivities for the Aquia aquifer, in pump tests conducted by the Maryland Geological Survey at two separate locations approximately 4 to 5 miles south of Site 1, ranged from 1 to 8 ft/day and 14 to 43 ft/day. Site-specific slug testing and aquifer pumping indicate hydraulic conductivities for wells at Site 1 are close to 1 ft/day. None of the groundwater aquifers are used for domestic water supply within the one mile radius of the site.

Figures 3 and 4 present a conceptual model of the site and show the different geological layers right beneath the pesticide shop. Of note are the cemented sand and iron layers near the water table, which are expected to retard the downward migration of the dense, non-aqueous phase liquid (DNAPL). Some of the highest contamination has been found in the vicinity of these lower-permeability layers.

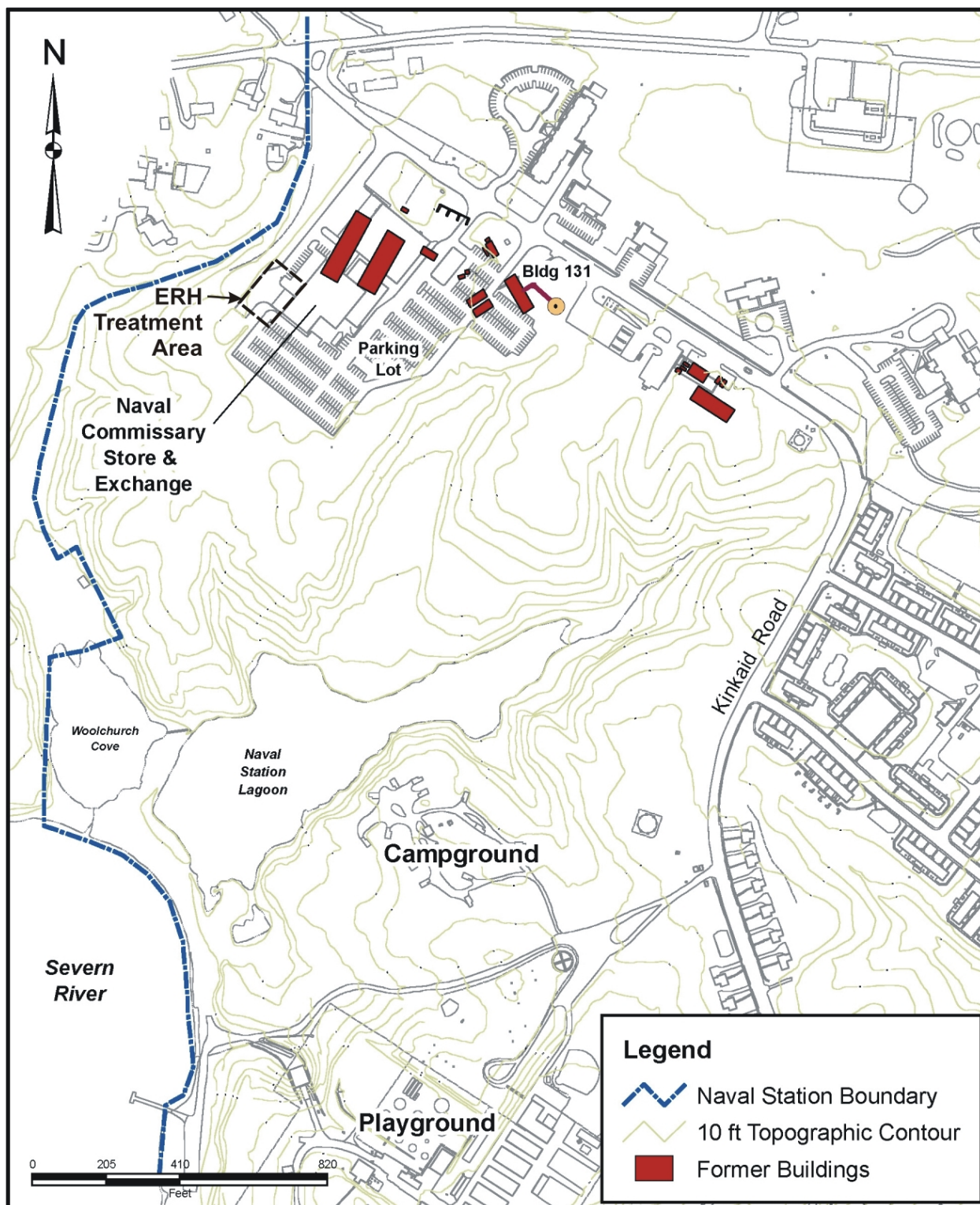


Figure 1. ERH Treatment Area in Site 1, U.S. Naval Academy Annapolis, MD

**Table 1. Generalized Lithologic and Hydrogeologic Units in Vicinity of Site 1,
Annapolis, Maryland**

Geologic Age			Stratigraphic Formation	Hydrologic Unit	General Lithology	Approximate Formation Elevation (ft- mean sea level) Not to Scale
System	Series	Group				
Tertiary	Paleocene	Pamunkey	Aquia	Aquia Aquifer	Glauconitic, greenish to brown sand with thin partially indurated 'rock' layers and silt layers.	+~60 (site) _Sea level -50 ⁽¹⁾
			Brightseat	Brightseat Leaky Confining Unit	Silt and clay, olive-gray to black, glauconitic.	-60 ⁽¹⁾
Cretaceous	Upper Cretaceous		Severn	Monmouth Aquifer (Poor)	Sand, silty to fine, with some glauconite.	-110 ⁽¹⁾
			Matawan	Matawan Confining Unit	Silt and fine sand, clayey, dark-green to black, glauconitic.	-170 ⁽¹⁾
			Magothy	Magothy Aquifer	Sand, light-gray to white, with interbedded thin layers of organic clay.	-300 ⁽¹⁾
	Lower Cretaceous	Potomac	Patapsco	Confining Unit	Tough, variegated clay for confining units. Fine to coarse brown sand with layer variegated clay for aquifers.	-360 ⁽¹⁾
				Upper Patapsco		
				Confining Unit		
				Lower Patapsco Aquifer		-1100 ⁽¹⁾
			Arundel Clay	Arundel Confining Unit	Clay, red, brown and gray, contains some iron stone nodules, plant remains and thin sandy layers.	
			Patuxent	Multiple-Layer Aquifer	Sand, gray and yellow, with interbedded clay, kaolinized feldspar, pyrite and lignite common; locally clay layers predominate.	-1800 ⁽²⁾
Triassic and/or Paleozoic to Precambrian			Basement Complex	Confining Unit	Shale, sandstone, gneiss, or granite.	

⁽¹⁾ Estimated elevations are feet below sea level based primarily on well records from numerous wells completed at Annapolis, the U.S. Naval Station and the Annapolis Neck and Broadneck Peninsula

⁽²⁾ Approximate elevation, feet below sea level

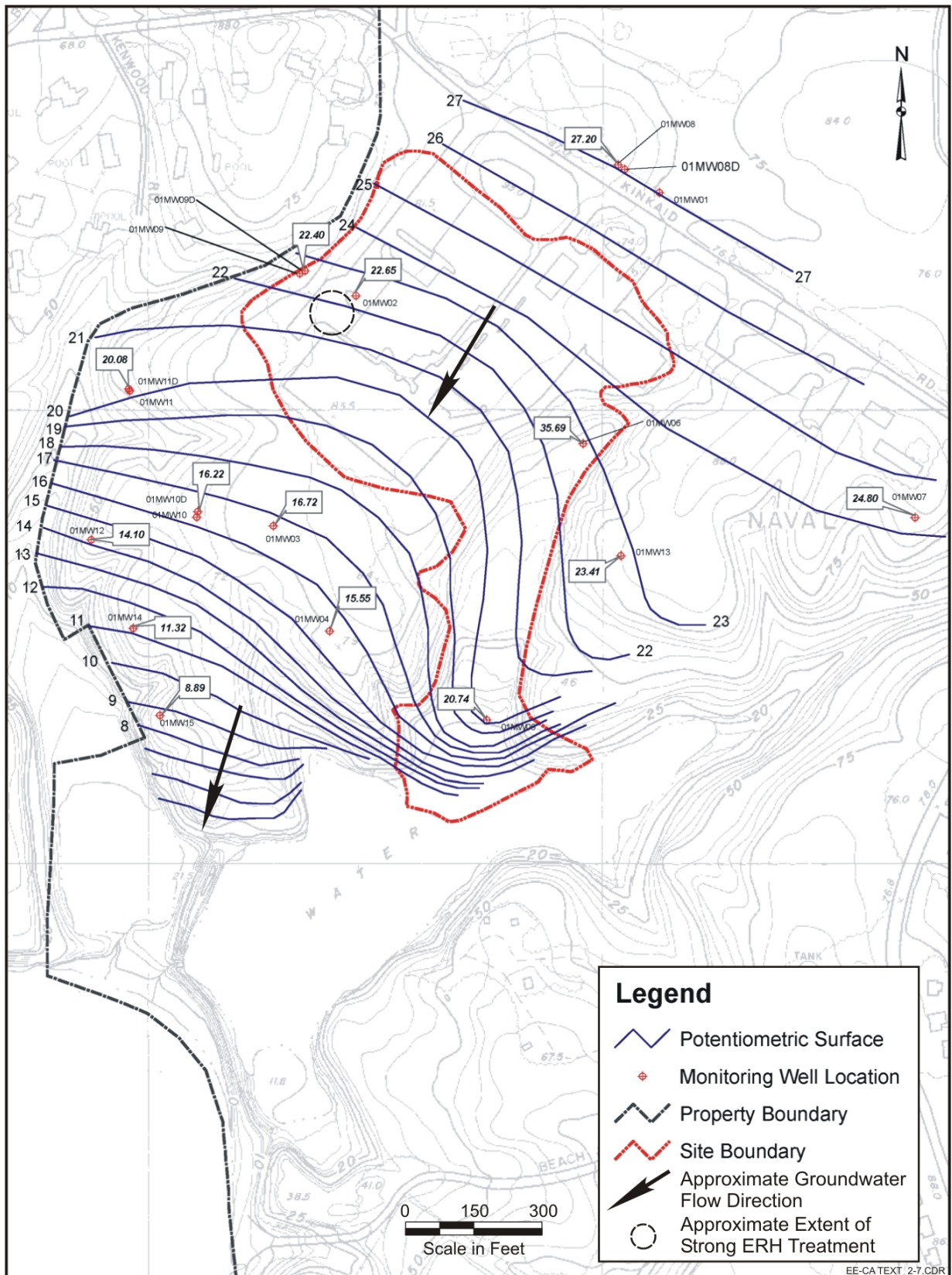


Figure 2. Groundwater Flow at Site 1

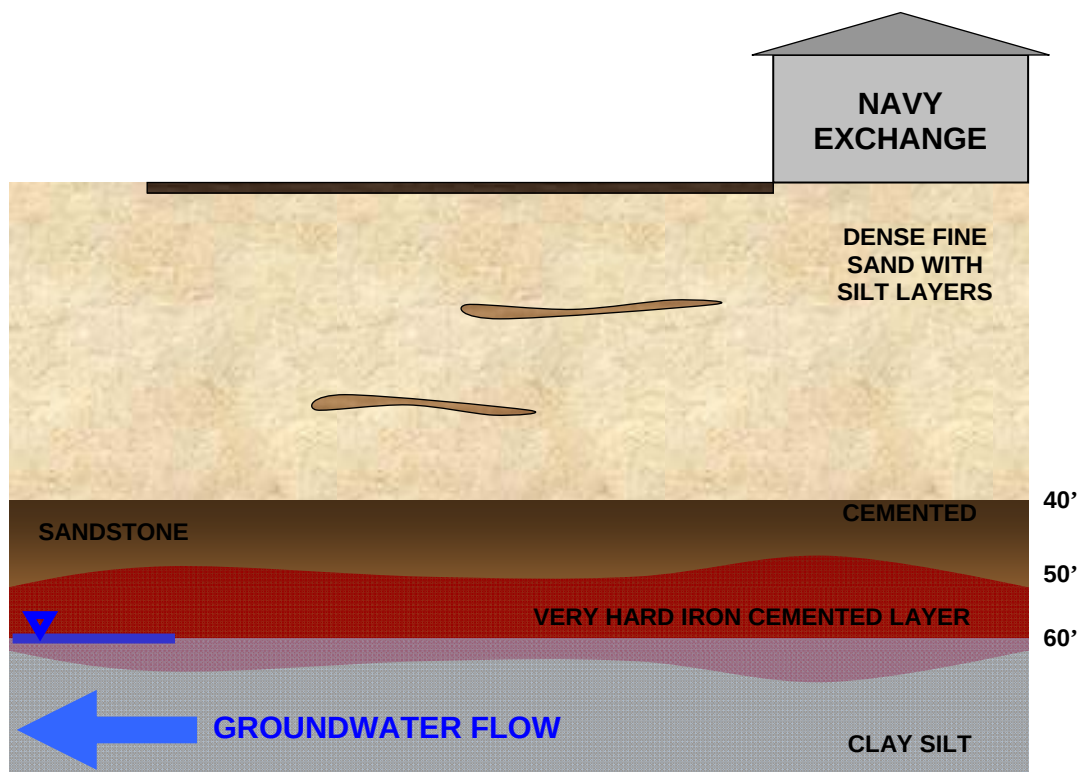


Figure 3. Conceptual Site Model

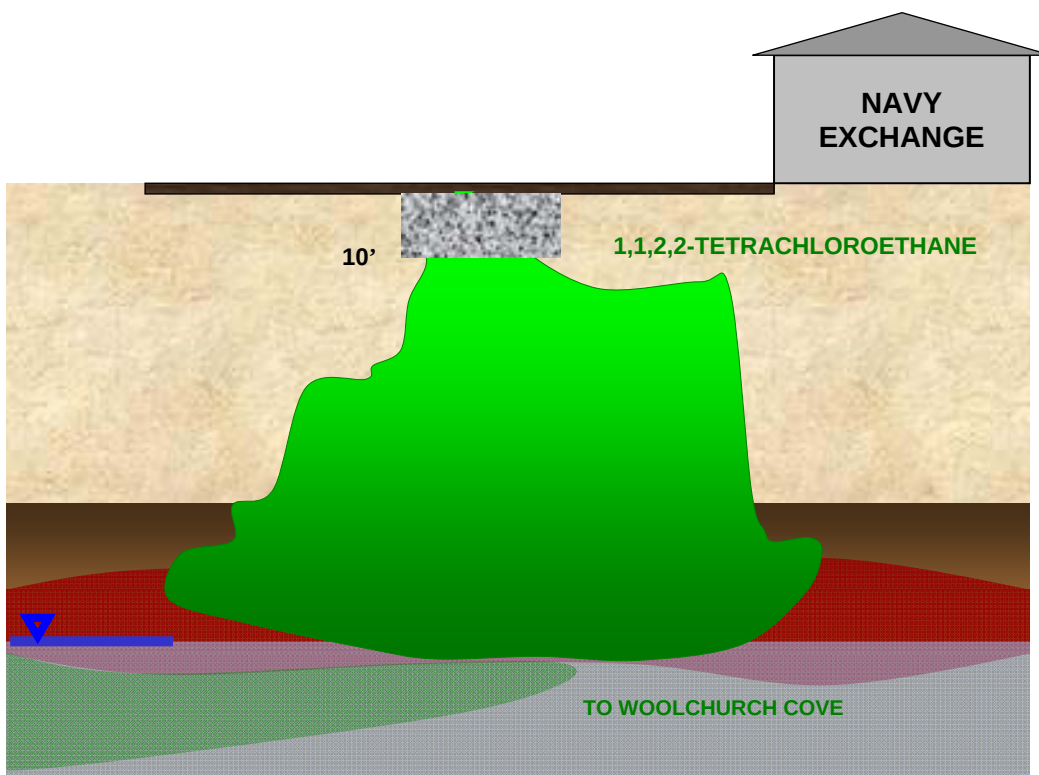


Figure 4. Conceptual Site Model with TeCA Plume Emanating from the Source

Section 3.0: CONTAMINANT DISTRIBUTION

The chlorinated volatile organic carbon (CVOC) Source Area is located in the northwestern portion of Site 1, west of the Commissary and Exchange Building 329. Soils and groundwater in this area have been contaminated primarily with 1,1,2,2-tetrachloroethane (TeCA), trichloroethene (TCE), and 1,1,2-trichloroethane (TCA). Figure 5 shows the variability of contamination in the baseline (pre-treatment) soil borings excavated in the source area. Prior to ERH treatment, soil contamination was generally encountered from 10 feet bgs to groundwater, which occurs at a depth of approximately 55 to 60 feet bgs. As shown in Table 2, maximum concentrations of CVOCs were detected in soil from 45 to 66 ft bgs.

Table 2. Maximum CVOC Concentration for Each Boring

Boring	Resulting TMP	Maximum Concentration (mg/kg)	Depth of maximum concentration (ft bgs)
B35	TMP-3	65	50
B36	TMP-2	98	48
B38	TMP-1	15	61
B39	TMP-4	169	66
B40	TMP-5	63	45

The highest baseline soil concentration encountered (169 mg/kg) was at 66 ft bgs in soil boring SB039. As seen in Figure 6a, SB039 is near the southwestern side of the ERH treatment area and near monitoring well MW-16 (Figure 6b), which demonstrated some of the highest pre-treatment dissolved concentrations of TeCA (approximately 45,000 µg/L) at the site. Although Figure 6b shows monitoring well MW-02 as located within the target ERH treatment area, this well is actually outside the electrode array but is still in the zone of influence of heating. The well encountered a moderate elevation in temperatures during treatment. In fact, there are no monitoring wells within the ERH treatment zone. The region targeted for ERH appears to be primarily the vadose zone, although the electrodes did penetrate to a depth of 70 ft bgs and targeted the top of the saturated zone. As shown in the conceptual model for the site, much of the contamination was assumed to be trapped in the vicinity of the cemented layers (sandstone and iron layers in Figures 3 and 4).

Section 4.0: TECHNOLOGY IMPLEMENTATION

The ERH system consisted both of surface and subsurface components. The surface components installed at the site were a steam condenser, cooling tower, 40 horsepower blower unit, power control unit (PCU), granular activated carbon (GAC) vessels for vapor treatment, data acquisition and remote assistance ports, ports for temperature and pressure monitoring, and make-up water condenser system. Most of the condensate, approximately 99% of it, was recycled back to the subsurface through drip lines for maintaining moisture content in the vadose zone soil and also used as cooling water. The chronology below lists all of the important dates in the ERH application at the site.

- | | |
|---|---------------------------------|
| • Mobilization and site setup | 07 Nov 2005 through 14 Nov 2005 |
| • Drilling program for ERH system | 15 Nov 2005 through 17 Jan 2006 |
| • Installation of subsurface ERH system | 16 Dec 2005 through 25 Jan 2006 |
| • ERH system fully operational | 28 Jan 2006 |

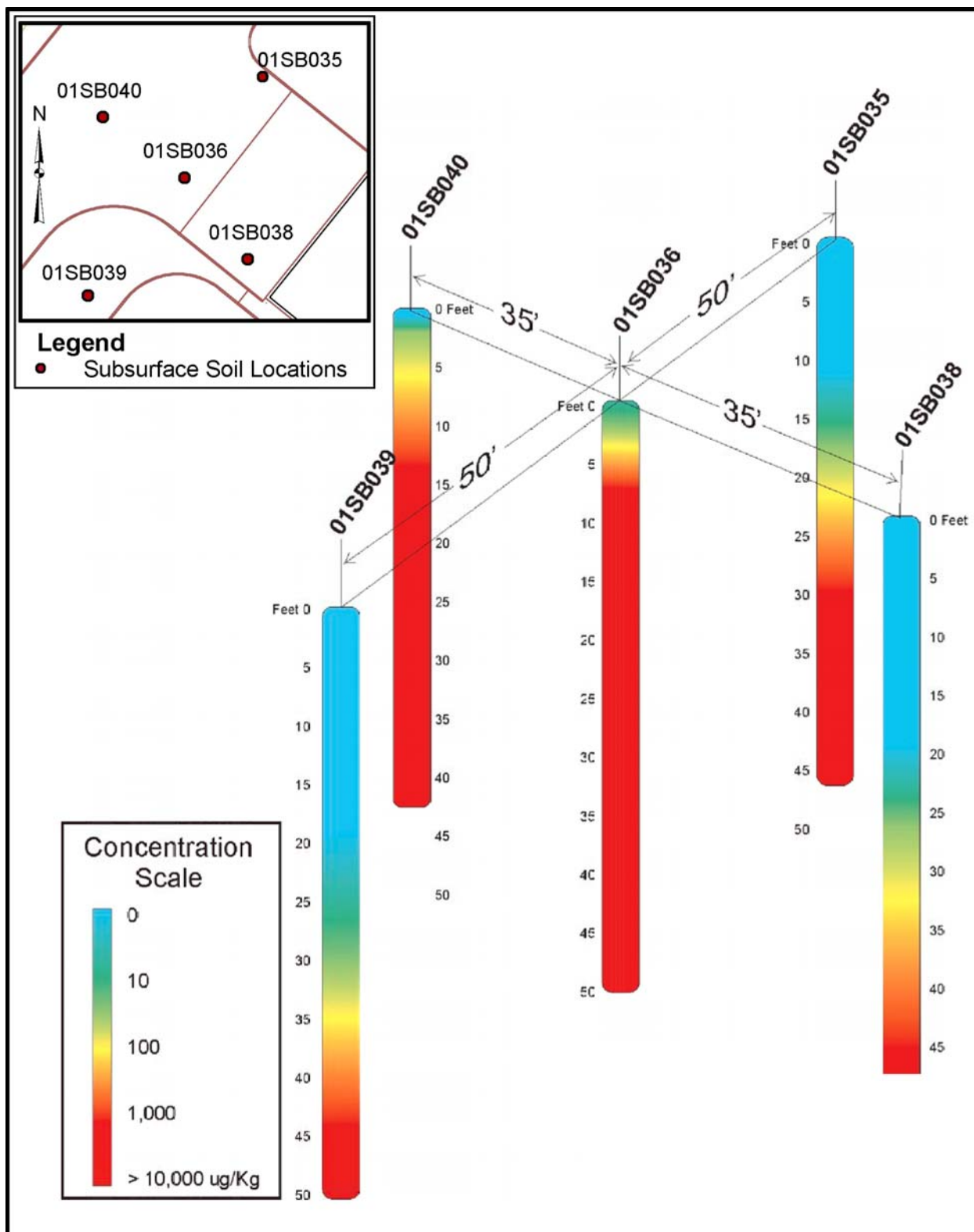


Figure 5. CVOC Contamination in Baseline Soil Borings

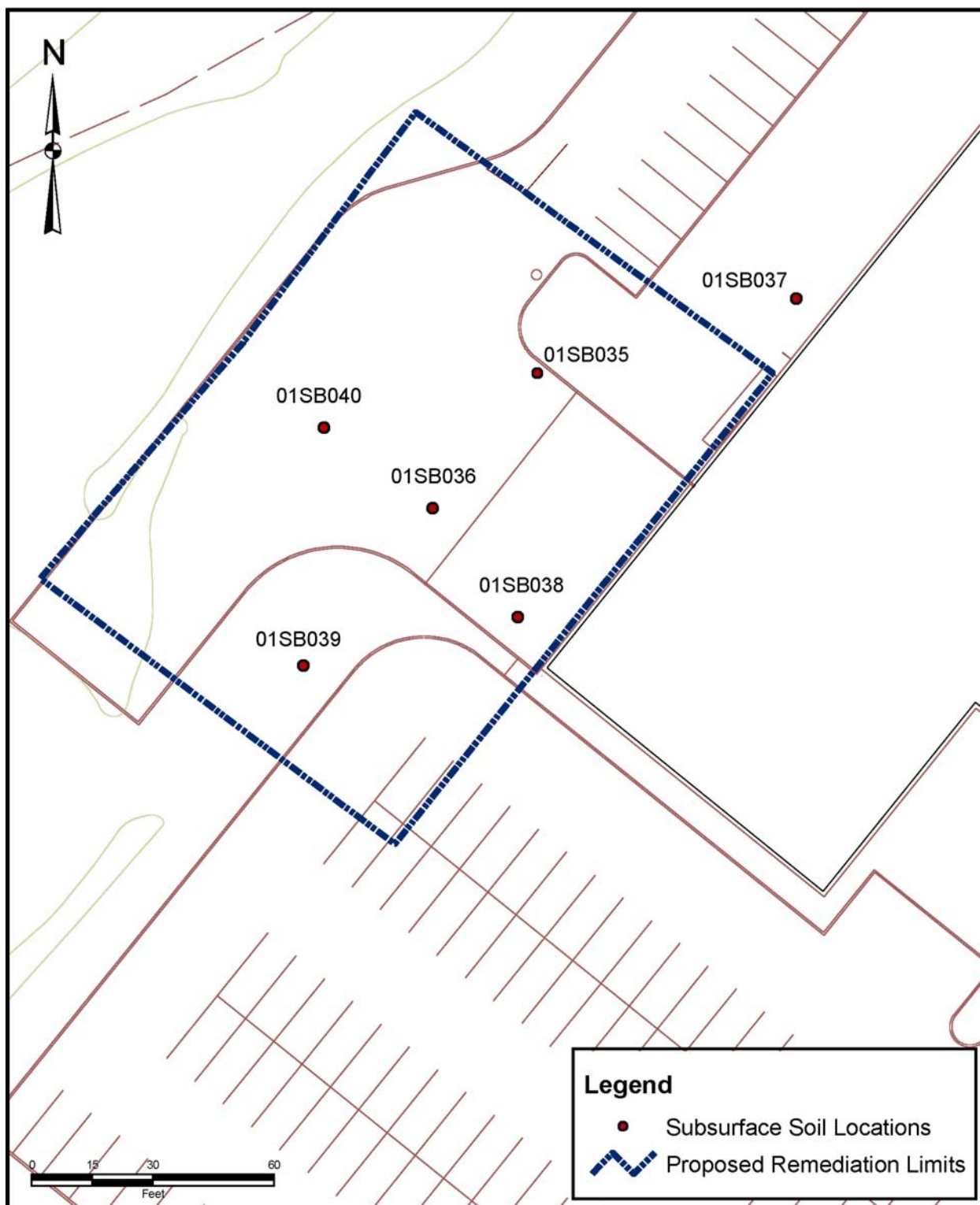


Figure 6a. Soil Boring Locations

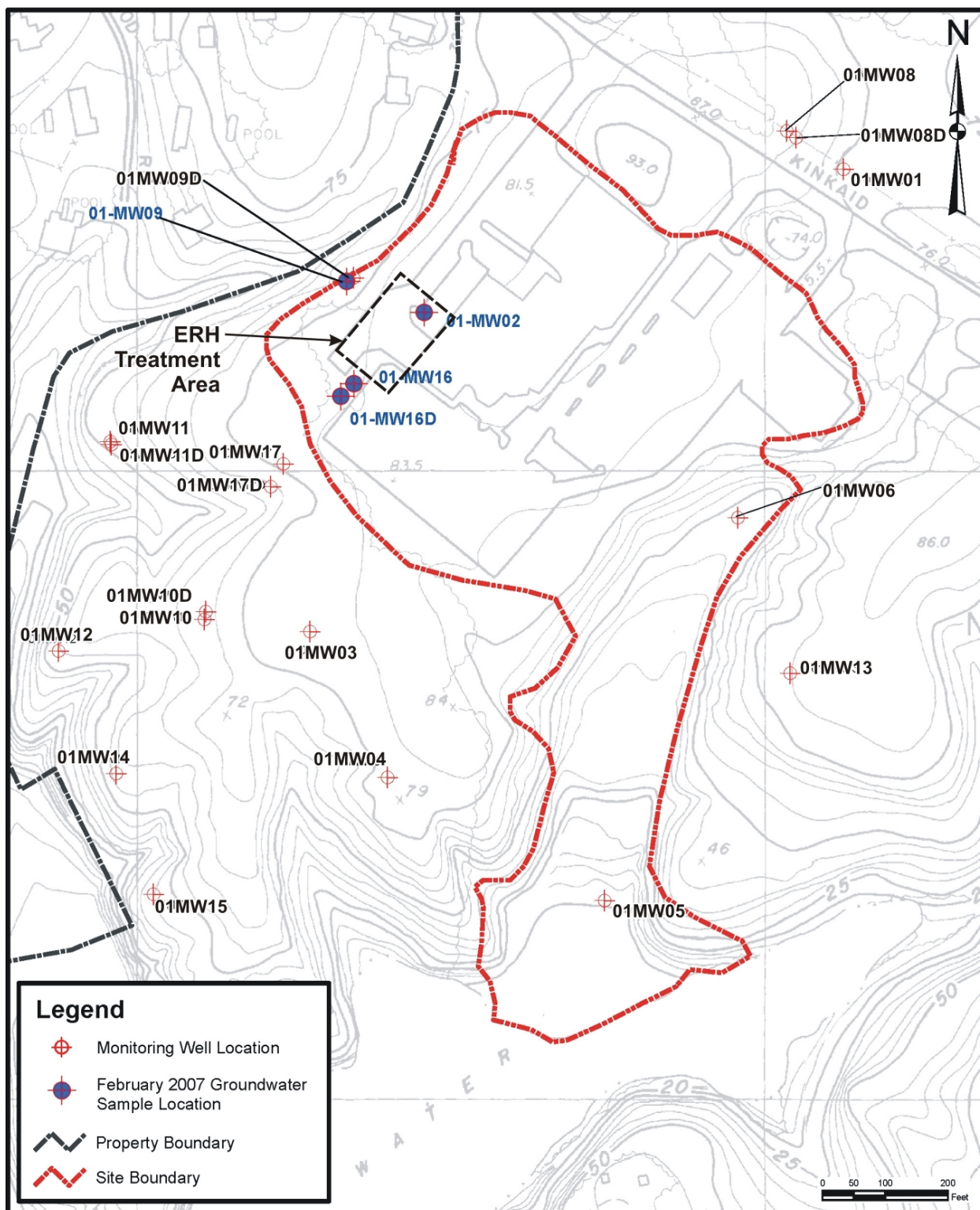


Figure 6b. Monitoring Wells Locations

- Discontinued ERH electrode operation 31 May 2006
- Shut down VR blower and steam condenser 10 June 2006

Electrodes were installed to a depth of between 70 and 75 feet bgs in 24 borings locations. The installation of the subsurface ERH system was conducted between November 2005 and January 2006. Each electrode also served as a vapor recovery point. The electrodes were composed of steel wells through which a three-phase electrical current was directed to the subsurface in a controlled manner. The ERH system was fully operational by the end of January 2006. Electrodes heated the primary treatment zone, located between 30 and 70 feet bgs. However, active heating was necessary from 10 to 70 feet bgs within portions of the treatment zone due to the conical shape of the CVOC-impacted zone. Therefore, the active treatment zone is different for different groups of electrodes. Figure 7 shows the location of all electrodes in the treatment area and Figure 8 exhibits the operational depths of the different electrodes; the heating interval of each electrode was targeted at those depths where contamination was encountered in the soil borings.

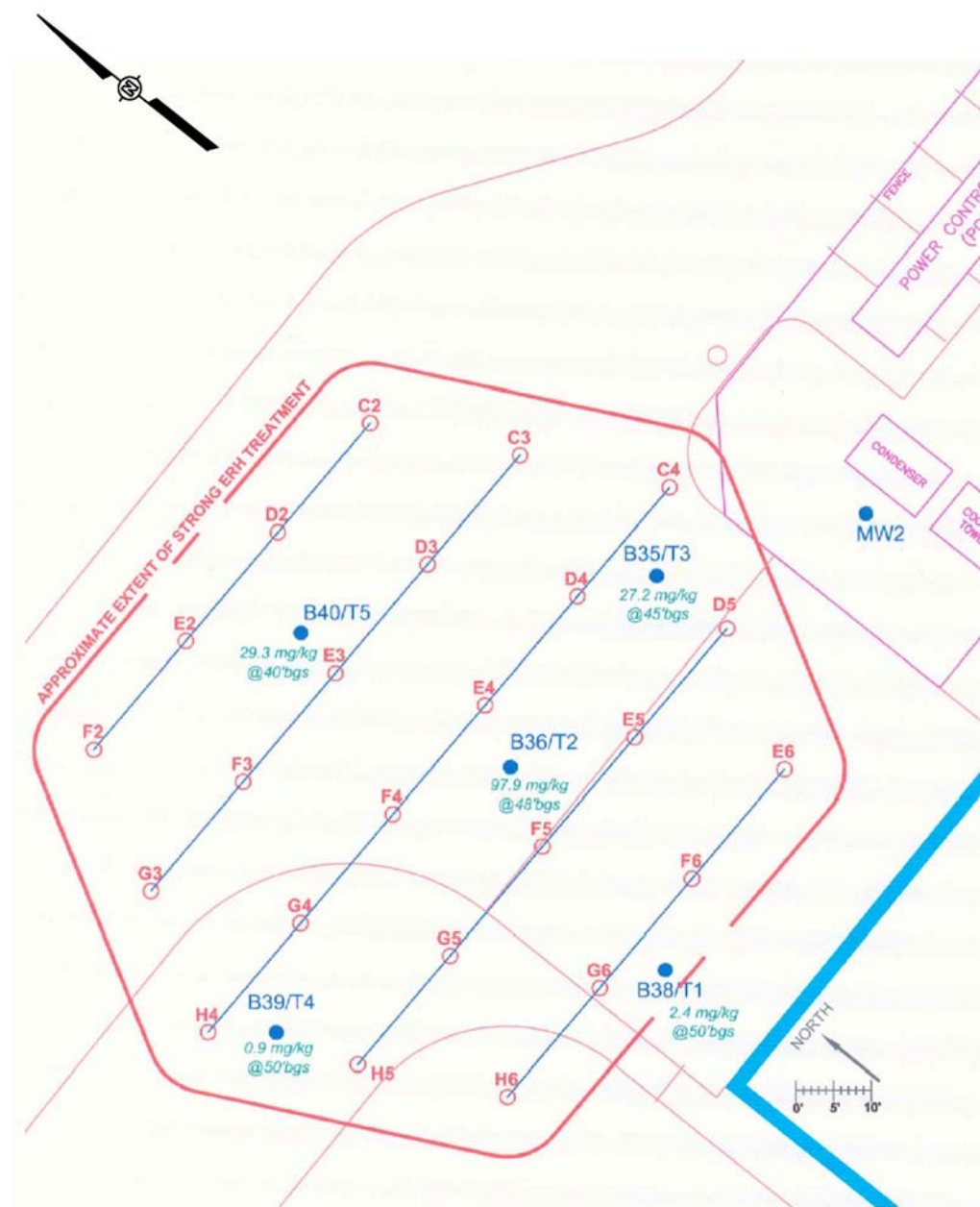
Temperature was monitored at the site by installing temperature monitoring points (TMPs) at five different soil boring locations. The TMPs consisted of thermocouples installed every 5 feet within the depth range of the treatment zone. A total of 58 thermocouples automatically recorded subsurface temperatures at the five TMPs. Figure 9 shows the average temperature recorded by the thermocouples during the heating phase. The designed target temperature for the application was 100 °C, the nominal boiling point of water.

Section 5.0: PERFORMANCE EVALUATION APPROACH

An organic vapor analyzer-flame ionization detector (OVA-FID) and Summa canisters were used to monitor CVOC concentrations at the inlet to the vapor-phase GAC vessels. Air samples collected using the 6-liter Summa canisters were analyzed for CVOCs using United States Environmental Protection Agency (U.S. EPA) Method TO-14A. Samples were also collected for similar investigations at the GAC vessel outlet. ERH system monitoring and temperature recording with the installed thermocouples also was done regularly. Five soil borings were drilled in the source area for pre- and post-ERH application sampling. Soil cores were collected at 5-foot intervals from 44 to 85 ft bgs. The five TMPs were installed in these same soil borings. Groundwater sampling was conducted during the operations and pre- and post-ERH application in wells (see Figure 6b) surrounding the ERH treatment area. In addition to existing wells (MW-02, MW-09, MW-10) in the vicinity, groundwater was collected from four recently installed shallow and deep monitoring wells (two clusters: MW-16 and MW-16D; MW-17 and MW-17D). None of the monitoring wells are within the ERH treatment area. MW-02 is immediately upgradient of the ERH area and MW-16 cluster is immediately downgradient. MW-16S was drilled with a screened interval from 55 to 70 ft bgs and targets the lower portion of the ERH treatment depth (uppermost portion of the saturated zone). MW-16D is screened from 85 to 101 ft bgs and is well below the target heating depth.

Section 6.0: TECHNOLOGY PERFORMANCE

As shown in Figure 9, the average temperature reached 45 °C around February 20, 2006, approximately 3 weeks after heating began (2 weeks, if the downtime to noise-proof the blower is excluded). The average temperature reached 70 °C, 90 °C, and 92 °C around March 5, March 20, and March 30, 2006 (approximately 4, 6, and 8 weeks after heating began). The average subsurface temperature reached



REFERENCE:

REFERENCED BASE MAP FROM THERMAL REMEDIATION SERVICES, INC.



Figure 7. Horizontal Layout of Electrodes

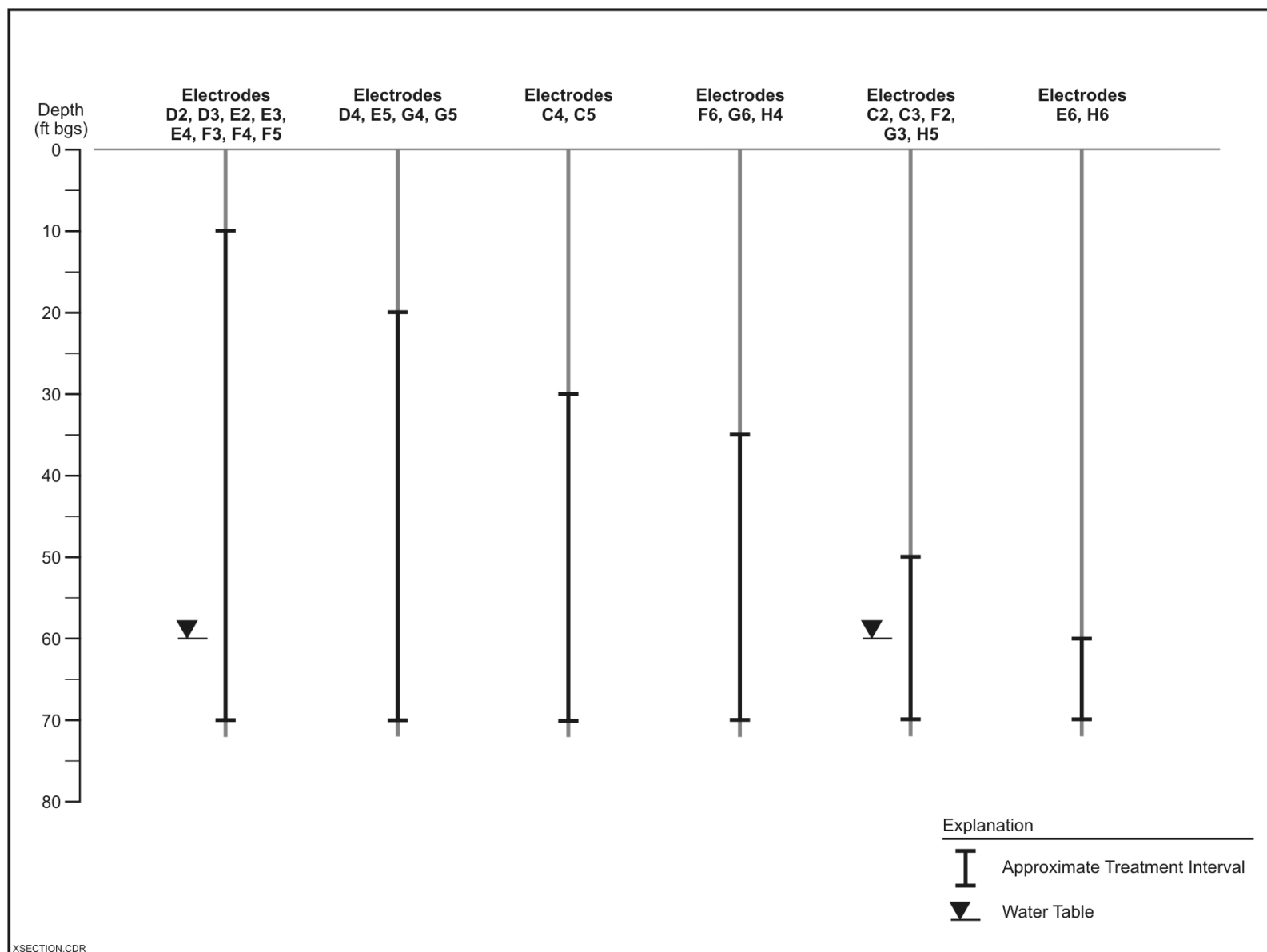


Figure 8. Vertical Heating Intervals of Various Electrodes

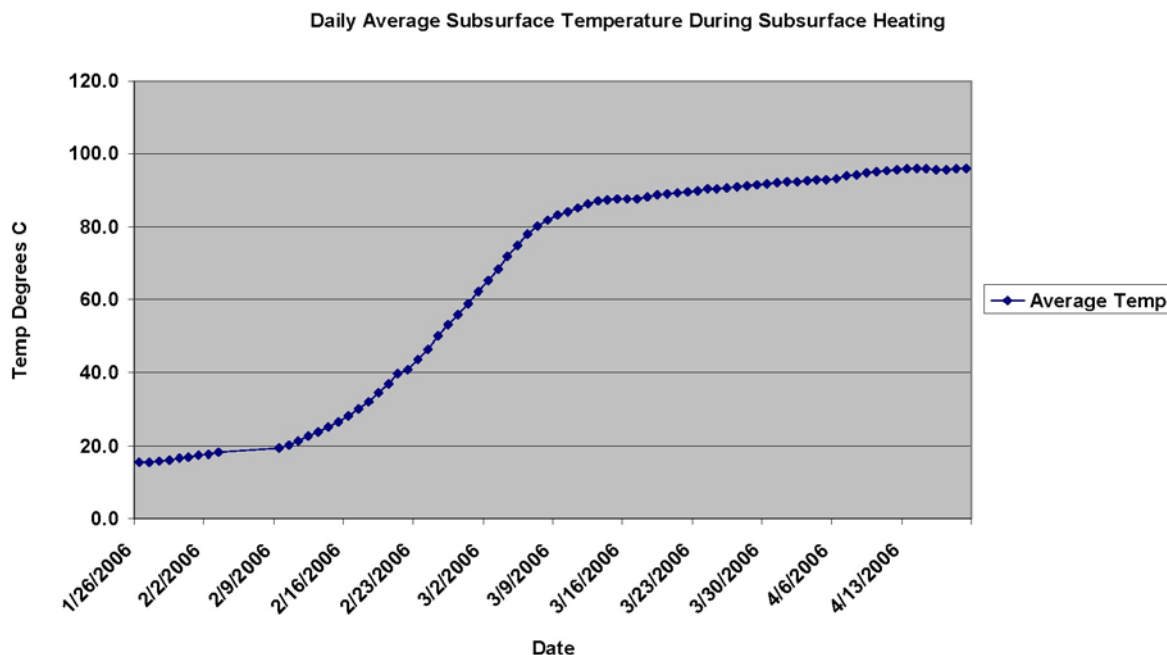


Figure 9. Daily Average Subsurface Temperature

99.2°C on May 9 (Shaw, 2006). This indicates that compared to some of the other sites reviewed, heating progressed relatively efficiently. The drip lines at the electrodes enabled efficient heating of both the vadose zone and the targeted portion of the saturated zone. Individual thermocouples started exceeding 100°C by March 8 (see Table 3), approximately 4 weeks after heating began. Therefore, the target depth interval (45 to 66 ft bgs, where the highest contamination is present) reached the target temperature quickly. By the time the ERH application was discontinued on May 31, most of the thermocouples below 35 ft bgs were showing temperatures greater than 99 or 100°C (see Table 4).

Figure 10 shows the daily concentration of total CVOC recovered in the extracted vapor over time, as measured by a field flame-ionization detector (FID) and by Summa canister collection and off-site analysis. Figure 11 shows the masses of individual constituents of the extracted vapor over time. The cumulative masses of the individual constituents are plotted in Figure 12. Although the Summa canisters consistently recorded a higher concentration of CVOCs, compared to the FID, these plots show some interesting trends.

Figure 10 shows that when the vapor extraction system first began on January 28, 2006 (when the subsurface was at ambient temperature), the daily recorded level of CVOCs in the extracted vapor was already relatively high at 1,000 parts per million by volume (ppmv) in the Summa canisters (concentration units are not provided in Figure 10, so ppmv is assumed for discussion purpose). This indicates that soil vapor extraction alone (without heating) was able to recover significant CVOC mass. Total CVOC concentrations in the vapor fluctuated around the same order of magnitude level throughout the heating, increasing to about 4,000 ppmv around mid-March (average ground temperature at 90°C) and decreasing to about 20 ppmv in mid-April (with average ground temperatures approaching 99°C). Some of the variability could possibly be attributable to daily fluctuations in the grab samples.

Figure 11 shows that when the soil vapor extraction system was first started (subsurface temperatures were still ambient), TeCA levels in the vapor (~ 20 lbs/day) were much higher than TCE levels (~ 5 lbs/day), even though TCE (9,910 Pa) has a higher vapor pressure than TeCA (647 Pa) and is

Table 3. Subsurface Temperatures on 03/07/06 (°C)

Depth (ft bgs)	TMP-1	TMP-2	TMP-3	TMP-4	TMP-5
-5		28			15
-10		45			22
-15		58			30
-20		61			30
-25		71	28		31
-30	30	79	34		34
-35	47	98	42	43	40
-40	87	99	73	67	46
-45	96	99	99	80	96
-50	99	100	99	97	100
-55	99	100	10	95	101
-60	103	102	103	99	105
-65	105	95	105	104	98
-70	108		93	78	69
-75	66		62	37	34

Table 4. Subsurface Temperatures on 05/31/2006 (°C)

Depth (ft bgs)	TMP-1	TMP-2	TMP-3	TMP-4	TMP-5
-5		46			35
-10		6			41
-15		83			58
-20		98			87
-25		99	82		99
-30	88	99	99		99
-35	98	98	99	45	99
-40	99	100	98	105	100
-45	99	100	100	103	100
-50	100	101	100	102	100
-55	101	102	100	99	102
-60	102	103	103	99	104
-65	103	104	104	102	105
-70	106		103	96	104
-75	92		66	70	77

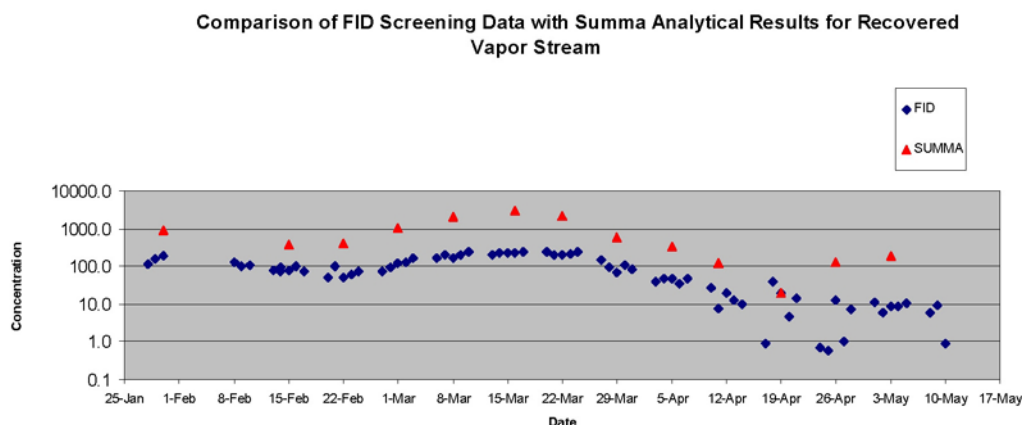


Figure 10. Total CVOC Concentrations in Recovered Vapor

therefore more volatile. This indicates that the initial mass of TeCA was greater than the initial mass of TCE in the vadose zone soil. This is borne out by the baseline (pre-treatment) soil sampling that showed much higher levels of TeCA than TCE in the soil (see Figures 13 through 16 that describe TeCA and TCE concentrations in soil samples).

However, TCE responded first to an increase in temperature and at 45 °C started to show increased concentrations in the vapor. This could be due to the higher volatility of TCE or the production of TCE from degradation of TeCA (Figure 17 shows the possible degradation pathways for TeCA). If TeCA is degrading to TCE, only one step in the degradation pathway appears to be activated, namely, the abiotic degradation (dehydrochlorination) of TeCA to TCE. There is no elevated level in the vapor of other byproducts, such as 1,2 DCE or TCA, which would have indicated that biologically intermediated reactions, such as hydrogenolysis or dichloroelimination, were stimulated (see Figures 11 and 12).

One interesting issue is what the soil sampling indicates about the treatment efficiency and about post-treatment residual mass of CVOCs. The pre-treatment soil sampling resulted in a total CVOC mass estimate of 850 lbs. The estimated CVOC mass recovered in the extracted vapor was 1,880 lbs or more than twice the estimated pre-treatment mass. Additional CVOC mass possibly was removed from the subsurface by in-situ degradation and this is not captured in the aboveground CVOC mass estimates in the vapor. This is typical of many ERH sites and of the uncertainties involved in estimating pre-treatment DNAPL mass. Given the higher-than-expected CVOC mass recovery, initial remediation objectives and expectations from the technology were clearly exceeded. However, the elevated levels of TeCA in the extracted vapor at the time of system shutdown leave open the possibility that there may still be some residual DNAPL in the subsurface. The pre- and post-treatment soil sampling indicate that both TeCA and TCE masses in the soil were considerably reduced due to the ERH treatment. However, the post-treatment CVOC mass is likely to be even more sporadically dispersed than the pre-treatment CVOC mass, leading to similar (or greater) uncertainties in the post-treatment CVOC mass estimate. Soil gas sampling (vadose zone) and groundwater monitoring (saturated zone) in the weeks and months following DNAPL source remediation generally would be a better indicator of residual CVOC mass in the treated aquifer.

At peak total CVOC concentrations in mid-March (see Figures 11 and 12 and Tables 5, 6, and 7), the extracted vapor contained maximum daily levels of TeCA (~ 46 lbs/day) and TCE (~ 46 lbs/day). This peak rate corresponds to the time when temperatures at several locations at the most contaminated depth interval (45 to 66 ft bgs) reached or exceeded 100 °C (although overall average temperature for the

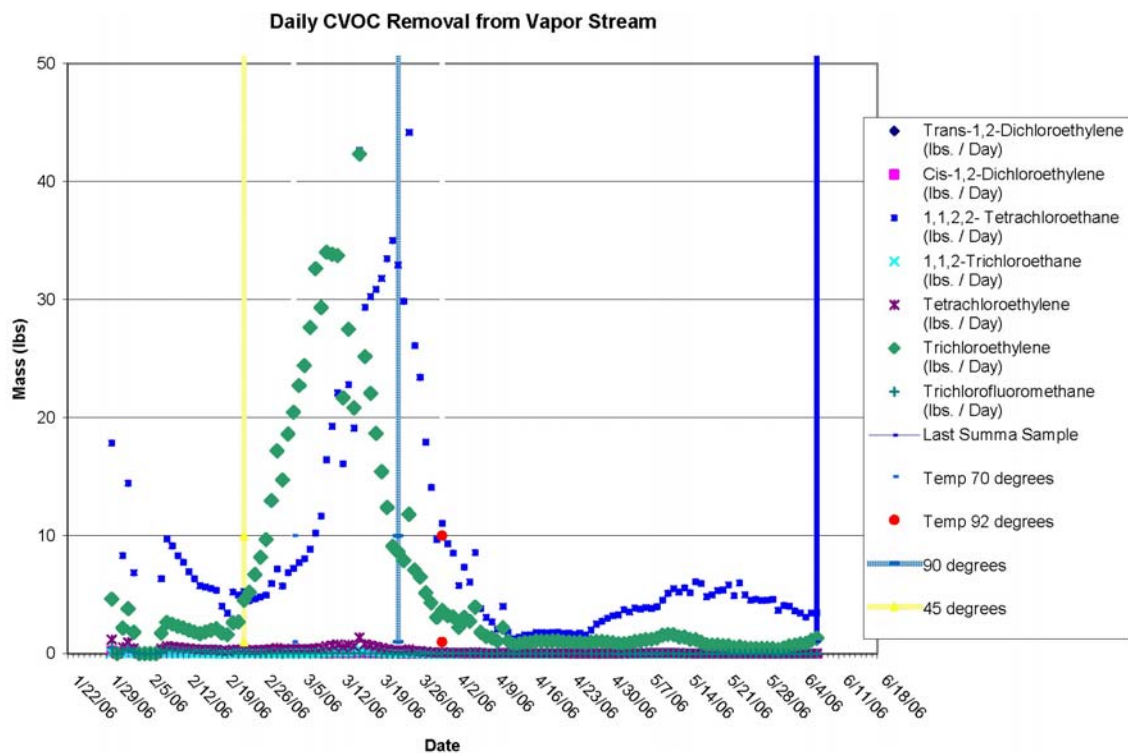


Figure 11. Concentration of CVOC Constituents in Recovered Vapor

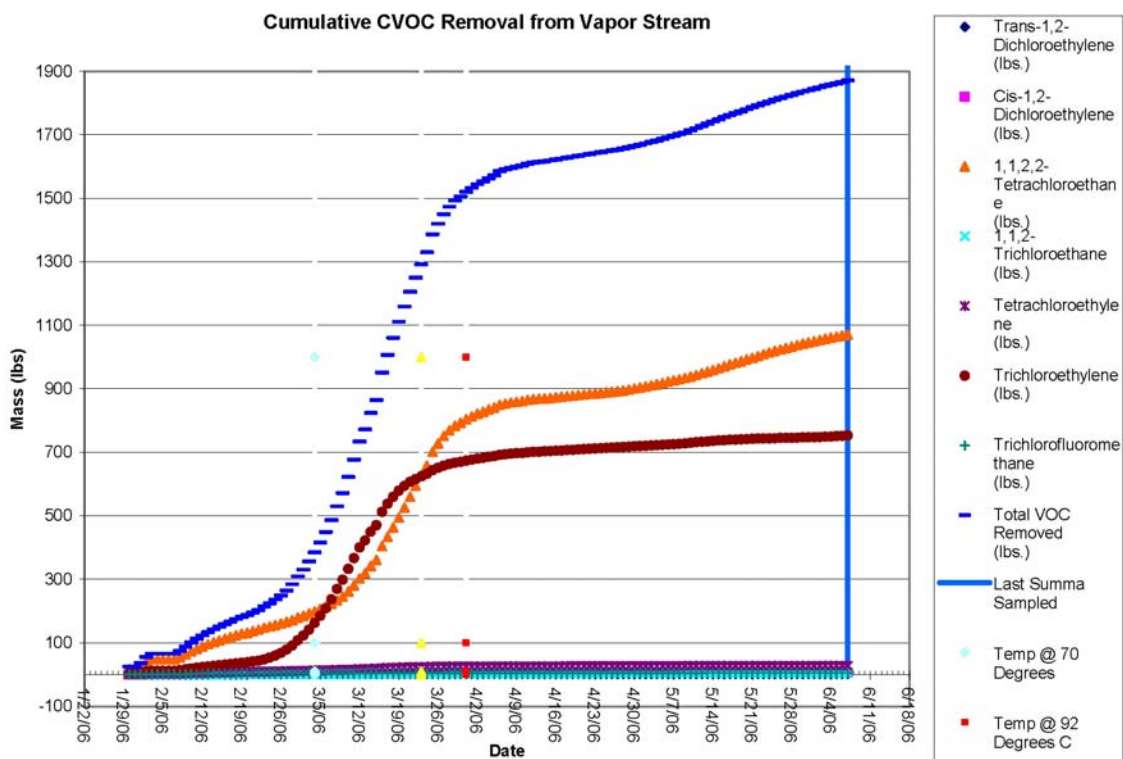


Figure 12. Cumulative CVOC Mass Recovered

Site 1 - SB40: TeCA in Pre- and Post-ERH Soils

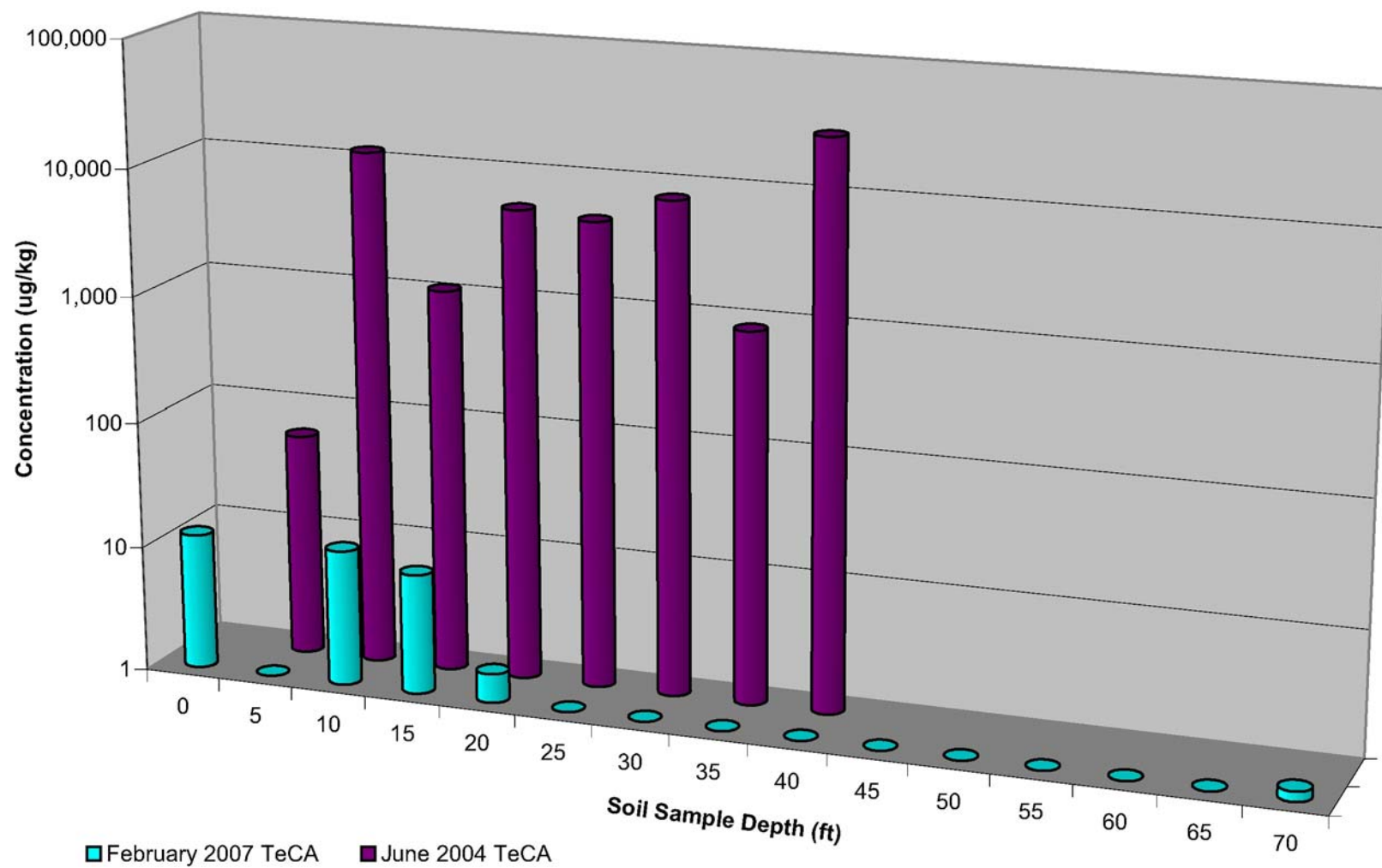


Figure 13. Site 1 – SB40: TeCA in Pre- and Post-ERH Soils

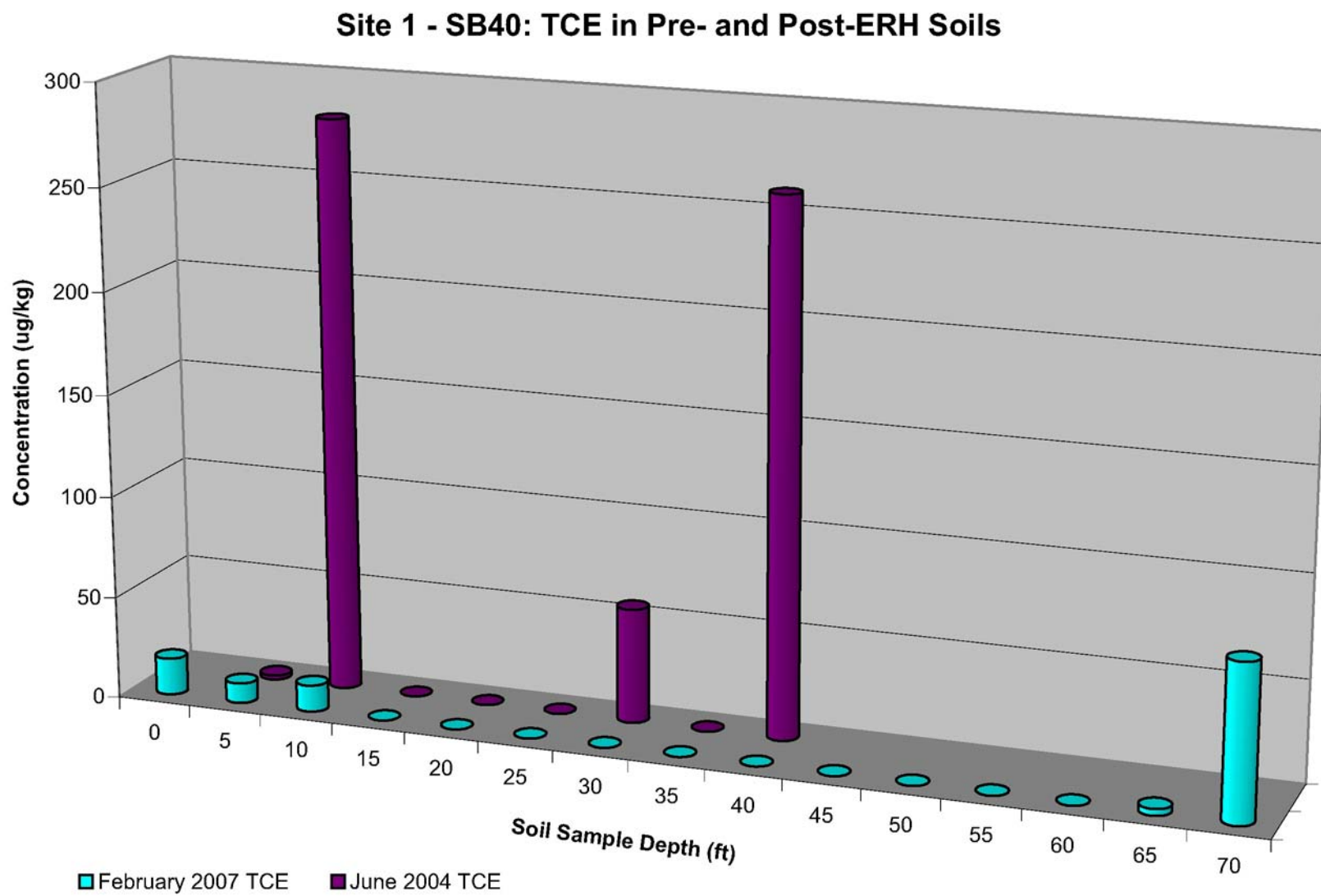


Figure 14. Site 1 – SB40: TCE in Pre- and Post-ERH Soils

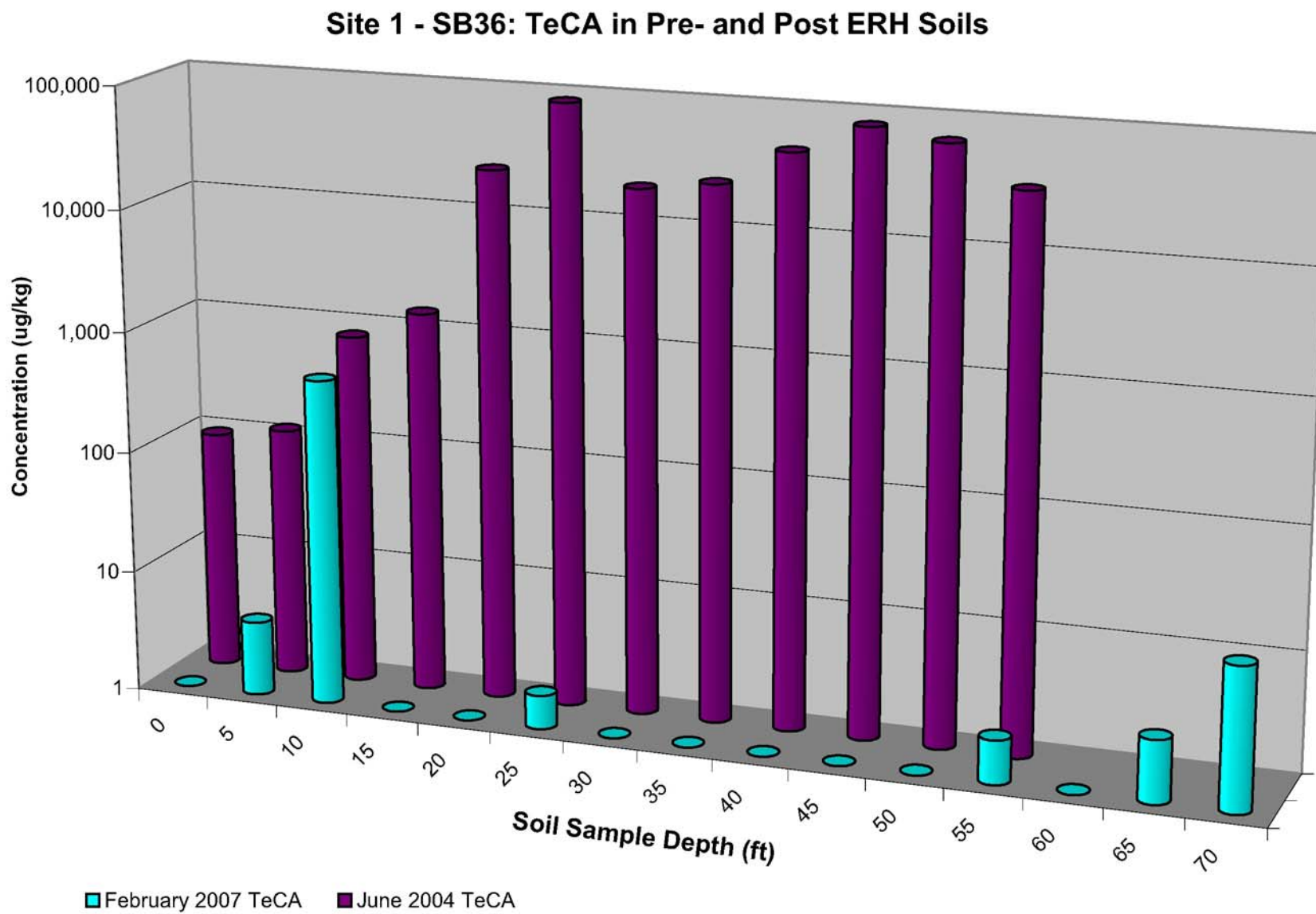


Figure 15. Site 1 – SB36: TeCA in Pre- and Post-ERH Soils

Site 1 - SB36: TCE in Pre- and Post ERH Soils

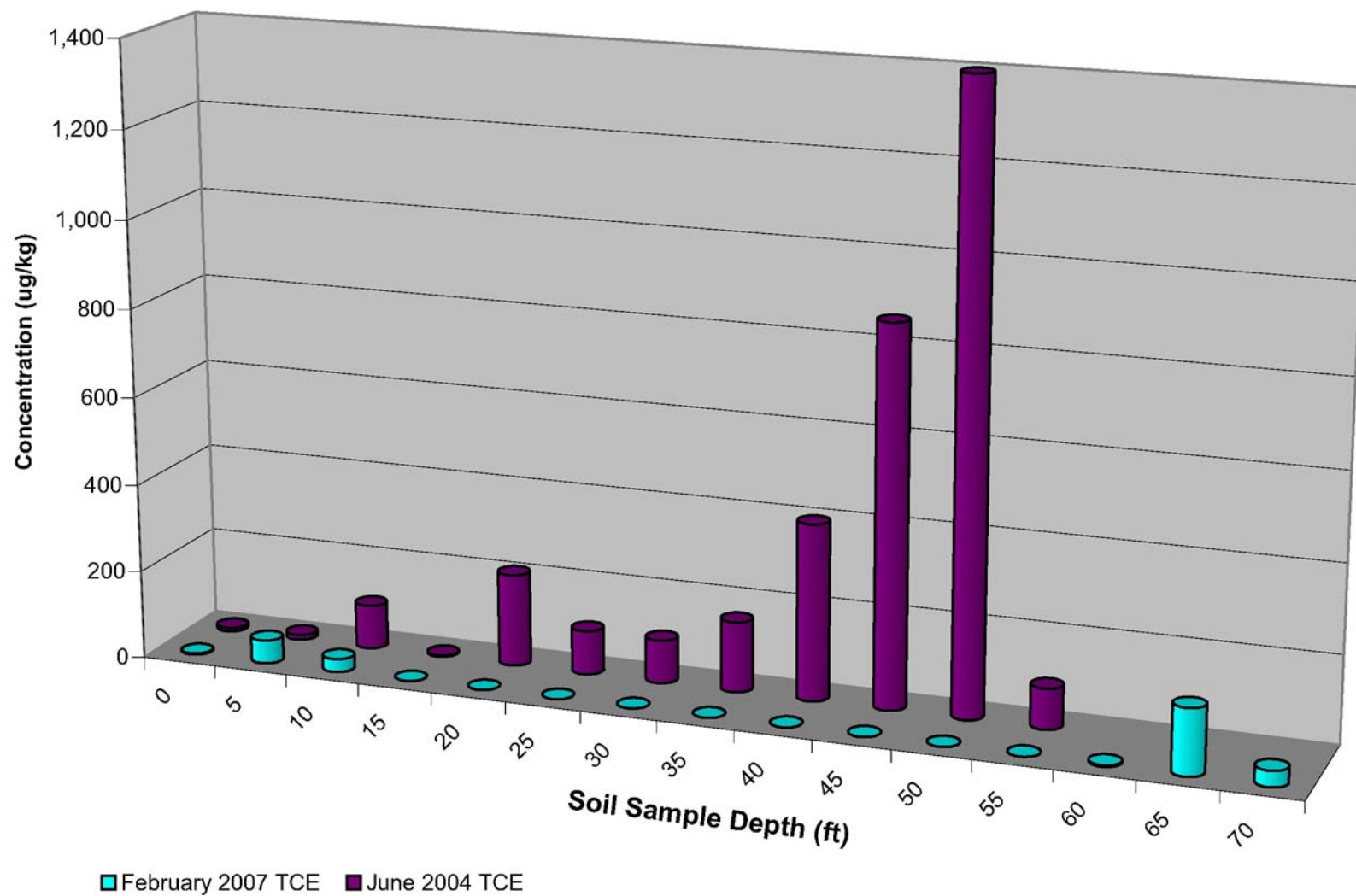


Figure 16. Site 1 – SB36: TCE in Pre- and Post-ERH Soils

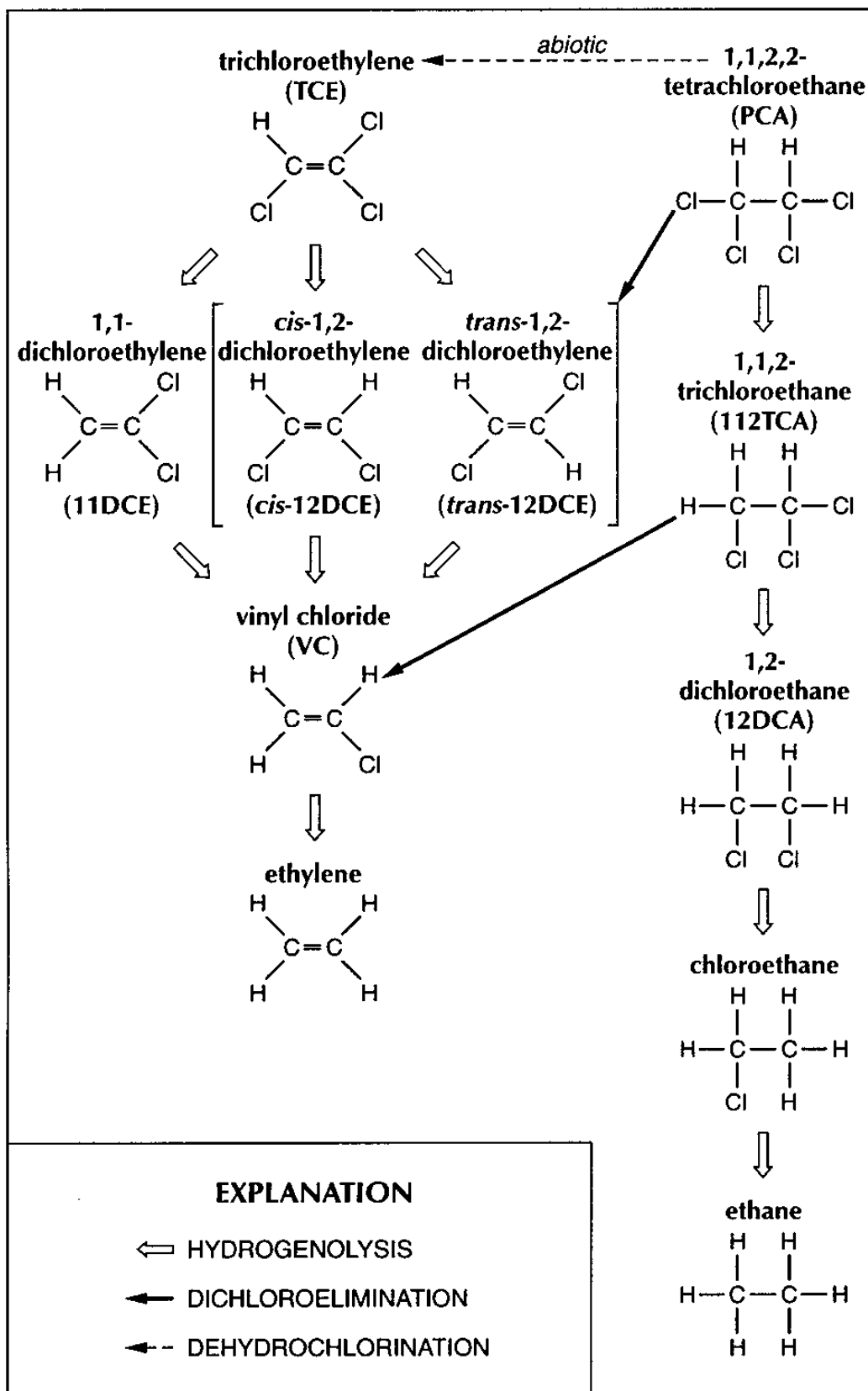


Figure 17. Degradation Pathway of TeCA (Source: Lorah and Olsen, 1999)

**Table 5. Vapor Stream Concentration
(Measured in ppb/v)**

Date	TeCa	TCE	Cis-1,2		PCE	Total VOCs	% TCE	Avg. Temp
			DCE	1,1,2,TCA				
1/31/06	99,100	32,900	2,610	493	6,710	141,813	23%	17
2/15/06	32,200	14,400	1,540	314	2,430	50,884	28%	26
2/22/06	34,400	23,900	903	263	2,320	61,786	39%	40
3/1/06	43,100	132,000	735	362	2,950	179,147	74%	61
3/8/08	69,800	285,000	835	545	3,120	359,300	79%	82
3/16/06	218,000	277,000	1,000	2,590	7,130	505,720	55%	88
3/22/06	246,000	81,700	545	649	2,080	330,974	25%	90
3/29/06	63,400	24,700	242	ND	653	88,995	28%	93
4/5/06	33,100	19,100	396	184	396	53,176	36%	95
4/11/06	10,600	8,120	209	91	216	19,236	42%	97
4/19/06	10,200	7,810	163	92	215	18,480	42%	98
4/26/06	11,400	8,250	133	66	150	19,999	41%	98
5/3/06	21,900	6,400	96	54	131	28,581	22%	98
5/10/06	25,600	11,400	212	104	409	37,725	30%	99
5/15/06	36,400	10,900	197	59	170	47,726	23%	99
5/24/06	38,800	4,860	98	38	109	43,905	11%	100
5/31/06	31,700	3,920	86	0	91	35,797	11%	100

Table 6. Vapor Stream Mass Removal Rate

Date	TeCA Removal lbs/day	TCE Removal lbs/day	cis-DCE Removal lbs/day	1,1,2,TCA Removal lbs/day	PCE Removal lbs/day	Total Removal lbs/day	Velocity (FPM)	Flow Rate (scfm)
1/31/06	14.3	3.7	0.2	0.1	1.0	19.3	3,680	235
2/15/06	4.6	1.6	0.1	0	0.3	6.8	3,681	235
2/22/06	6.6	.6	0.1	0	0.4	10.9	5,420	314
3/1/06	6.5	15.7	0.1	0	0.4	22.8	4,260	247
3/8/06	9.9	31.6	0.1	0.1	0.4	42.0	4,065	230
3/16/06	46.4	46.3	0.1	0.4	1.5	94.8	6,125	346
3/22/06	33.5	8.7	0.1	0.1	0.4	42.7	3,920	222
3/29/06	12.1	3.7	0.0	0.0	0.1	16.0	5,820	311
4/5/06	5.4	2.4	0.0	0.0	0.1	7.9	4,800	264
4/11/06	2.8	1.7	0.0	0.0	0.1	4.6	7,750	427
4/19/06	1.7	1.0	0.0	0.0	0.0	2.8	5,000	275
4/26/06	1.5	0.8	0.0	0.0	0.0	2.4	3,846	212
5/3/06	3.6	0.8	0.0	0.0	0.0	4.5	4,878	269
5/10/06	4.3	1.5	0.0	0.0	0.1	5.9	5,516	275
5/15/06	4.9	1.2	0.0	0.0	0.0	6.1	4,140	220
5/24/06	6.1	0.6	0.0	0.0	0.0	6.7	4,787	255
5/31/06	4.0	0.4	0.0	0.0	0.0	4.4	3,871	206

Table 7. Vapor Stream Cumulative Mass Removal Estimate

Sample Date	TeCA Mass Removed (lbs)	TCE Estimated Mass Removed (lbs)	Cis 1,2-DCE Estimated Mass Removed (lbs)	1,1,2-TCA Estimated Mass Removed (lbs)	PCE Estimated Mass Removed (lbs)	Total Estimated Mass Removal (lbs)
1/31/06	40.0	13.7	0.75	0.25	2.75	57.5
2/15/06	80.9	22.9	1.5	0.4	5.6	111.2
2/22/06	39.1	18.2	0.8	0.3	2.7	61.1
3/1/06	46.0	67.6	0.6	0.3	3.1	117.6
3/8/06	57.5	165.9	0.5	0.4	3.1	227.3
3/16/06	212.6	294.3	0.7	1.9	7.3	516.9
3/22/06	267.7	184.3	0.6	1.7	6.0	460.3
3/29/06	158.6	43.2	0.2	0.2	1.7	203.7
4/5/06	61.3	21.5	0.2	0.1	0.7	83.8
4/11/06	24.3	12.2	0.2	0.1	0.4	37.2
4/19/06	18.1	10.9	0.2	0.1	0.4	29.7
4/26/06	11.2	6.6	0.1	0.1	0.2	18.2
5/3/06	17.2	5.6	0.0	0.0	0.1	23.1
5/10/06	28.8	8.5	0.1	0.1	0.3	37.8
5/15/06	22.0	6.3	0.0	0.0	0.2	28.7
5/24/06	49.4	7.9	0.0	0.0	0.2	57.6
5/31/06	35.9	3.5	0.0	0.0	0.1	39.6
Total						2,111

treatment region was below 99°C). After this peak extraction rate, concentrations of both TeCA and TCE in the vapor declined sharply to levels below those at the start of heating. TeCA levels rebounded to a lesser degree in late April (probably as subsurface temperatures rose further) and remained elevated through the remaining duration of vapor extraction (see Tables 5, 6, and 7). TCE levels remained elevated at the time of system shutdown, but showed a declining trend.

TeCA has a boiling point of 147°C, which is well above that of the boiling point of water and well above the maximum temperature of 106°C recorded in the subsurface thermocouples. This would present a challenge for a thermal technology if volatilization or boiling were the only mechanism for contaminant removal, especially in the vadose zone where steam generation and steam stripping of CVOCs may be expected to have a limited effect (unlike in the saturated zone). However, with other mechanisms, such as abiotic degradation at elevated temperatures potentially coming into play, treatment of TeCA appears more viable. The interim removal action report (Shaw, 2006) mentions that chloride concentrations in the soil increased in the post-treatment soil samples, but the data were not available for review. Increased chloride levels, if significant, could imply that TeCA and/or other CVOCs are being dechlorinated. Also, if TeCA is degrading to TCE, the expected trend would be decreasing TeCA levels and increasing TCE levels; instead, TeCA levels in the recovered vapor continued to increase long after TCE levels started declining. This could indicate that TeCA was initially removed by degradation to TCE at moderate temperatures; then, as temperatures increased further, volatilization of TeCA was the predominant mechanism.

Treatment of any CVOc contamination below the water table was not an objective of the ERH treatment. Groundwater monitoring wells are present around, but most of them are not within the footprint of the target treatment zone (see Figure 6b for monitoring well locations). MW-02 is the only

well within the direct influence of the ERH treatment (although outside the ERH electrode array). Many of these wells have long (15-foot) screens; therefore, localized CVOC concentrations indicative of DNAPL are likely to be vertically averaged and more difficult to discern. The CVOC trends in some of these wells are described in Figures 18 through 25. Only the top 15 ft or so of the saturated zone (60 to 75 ft bgs; in the cemented sand and iron layers and underlying sand as shown in Figures 3 and 4) was targeted for ERH treatment. MW-16 is the closest downgradient well and is screened near the water table. This is also the well that showed the maximum impact of the neighboring ERH treatment in terms of a rise in water temperature (see Figure 26) from 15 to 50°C (with a time lag after the end of ERH treatment, as the heated water from the ERH zone moved downgradient). In June 2006, when the ERH system was shut down and the average subsurface temperature in the ERH zone was 99°C, the temperature in MW-16 was 35°C and TeCA levels (Figure 24) had dropped from 45,000 to ~5,000 µg/L. During the same time (January-June 2006), TCE levels increased substantially from ~3,000 µg/L to ~25,000 µg/L, indicating that TCE was produced from the abiotic degradation of TeCA. As in the aboveground recovered vapor phase, other degradation products (e.g., TCA, cis-DCE, and trans-DCE) indicative of biologically intermediated degradation did not show any noticeable elevation. In the months following the end of ERH treatment (June-November 2006), both TeCA and TCE levels dropped substantially, while water temperature rose to 51 °C. This may indicate continuing influx of treated water from the ERH treatment zone.

MW-16 has the clearest trend pointing to potential degradation of TeCA to TCE and eventual removal of both TeCA and TCE from the subsurface. Most of the other wells sampled were either too far upgradient (or cross gradient) from the ERH zone for there to be a substantial impact or exhibited trends that were not as easily explained. For example, both TeCA and TCE levels in MW-02 (the upgradient well in the ERH zone) increased more than fivefold and tenfold, respectively, from January to June 2006. During this time, the temperature in the well increased from 15 to 37°C (Figure 26). It appears that in both MW-02 and MW-16, the rise in temperature from 15 to about 35 or 37°C was due to the neighboring ERH application. Once the ERH application ended, temperature in upgradient well MW-02 started decreasing, but temperature in downgradient well MW-16 kept increasing as more of the heated water from the ERH zone moved downgradient. The sharp increase in TCE level in MW-02 can be attributed to TeCA degradation, but the sharp increase in TeCA level may indicate redistribution of TeCA outside the ERH zone. The subsequent drop in both TeCA and TCE may indicate that the redistribution probably involved dissolved phase CVOCs, not DNAPL. MW-02 is the only well where there was some indication of cis-1,2 DCE levels increasing during the timeframe of the ERH application.

The trends in some of the other surrounding wells (MW-03, MW-09, MW-10, MW-14, and MW-15) are more difficult to explain. Many of these wells are probably too far to be impacted by the ERH treatment. However, many of these wells experience substantial shifts in TeCA and TCE concentrations.

Section 7.0: COST

The actual cost of the entire remediation was reported as \$1.8M (Melton, 2008).

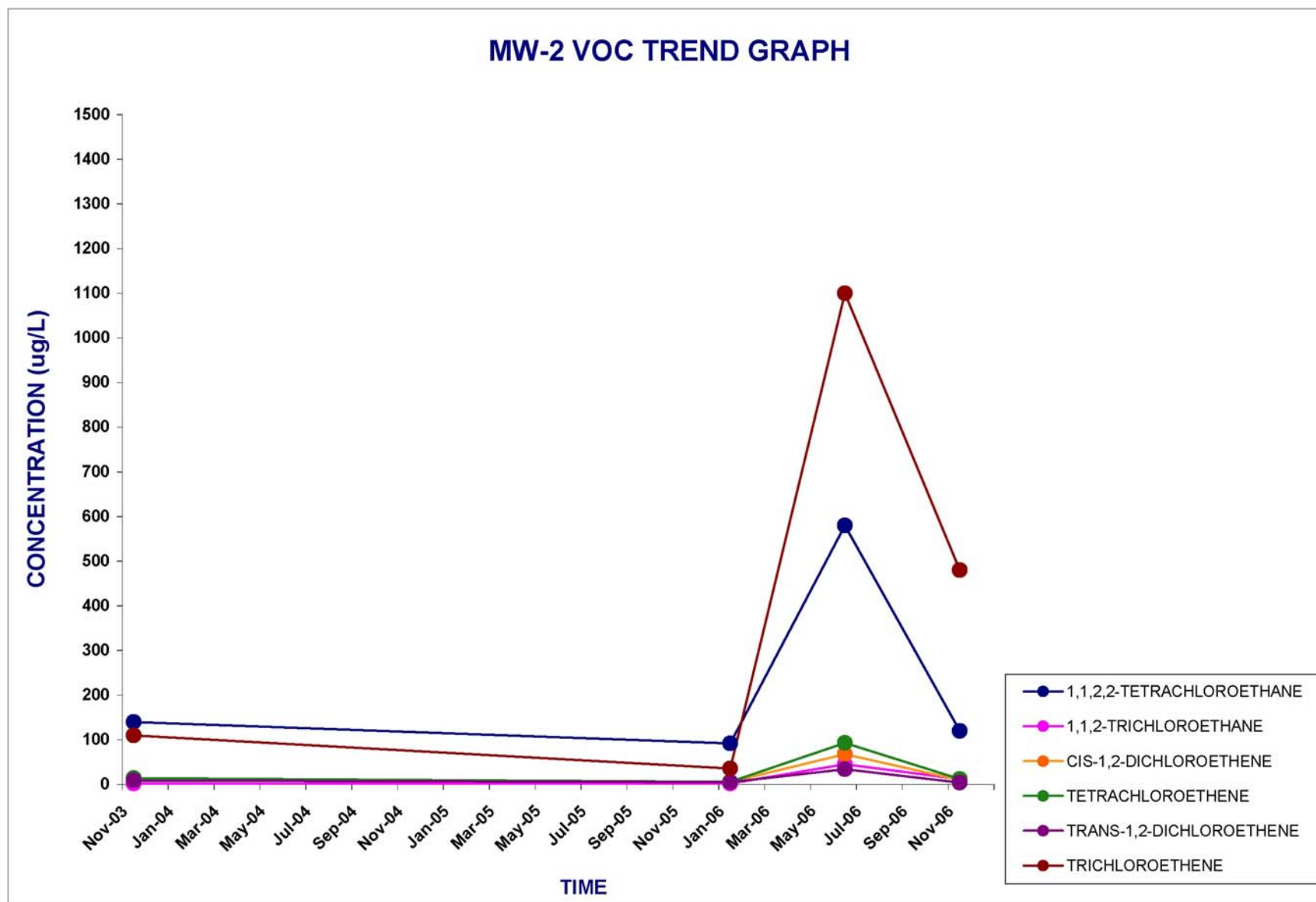


Figure 18. MW-02 VOC Trend Graph

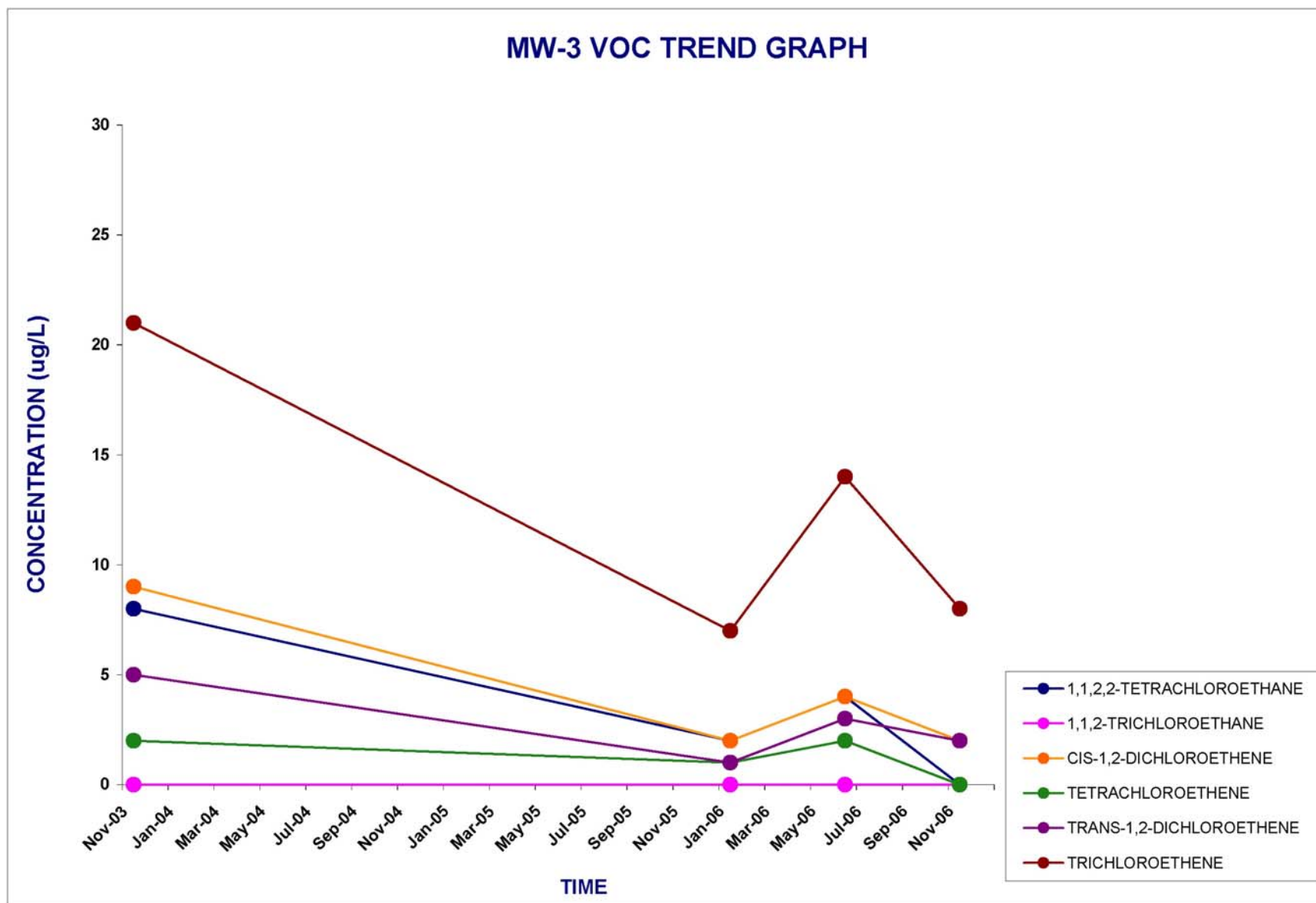


Figure 19. MW-03 VOC Trend Graph

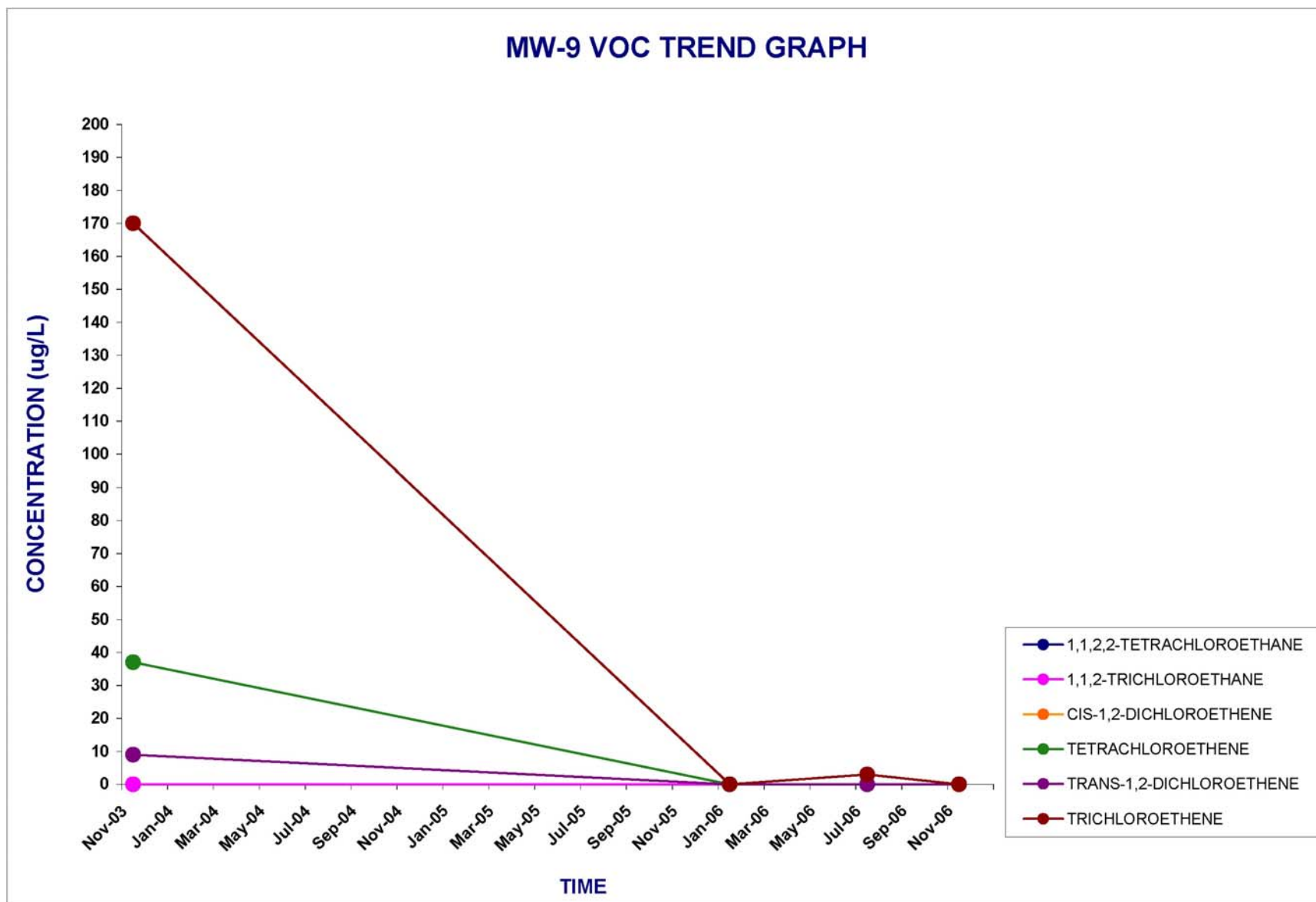


Figure 20. MW-9 VOC Trend Graph

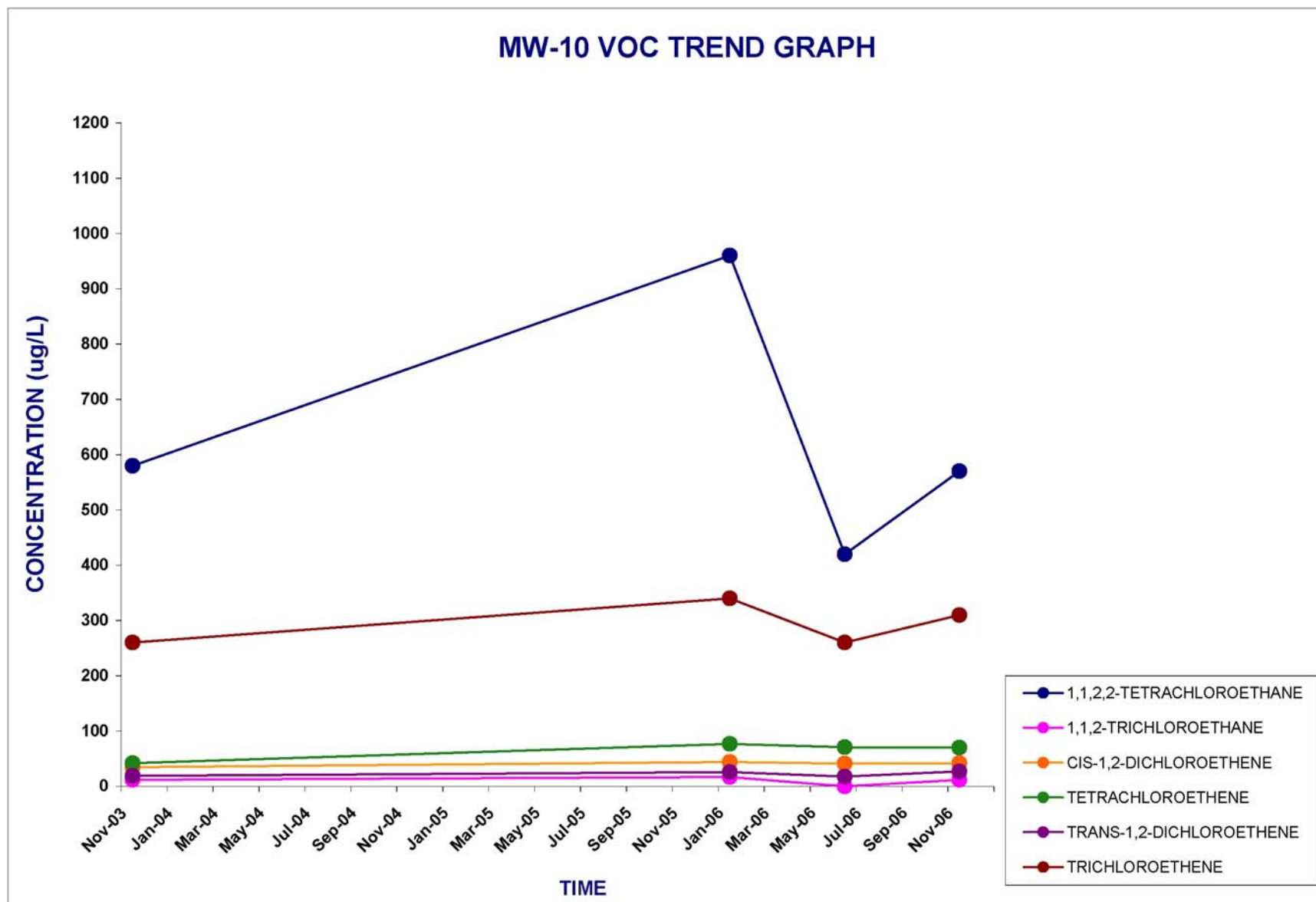


Figure 21. MW-10 VOC Trend Graph

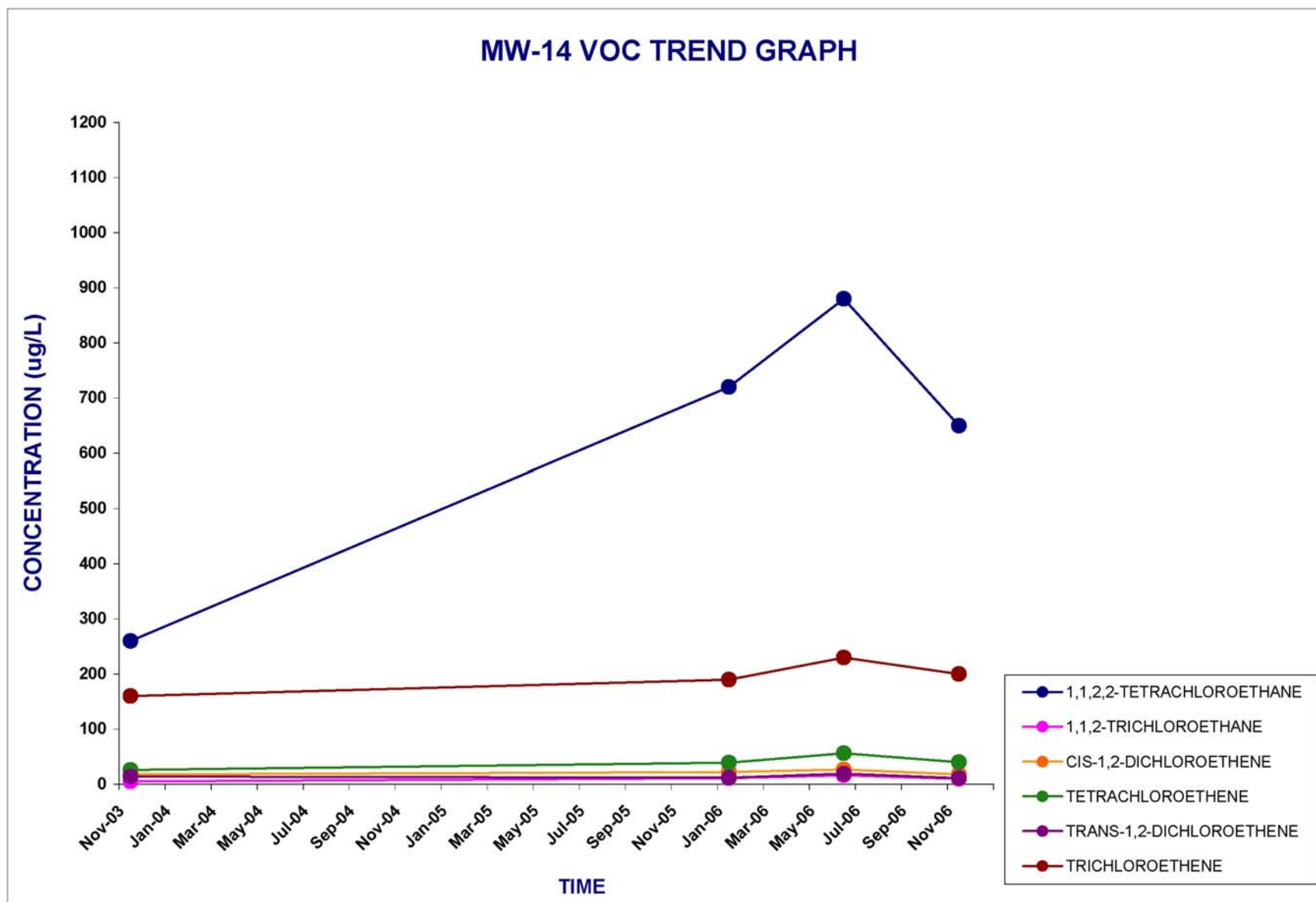


Figure 22. MW-14 VOC Trend Graph

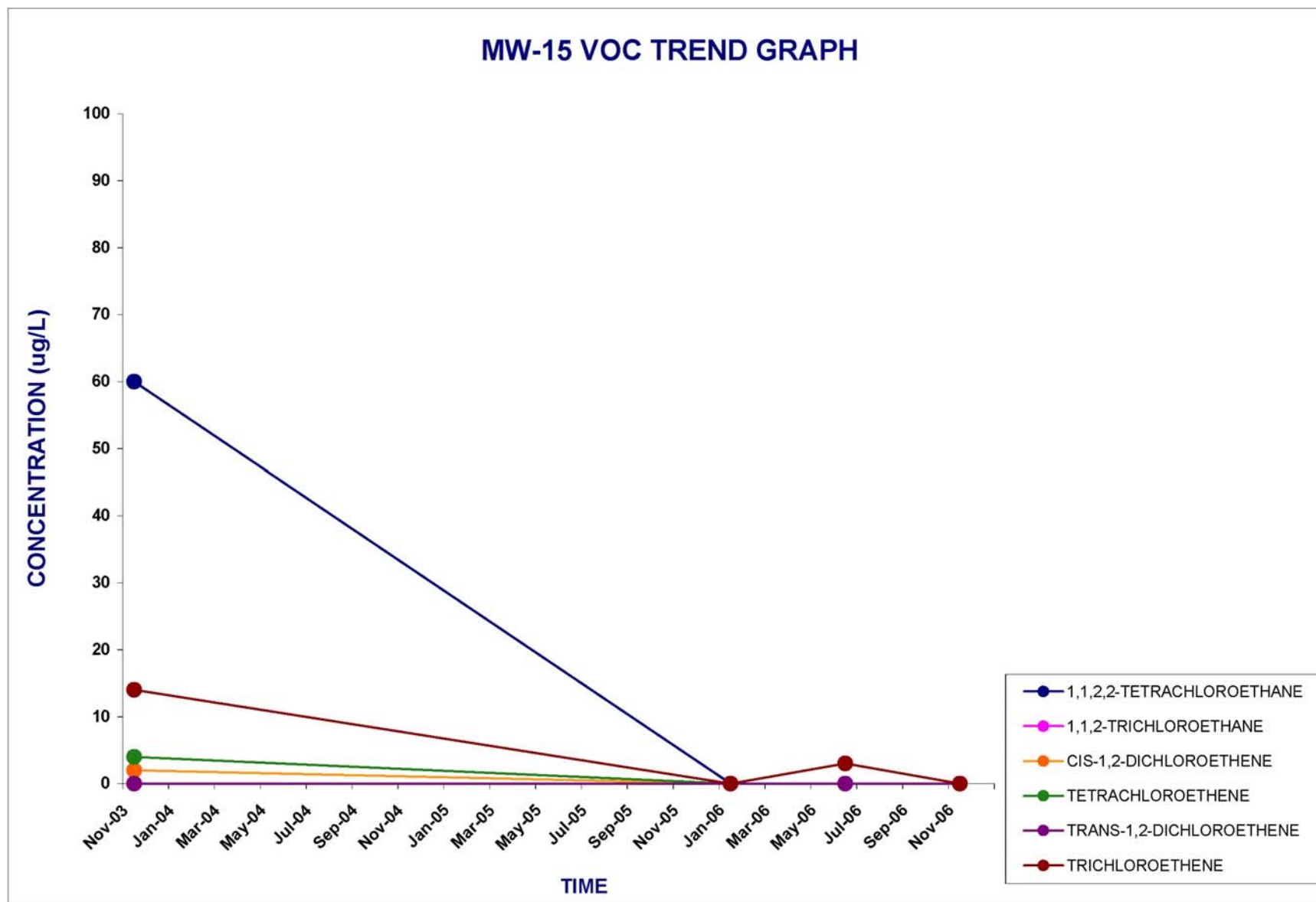


Figure 23. MW-15 VOC Trend Graph

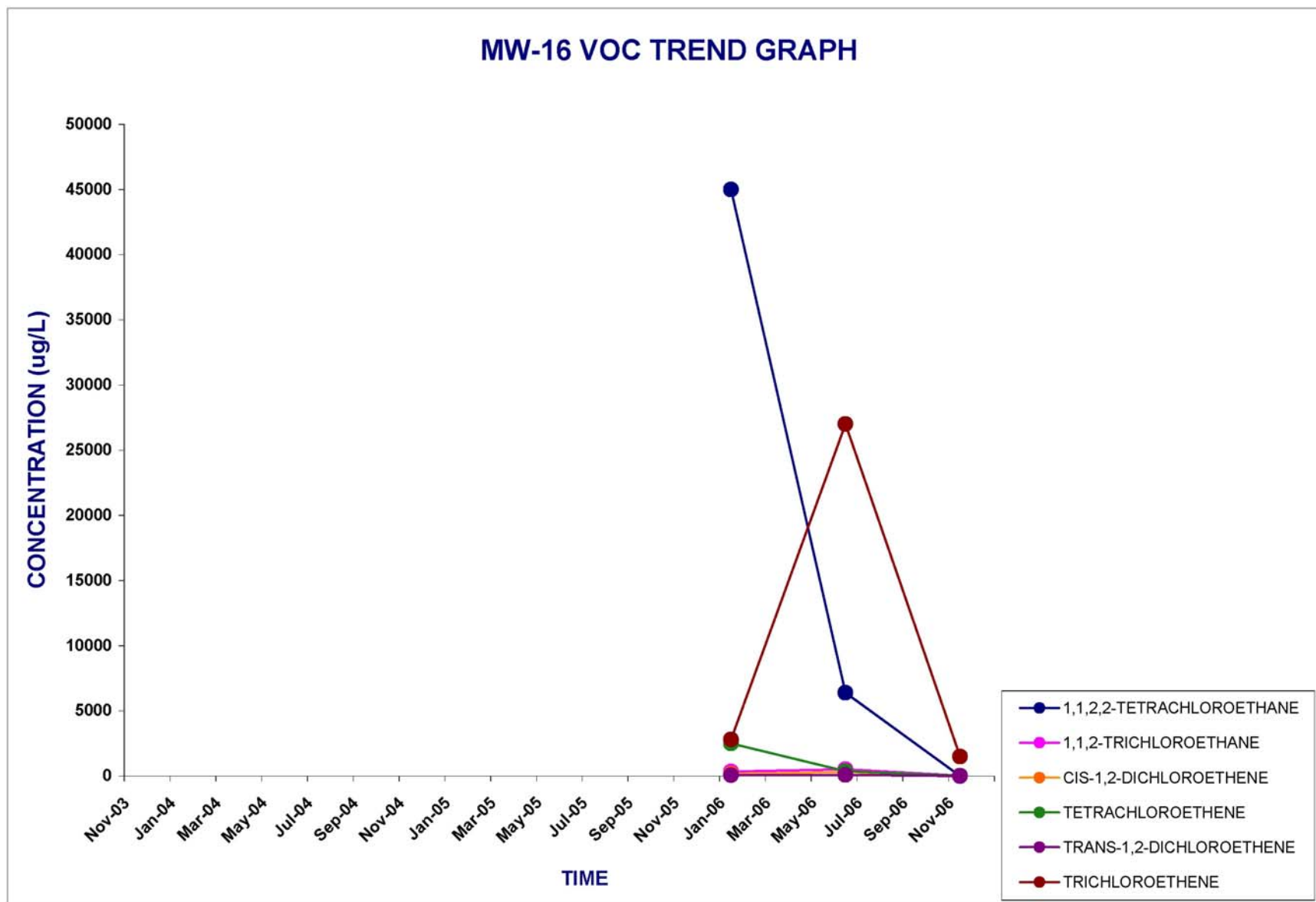


Figure 24. MW-16 VOC Trend Graph

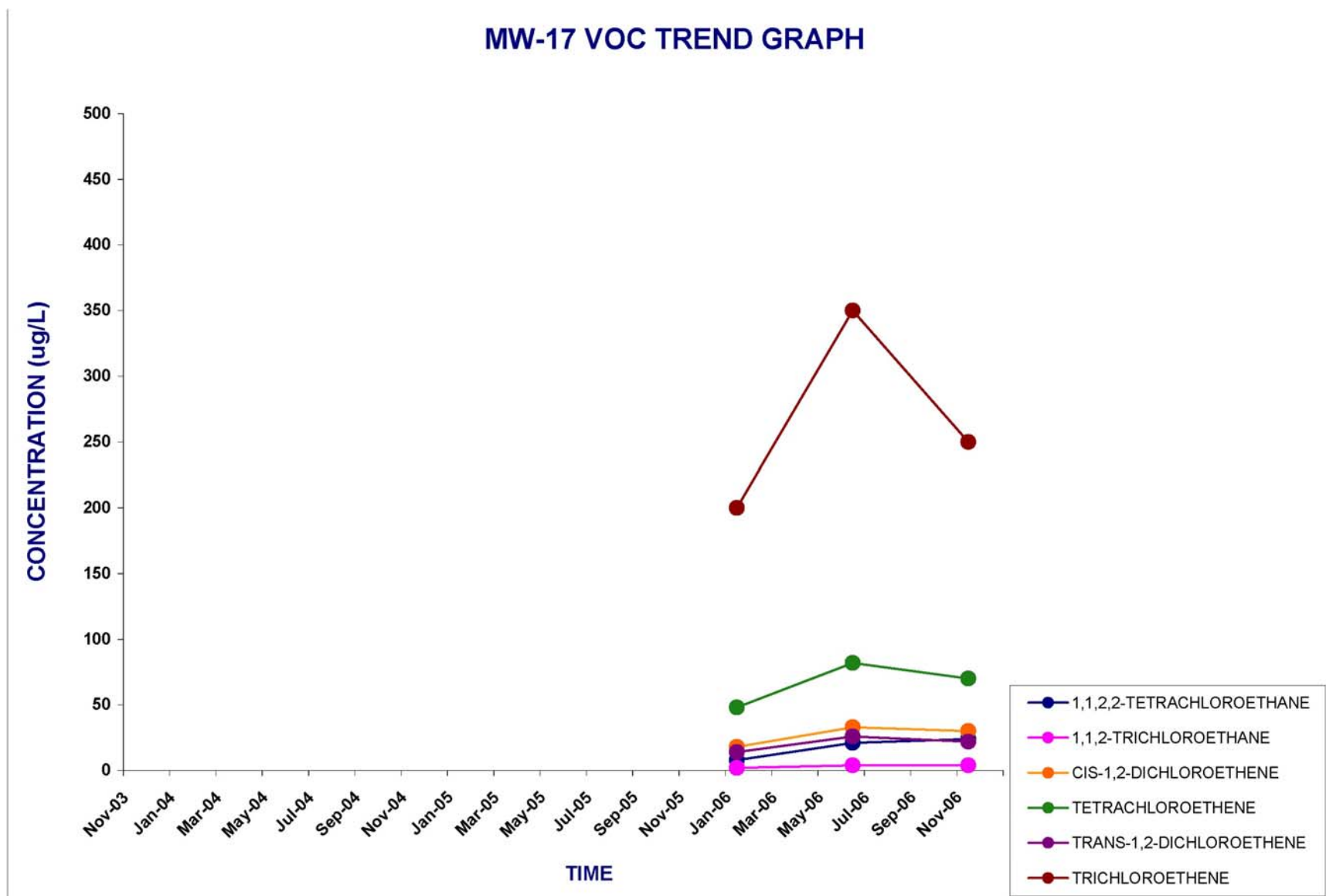


Figure 25. MW-17 VOC Trend Graph

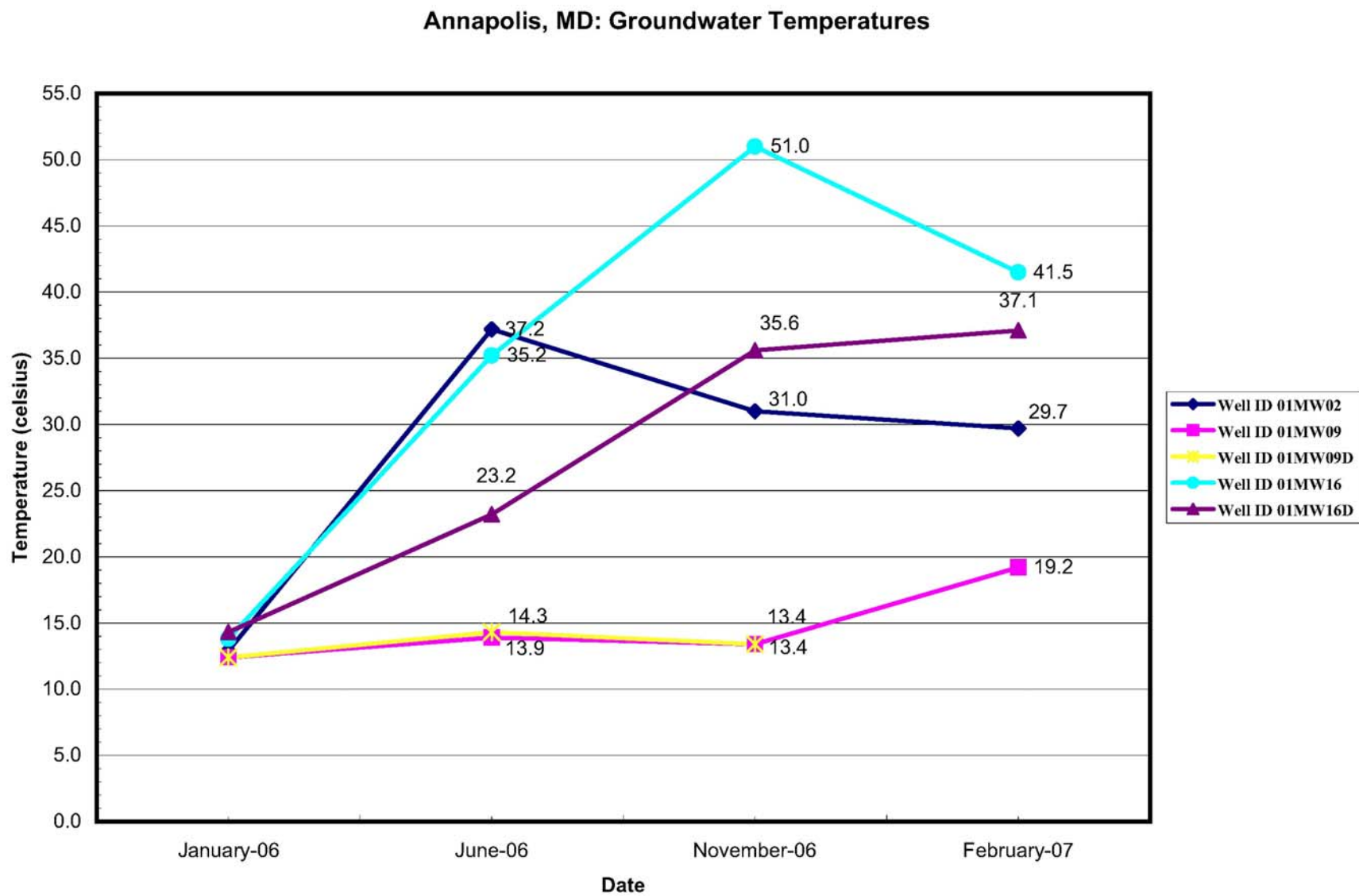


Figure 26. Groundwater Temperatures for Annapolis, MD

Section 8.0: DISCUSSION

The Site 1 interim removal action at Annapolis is an excellent example of the well-calibrated use of ERH for treatment of a DNAPL source under difficult site conditions. The primary contaminant, TeCA, is relatively less volatile compared to other chlorinated solvents, and has a nominal boiling point of 147°C, well above that of the boiling point of water. Adding to the difficulty was the fact that much of the contamination appeared to be trapped in the vadose zone and in cemented sand and iron layers straddling the water table. Despite these challenges, an estimated 1,880 lbs of total CVOC mass was recovered in the aboveground vapor. There is some indication in the vapor phase (aboveground) and in the surrounding aqueous phase (perimeter monitoring wells) that additional TeCA mass was removed from the subsurface through conversion to TCE by abiotic degradation reactions that were probably stimulated at the elevated temperatures. A possible scenario is that TeCA was removed from the soil initially by degradation to TCE at moderately higher temperatures and subsequently by volatilization at higher temperatures.

As with most DNAPL sites, there are some uncertainties that probably are a consequence of the limitations inherent in performance monitoring at DNAPL source sites. To summarize:

- One uncertainty relates to the type of degradation reactions that were stimulated at elevated temperatures and what the ultimate fate of the TCE, presumably produced by TeCA degradation, was. At moderately elevated temperatures, TeCA levels in both aboveground vapor and surrounding aqueous phases declined and TCE levels rose. This would indicate that TCE is either being produced due to TeCA degradation or simply that the more volatile TCE is responding first to elevated temperatures. However, at higher temperatures, alternative periods of both declining and increasing TeCA concentrations in the vapor phase did not show concomitant increases in TCE levels. Also, there was no noticeable elevation of other TeCA degradation products, such as TCA, cis-DCE, and trans-DCE, or of TCE degradation products, such as cis-DCE and vinyl chloride. These byproducts of biologically-driven reductive dechlorination reactions are generally evident during elevated temperatures at other ERH sites.
- Another uncertainty relates to how much residual DNAPL mass still remains in the treatment zone following ERH treatment. The limited soil sampling indicates that relatively little DNAPL is left in the soil after ERH treatment. However, when ERH was stopped, TeCA and total CVOC levels were still elevated and cumulative CVOC mass recovery was increasing.
- A third uncertainty relates to the subsurface zone targeted for DNAPL treatment. Some of the pre-treatment soil borings (e.g., SB-39) exhibited considerable CVOC mass at the fringe of the target treatment zone. Pre-treatment TeCA concentrations in monitoring well MW-16 were relatively high and indicative of DNAPL on the downgradient side; although these concentrations decline substantially due to influx of treated water from the upgradient ERH zone, they could rebound in subsequent months. As with many sites, there possibly could be additional DNAPL in the region surrounding and below the target treatment zone.

If budgets permit, some soil gas sampling within and around the treatment zone and installation of monitoring wells screened at shorter intervals within and below the treatment zone may help address some of these uncertainties. A microbial evaluation with polymerase chain reaction (PCR) analysis for presence of microbial communities involved in CVOC dehalogenation would also be desirable. Overall, the ERH application was well executed and has contributed towards considerable improvement of the soil and groundwater quality at this site.

Section 9.0: REFERENCES

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