PeroxyChem

ISCR BENCH STUDY FOR THE TREATMENT OF CVOCS IN GROUNDWATER AND SOIL

FROM THE SITE

FINAL REPORT

Prepared for:

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***Submitted by*:**
PeroxyChem
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EXECUTIVE SUMMARY

A bench study was completed at the PeroxyChem laboratory in Tonawanda, NY, USA, for the treatment of soil and groundwater impacted with chlorinated volatile organic compounds (CVOCs), including 1,1-Dichloroethane (1,1-DCA) and Chloroethane (CA), collected from the site. The purpose of the study was to evaluate PeroxyChem's EHC® and EHC® Plus for the treatment of chlorinated volatile organic carbons (CVOCs) in the impacted soil and groundwater from the site.

For the bench test, one control, two dosages each of EHC and EHC Plus were evaluated with the site samples in a column study. The effectiveness of the treatment was assessed using data collected in three sampling events over 83 days.

Below are summaries of the % removal of CVOCs relative to the Site groundwater for each treatment condition.

Treatment	Day	% GW COC Removal
0.5% EHC	27	43.0%
	55	27.7%
	83	5.6%
1.5% EHC	27	45.7%
	55	34.0%
	83	22.2%
0.5% EHC Plus	27	53.4%
	55	28.0%
	83	5.6%
1.0% EHC Plus	27	73.2%
	55	32.3%
	83	5.0%

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1 INTRODUCTION

1.1 Project Background

PeroxyChem Environmental Solutions conducted a bench-scale study to evaluate EHC and EHC Plus for the treatment of groundwater and soil impacted with chlorinated volatile organic compounds (CVOCs). Impacted groundwater and soil samples were collected from the site by AECOM. This report was prepared for AECOM and presents the results and data interpretation of the EHC and EHC Plus bench-scale study completed between July 2019 and December 2019.

1.2 EHC Technology Background

EHC in situ chemical reduction (ISCR) reagent is the original patented combination of controlled-release organic carbon and zero valent iron (ZVI) used for the treatment of groundwater and saturated soil impacted by persistent halogenated compounds, including chlorinated solvents, pesticides and organic explosives. The EHC formula is the culmination of years of research and successful field use. EHC is comprised of a synergistic mixture of micro-scale ZVI and a solid organic carbon source, stimulating both abiotic and biotic dechlorination mechanisms.

EHC can address a wide range of contaminant concentrations and has successfully been applied to treat large dilute plume areas, groundwater hotspots, and high concentration source areas.

1.3 EHC Plus Technology Background

EHC® Plus is a combination of EHC Reagent plus powdered activated carbon (PAC). This combined remedy approach can be used for the treatment of groundwater and saturated soil impacted by persistent halogenated compounds, including chlorinated solvents, pesticides and organic explosives.

EHC Plus offers synergistic mechanisms through abiotic and biotic de-chlorination of CVOCs. In addition, PAC within EHC Plus promotes adsorption /sequestration pathways to promote polishing of CVOCs to very low remedial goals (RGs), that are often challenging at contaminated sites.

2 PROJECT OBJECTIVES

The aim of this bench-scale study was to assess EHC and EHC Plus for the treatment of CVOCs. Specific objectives included:

- determination of the efficiency of EHC and EHC Plus at treating contaminants
- compare doses of EHC and EHC Plus to degrade contaminants concentrations, and;
- provision of a comprehensive final report.

3 BASELINE SAMPLING

3.1 Sample Receipt and Sampling

On July 23, 2019, four coolers were received. The samples consisted of 20 x 1L HDPE bottles of contaminated site groundwater (ID# MHC-23) and 20 x 1L HDPE bottles of contaminated site groundwater (ID# BIW-5D). A 5 gallon pail of contaminated soil (ID# SB-2 / SB-3) was also received. All samples were received on ice and placed into cold room storage upon receipt.

The composite groundwater was prepared by pumping an equal amount of each groundwater (ID# MHC-23 and BIW-5D) from the bottles into a Tedlar bag. After sampling, the composite groundwater was placed into cold room storage.

The site soil was moist, sticky gray hard clay / sand with free standing water on top. No odor was detected. The soil was quickly transferred to an anaerobic bag with the headspace removed and homogenized well.

The homogenized soil was sampled in duplicate for VOCs (Method 8260) and pH. The Site composite groundwater was sampled for VOCs (Method 8260), sulfate, alkalinity, nitrate, TOC, ferrous iron, pH and oxidation reduction potential (ORP). All samples were submitted to TestAmerica on ice via courier and under standard chain of custody. The pH and ORP were measured in-house.

3.2 Results

The summaries of results from the baseline sampling are shown below in **Tables 1 and 2**.

Table 1: VOC concentrations, geochemical parameters, pH and ORP in the composite groundwater

Analysis	Parameter	50:50 Blend Composite Groundwater	Units
VOCs	1,1,1-Trichloroethane	810	µg/L
	1,1-Dichloroethane	7,200	µg/L
	1,1-Dichloroethene	190	µg/L
	1,2-Dichloroethane	490	µg/L
	Acetone	310 J	µg/L
	Chloroethane	15,000	µg/L
	Methyl tert-butyl ether	24 J	µg/L
	Methylene Chloride	100 J	µg/L
	Vinyl chloride	58	µg/L
	Total VOCs =	**24,182**	**µg/L**
General Chemistry	Sulfate	1.9	mg/L
	Nitrogen, Nitrate Nitrite	ND (0.10)	mg/L
	Nitrogen, Nitrate	ND (0.10)	mg/L
	Nitrogen, Nitrite	ND (0.02) H	mg/L
	TOC Dup	58	mg/L
	Alkalinity	480	mg/L
	Ferrous Iron	14 HF	mg/L
Lab Parameters	pH	6.62	SI Units
	ORP	-59.9	mV

J Result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value.
HF = Field parameter with a holding time of 15 minutes. Test performed by laboratory at client's request.
H = Sample was prepped or analyzed beyond the specified holding time

Table 2: VOC concentrations and pH in the homogenized soil

Analysis	Parameter	Homogenized Soil	Homogenized Soil - Dup	Units
VOCs	1,1,1-Trichloroethane	ND (75)	ND (79)	µg/Kg
	1,1-Dichloroethane	ND (75)	ND (79)	µg/Kg
	1,1-Dichloroethene	ND (75)	ND (79)	µg/Kg
	1,2-Dichloroethane	ND (75)	ND (79)	µg/Kg
	Acetone	ND (750)	ND (790)	µg/Kg
	Chloroethane	ND (75)	ND (79)	µg/Kg
	Methyl tert-butyl ether	ND (75)	ND (79)	µg/Kg
	Methylene Chloride	ND (380)	ND (400)	µg/Kg
	Vinyl chloride	ND (75)	ND (79)	µg/Kg
	Total VOCs =	**0.00**	**0.00**	**µg/Kg**
Lab Parameters	Percent Solids	79.7	77.2	%
	pH (Slurry method)	8.92		SI Units

4 ISCR COLUMN TREATABILITY STUDY

4.1 Set Up - Method

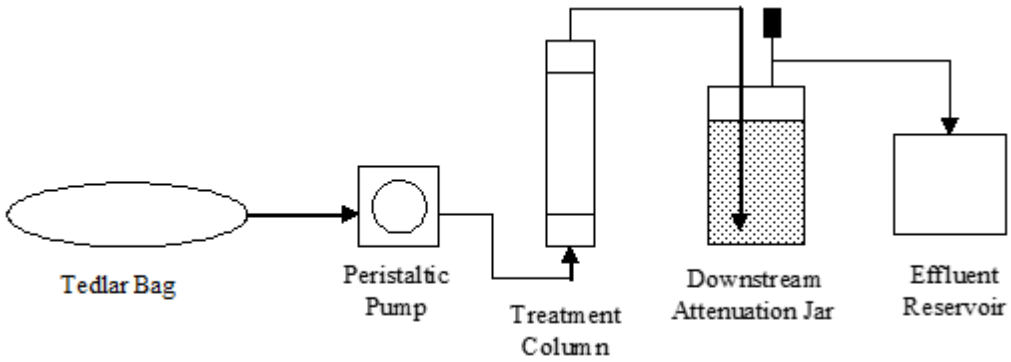
On August 29, 2019, a column study was set up as outlined below (**Table 3**). For the study, one control, two dosages of EHC and two of EHC Plus were evaluated. An unamended downstream soil jar followed each column. The column systems with up-flow treatment were set up as shown in **Figure 1** below.

In agreement with AECOM, due to the nature of the site soil, the soil was blended 50:50 with clean fine silica sand in a kitchen mixer prior to placement in the columns and downstream soil jars (**Pictures 1 & 2**).
The columns were hooked up to the site groundwater feed and water was pumped into each column at ~200mL/day until each system was saturated (day 0). Feed bags were kept in the cold room at ~4C until the previous feed bag for the column system was nearly empty. **Picture 3** shows the setup on day 0. For the remainder of the study, an ~50 mL/day flow rate was maintained to obtain a longer residence time. The systems were sampled according to **Table 4** below.

Table 3: Summary of Column Study

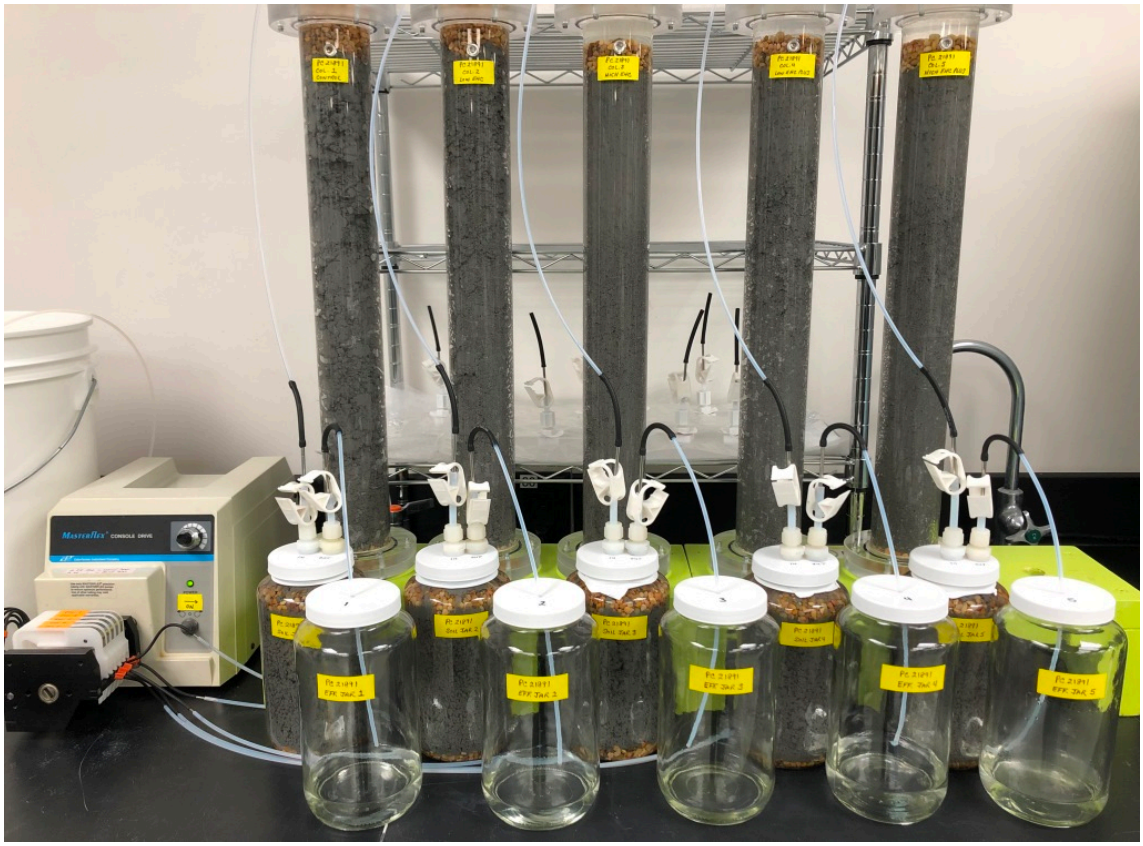
Column #	Description	Column Details		Soil Jar Unamended
1	Control	50: 50 blend site soil / fine silica sand	---	50: 50 blend site soil / fine silica sand
2	0.5% EHC		blended with 0.5% EHC	
3	1.5% EHC		blended with 1.5% EHC	
4	0.5% EHC Plus		blended with 0.5% EHC Plus	
5	1.0% EHC Plus		blended with 1.0% EHC Plus	

Figure 1: Schematic of treatment column apparatus.



Picture 1: Before site soil / sand blending

Picture 2: After site soil / sand blending



Picture 3: Systems saturated, Day 0

Table 4: Sampling schedule

Sample Location	Day	Actual Date	Field Parameters	Analysis
Feed Soil Jars 1 -> 5 effluents	10	9/9/2019	ORP & pH	
Feed Soil Jars 1 -> 5 effluents	18	9/17/2019	ORP & pH	
Feed Soil Jars 1 -> 5 effluents	27	9/26/2019	ORP & pH	VOCs
Feed Soil Jars 1 -> 5 effluents	55	10/24/2019	ORP & pH	VOCs / TOC / Ferrous Iron
Feed Soil Jars 1 -> 5 effluents	83	11/21/2019	ORP & pH	VOCs

4.2 Results

Below in **Figures 2-4** are the total COC and pH/ORP data from the feed and system effluents. Full analytical results and readings are provided in **Tables 6-10** in the Appendix.

Figure 2: COCs in Groundwater

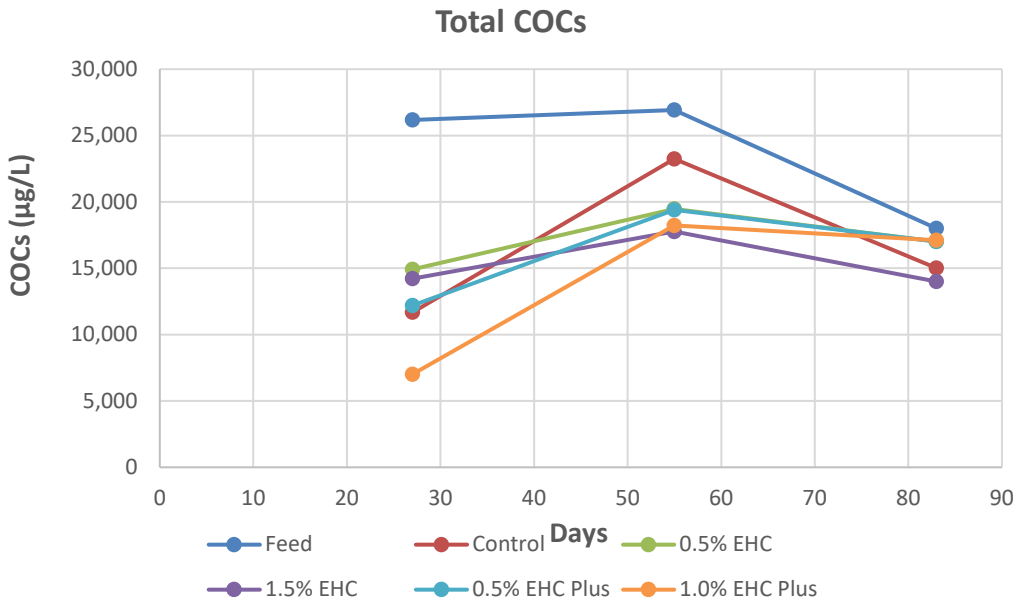
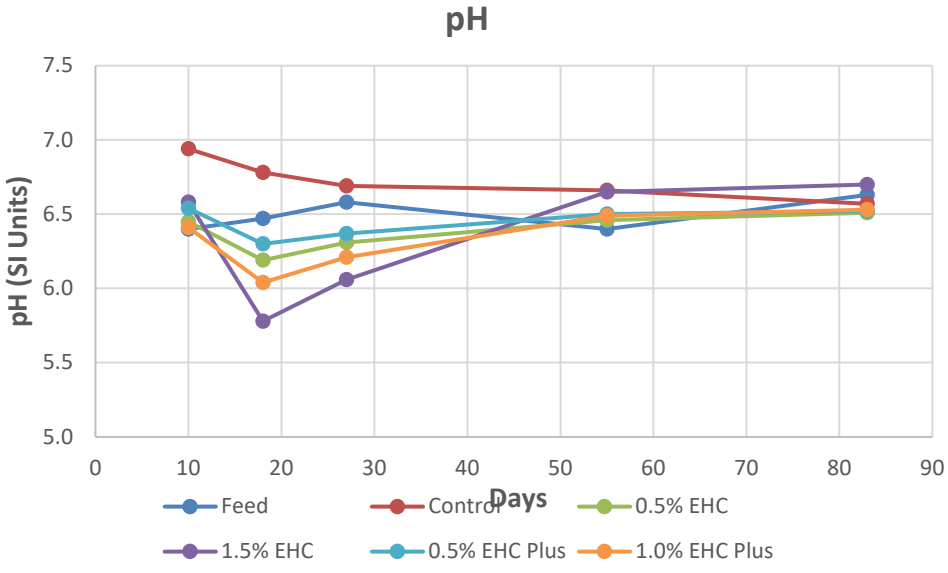
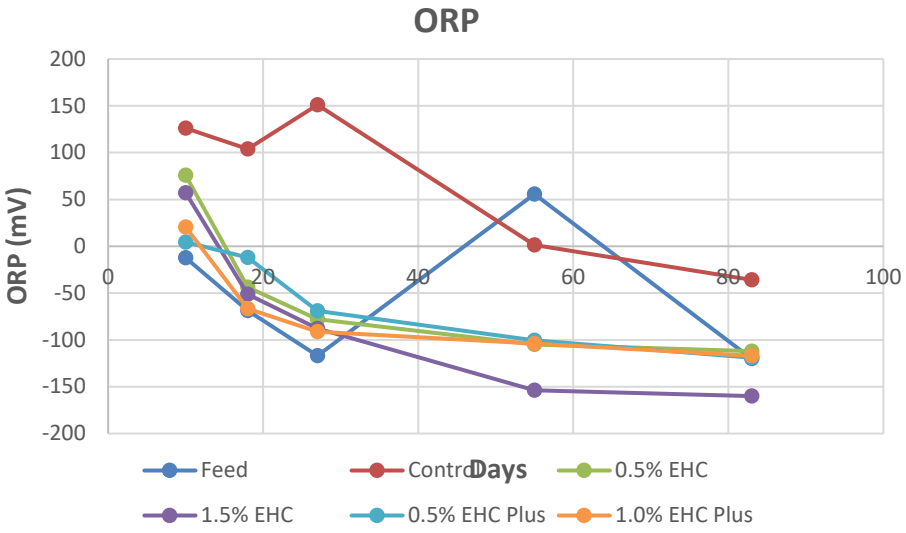


Figure 3: pH in Groundwater



The pH in the treatment systems stayed within an acceptable range for remediation. No pH modifier was needed for the treatments.

Figure 4: ORP in Groundwater



The received Site GW was slightly anoxic. Feed anoxic conditions were difficult to maintain possibly due to the column study being run at room temperature. Each of the treatment conditions reached consistent anoxic levels over time.

Table 5: GW COC % removal summary relative to the feed

Treatment	Day	% GW COC Removal
0.5% EHC	27	43.0%
	55	27.7%
	83	5.6%
1.5% EHC	27	45.7%
	55	34.0%
	83	22.2%
0.5% EHC Plus	27	53.4%
	55	28.0%
	83	5.6%
1.0% EHC Plus	27	73.2%
	55	32.3%
	83	5.0%

5 SUMMARY

The purpose of this bench study was to evaluate two EHC and EHC Plus dosages for the removal of CVOCs in groundwater and soil samples collected from the client's site. The following summary is provided based on the results presented here.

The losses in the control column were suspected to be caused by contaminant binding to the disturbed site soil. Under field conditions, this is unlikely to occur due to the very dense sticky clay present at the site. The loses in the feed may be due to biotic action when the feed bags are stored at room temperature. The typical set ups for EHC and EHC Plus in columns is to blend the soil with the amendment to ensure even distribution. Given that the native soil (clay) had little to no VOCs (based on baseline soil characterization), It is suspected that the sticky site clay soil may have coated the amendment particles minimizing site groundwater contact and contaminant destruction. This coating of the amendment would not be anticipated in the field due to the injection application and no direct mixing with the soil.

With the above-mentioned lab-artifact, we started comparing reduction in COC concentrations under different test conditions against the inlet/feed concentrations. Day 83 data summary indicate that that the total CVOCs were reduced anywhere between 6-15%. It is important to note that Chloroethane (CA) contributes to more than 95% of the COC mass remaining and all other constituents have been treated below target levels.

CA is a recalcitrant compound relative to other COCs of concern, it does not bind readily with activated carbon and requires stronger reducing conditions with the right mixture of native microbes/functional genes to be mineralized through the biological pathway. Abiotic dechlorination is usually slower than microbial processes but is documented to occur. Abiotic agents that may enhance the reductive dechlorination of chlorinated ethanes and ethenes are zero-valent metals, sulfide minerals or green rusts which could be created by possible biogeochemical cycling of iron and sulfur compounds which is something that can be engineered in the substrate formulation.

The combination of factors mentioned above possibly resulted in accumulation/stall of CA which can be addressed using quick amended batch study with a suite of different approaches

Based on feedback from AECOM, PeroxyChem recommends running an additional study using batch reactors with a biologically inactivated control jar to minimize some of the suspected interferences encountered in the column study outlined as follows:

- Control (no biocide)
- EHC Plus- Promoting ISCR with sequestration
- GeoForm Extended Release- Promoting ISCR with biogeochemical component through creation of reactive Iron sulfides.
- Klozur KP- ISCO (would need KDT/Soil Oxidant demand testing for $1000)

All technologies will have one conservative loading/application rate. Both soil and groundwater will be analyzed post treatment (single time-point) . The costs are summarized as follows:

Table 5a: Proposed Batch study

A. ANALYTICAL				
Parameter	**Qty**	**Lab**	**Unit price**	**Subtotal**
VOCs Soil (Method 8260C)	4	TestAmerica	$100	$400
VOCs GW (Method 8260C)	5	TestAmerica	$100	$500
persulfate	1	TestAmerica	$40	$40
KDT	1	PeroxyChem	$1,000	$1,000
pH/ORP	5	PeroxyChem	$20	$100
Other Costs				
Chemicals and supplies	1	--	$250	$250
Shipping to Test America	2	--	$75	$150
Total Analytical and Other Direct Costs				**$2,440**
B. LABOR				
	Units	**Number**	**Unit price**	**Subtotal**
Project Manager	hours	5	$140	$700
Technician	hours	10	$80	$800
Office Support	hours	1	$55	$55
Total Labor				**$1,555**
TOTAL				**$3,995**

On behalf of PeroxyChem, thank you for your interest in our products and technologies, the opportunity to submit this report and for considering Health, Safety and the Environment when sending samples to our lab. Please do not hesitate to contact PeroxyChem if you have any questions regarding this proposal.

Yours truly,
PeroxyChem

Via email
Brianna Desjardins and Ravi Srirangam, PeroxyChem

6 APPENDIX

Table 6: Day 10 Groundwater pH & ORP Readings

Analysis	Parameter	Feed	Control	0.5% EHC	1.5% EHC	0.5% EHC Plus	1.0% EHC Plus	Units
Lab Parameters	pH	6.40	6.94	6.45	6.58	6.54	6.41	SI Units
	ORP	-12.4	126	75.7	57.2	4.4	20.5	mV

Table 7: Day 18 Groundwater pH & ORP Readings

Analysis	Parameter	Feed	Control	0.5% EHC	1.5% EHC	0.5% EHC Plus	1.0% EHC Plus	Units
Lab Parameters	pH	6.47	6.78	6.19	5.78	6.3	6.04	SI Units
	ORP	-68.8	104	-43.9	-51.3	-11.9	-66.5	mV

Table 8: Day 27 Groundwater Summary

Analysis	Parameter	Feed	Control	0.5% EHC	1.5% EHC	0.5% EHC Plus	1.0% EHC Plus	Units
VOCs	1,1,1-Trichloroethane	910	22	8.3 J	ND (20)	ND (20)	ND (20)	µg/L
	1,1-Dichloroethane	7,500	1,600	3,800	3,900	190	8.8 J	µg/L
	1,1-Dichloroethene	160	ND (20)	ND (20)	12 J	ND (20)	ND (20)	µg/L
	1,2-Dichloroethane	540	39	100	260	ND (20)	ND (20)	µg/L
	Chloroethane	17,000	10,000	11,000	10,000	12,000	7,000	µg/L
	cis-1,2-Dichloroethene	ND (50)	ND (20)	ND (20)	21	ND (20)	ND (20)	µg/L
	Vinyl chloride	60	12 J	8.2 J	12 J	ND (20)	ND (20)	µg/L
	Total COCs =	**26,170**	**11,673**	**14,916.5**	**14,205**	**12,190**	**7,009**	**µg/L**
	COC % Removal =			**-27.8%**	**-21.7%**	**-4.4%**	**40.0%**	
	2-Butanone (MEK)	180 J	190	250	550	ND (100)	150	µg/L
	Acetone	360 J	330	2,600	980	460	2,200	µg/L
	Methyl tert-butyl ether	23 J	23	25	22	17 J	14 J	µg/L
Lab Parameters	pH	6.58	6.69	6.31	6.06	6.37	6.21	SI Units
	ORP	-117	151	-77.8	-87.9	-69.2	-91.2	mV

J = Result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value.

Table 9: Day 55 Groundwater Summary

Analysis	Parameter	Feed	Control	0.5% EHC	1.5% EHC	0.5% EHC Plus	1.0% EHC Plus	Units
VOCs	1,1,1-Trichloroethane	520	190	ND (50)	ND (50)	ND (50)	ND (50)	µg/L
	1,1-Dichloroethane	6,400	7,700	160	190	1,300	200	µg/L
	1,1-Dichloroethene	130	ND (50)	ND (50)	42 J	ND (50)	ND (50)	µg/L
	1,2,4-Trimethylbenzene	65 J B	ND (50)	ND (50)	ND (50)	ND (50)	ND (50)	µg/L
	1,2-Dichloroethane	490	290	270	450	98	26 J	µg/L
	1,3,5-Trimethylbenzene	60 J	ND (50)	ND (50)	ND (50)	ND (50)	ND (50)	µg/L
	Chloroethane	19,000	15,000	19,000	17,000	18,000	18,000	µg/L
	cis-1,2-Dichloroethene	ND (100)	ND (50)	ND (50)	46 J	ND (50)	ND (50)	µg/L
	Naphthalene	74 J B	ND (50)	ND (50)	ND (50)	ND (50)	ND (50)	µg/L
	n-Butylbenzene	54 J B	ND (50)	ND (50)	ND (50)	ND (50)	ND (50)	µg/L
	Styrene	47 J B	ND (50)	ND (50)	ND (50)	ND (50)	ND (50)	µg/L
	Vinyl chloride	83 J	62	36 J	40 J	ND (50)	ND (50)	µg/L
	Total COCs =	**26,923**	**23,242**	**19,466**	**17,768**	**19,398**	**18,226**	**µg/L**
	COC % Removal =			**16.2%**	**23.6%**	**16.5%**	**21.6%**	
	2-Butanone (MEK)	ND (500)	ND (250)	150 J	300	220 J	190 J	µg/L
	Acetone	410 J	390 J	150 J	450 J	380 J	210 J	µg/L
	Methyl tert-butyl ether	ND (100)	33 J	21 J	25 J	21 J	20 J	µg/L
Inorganics	TOC Dup	65	45	130	310	110	93	mg/L
	Ferrous Iron	ND (0.050) HF	ND (0.050) HF	ND (0.050) HF	1.0 HF	ND (0.050) HF	ND (0.050) HF	mg/L
Lab Parameters	pH	6.40	6.66	6.46	6.65	6.50	6.49	SI Units
	ORP	55.7	1.5	-105	-154	-100	-104	mV

J = Result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value.

B = Compound was found in the blank and sample.

HF = Field parameter with a holding time of 15 minutes. Test performed by laboratory at client's request.

Table 10: Day 83 Groundwater Summary

Analysis	Parameter	Feed	Control	0.5% EHC	1.5% EHC	0.5% EHC Plus	1.0% EHC Plus	Units
VOCs	1,2-Dichloroethane	ND (50)	ND (50)	ND (50)	ND (50)	ND (50)	100	µg/L
	Chloroethane	18,000	15,000	17,000	14,000	17,000	17,000	µg/L
	Total COCs =	**18,000**	**15,000**	**17,000**	**14,000**	**17,000**	**17,100**	**µg/L**
	COC % Removal =			**-13.3%**	**6.7%**	**-13.3%**	**-14.0%**	
	2-Butanone (MEK)	ND (250)	ND (250)	ND (250)	ND (250)	120 J	ND (250)	µg/L
	Acetone	ND (500)	ND (500)	ND (500)	ND (500)	170 J	ND (500)	µg/L
Lab Parameters	pH	6.63	6.57	6.51	6.70	6.52	6.53	SI Units
	ORP	-120	-36	-112	-160	-119	-117	mV

J = Result is less than the RL but greater than or equal to the MDL and the concentration is an approximate value.