Shaw™

Shaw Environmental & Infrastructure, Inc.

Final Chemical Oxidation Treatability Report, Soil and Groundwater at the Texarkana Wood Preserving Superfund Site, *Texarkana, Texas*

June 2004

Prepared for:

Texas Commission of Environmental Quality

12100 Park 35 Circle, Bldg. D
Austin, TX

Shaw Technology Applications Laboratory
304 Directors Drive
Knoxville, TN 37923

181362

Table of Contents

1.0 INTRODUCTION

1.1 Site Description

The Texarkana Wood Preserving Company (TWPC) Superfund site was used for various lumber-related activities since the early 1900s. Creosoting operations apparently began at the site prior to 1954 in the southwest corner of the property. The TWPC took over the operation in 1961 and used a combination of creosote and pentachlorophenol (PCP) to treat wood in large pressure cylinders. Two large ponds were created to hold wastewater which was released to nearby Days Creek. Operations were moved north of the old facility in 1973 to facilities in the center of the west side of the site. A large diked area was created to contain the pressure treating cylinders and wastewater equipment. Two pretreatment storage ponds and three evaporation ponds were constructed as part of a zero discharge wastewater treatment system

Operations at the site ceased in 1984 when the company went bankrupt. Several investigations at the site documented the presence of polynuclear aromatic hydrocarbons, (PAHs), PCP, and dioxins in waste impoundments and site soils. The Texas Commission on Environmental Quality (TCEQ), Superfund Cleanup Section (SCS) through a Cooperative Agreement with the United State Environmental Protection Agency (EPA) is undertaking treatability study and additional characterization in support of the refinement of remedy at the TWPC site. The proposed remedial alternative being considered by the TCEQ and EPA, is a combination of 1) stabilization of the soil areas impacted with NAPL 2) control of the high concentrations of dissolved phases/NAPL through containment using slurry wall, 3) Chemical oxidation of groundwater contamination outside of the NAPL-impacted area, and 4) monitoring and restoring through natural attenuation of the less contaminated dissolved phase. The data presented in this report was initially intended for remedial alternative 3 above; the bench scale treatability testing of chemical oxidation of groundwater contamination outside of the NAPL-impacted area (XH-16-02). After presenting preliminary results for the initial investigation demonstrating the effectiveness of chemical oxidation in PAH reduction, Shaw Environmental was asked to also evaluate chemical oxidation on a highly impacted NAPL site, X-K7-01. This report summarizes details and results from all tests performed on site soil and groundwater with the oxidants potassium permanganate and sodium persulfate to assess in-situ chemical oxidation (ISCO) technologies for application at the Texarkana site.

The testing was conducted at Shaw Environmental Technology Development Laboratory (TDL) in Knoxville, Tennessee. Chemical and physical analyses of samples were performed at Microbac Laboratory in Maryville, Tennessee and Shaw E&I’s Environmental Technology Development Laboratory (TDL) in Knoxville, Tennessee.

1.2 Site Media Characterization and Description

The waste streams consist of soil and groundwater samples from the former wood perserving facility. A sample of contaminated groundwater and soil from outside of the NAPL-impacted areas were obtained from Sampling Point H-16 (9 to 12.5') and a sample of soil from the NAPL-impacted area was obtained from Sampling Point K-7 (10-16'). These samples were received at Shaw's Technology Applications Laboratory in Knoxville, TN on August 11,2003. The soil and groundwater samples from outside of the NAPL-impacted area were identified as XH-16-02, while the NAPL-impacted soil sample was identified as X-K7-01. The groundwater was received in one 5-gallon HDPE cubitainer. The water was a yellow-brown color with an orange-brown iron discoloration on the cubitainer. The soil samples were each triple bagged and contained in a 5-gallon pail. The soil samples were gray-tan colored, wet sandy material with small pebbles. Both samples had strong organic DNAPL odors when opened. TDL identification numbers were assigned as follows:

Soil	TDL 5226	X-H16-02	(Low level PAHs)
Soil	TDL 5225	X-K7-01	(High Level PAHs)
Groundwater	TDL 5221	X-H16-02	

1.3 Remedial Technology Description

Chemical oxidation can be accomplished with a number of different oxidizers. These include calcium peroxide, hydrogen peroxide, ozone, sodium persulfate, and sodium or potassium permanganate. Based on the fact that exchange of the contaminants from soil surfaces and pore space to the dissolved phase will be the primary rate-controlling step, persistent oxidizers such as permanganate or persulfate should be considered for the TWPC site. Permanganate ion (MnO4-) is a moderate strength oxidizer. The standard reduction potential is shown below for the half-reaction in acidic solution for comparison with other oxidants. It is about the same as that for hydrogen peroxide. In basic solution the standard reduction potential is +0.588 V.

$$MnO4- \; + \; 3e- \; + \; 4H+ \rightarrow MnO2 \; + \; 2H2O \qquad E° = +1.68\ V$$

Permanganate

Permanganate is generally slower to react than peroxide (Fenton's Reagent) and is more selective with respect to the compounds with which it reacts. Permanganate ion is an oxidizing agent with a unique affinity for oxidizing organic compounds containing carbon-carbon double bonds, alkyl substitution of aromatics, aldehyde groups or hydroxyl groups. As an electrophile, the permanganate ion is strongly attracted to the electrons in carbon-carbon double bonds found in chlorinated alkenes, borrowing electron density from these bonds to form a bridged, unstable oxygen compound known as a hypomanganate diester. This intermediate product further reacts by a number of mechanisms including hydroxylation, hydrolysis or cleavage. Under normal subsurface pH and temperature conditions, the carbon-carbon double bond of alkenes is broken spontaneously and the unstable intermediates are converted to carbon dioxide through either hydrolysis or further oxidation by the permanganate ion. The product of permanganate reaction is an insoluble manganese dioxide (MnO_2) solid. The MnO_2 is left in the subsurface matrix following treatment and is environmentally stable.

There are two commercially available forms of permanganate, the potassium salt, $KMnO_4$, and the sodium salt, $NaMnO_4$. Permanganate reagent is applied as either a 2-3 percent aqueous solution of potassium permanganate or a 10-40 percent solution of sodium permanganate. The solutions are quite stable and relatively safe to handle in comparison to high concentration hydrogen peroxide reagents (30-50%). Due to the permissive nature of the saturated zone at the TWPC site, the use of high volumes of oxidant solution will not be precluded. Therefore, potassium permanganate would be preferred due to its lower cost. Because permanganate is more stable and somewhat slower reacting then hydrogen peroxide or ozone, it has good subsurface delivery properties. It reacts with natural organic matter in soil and groundwater, so dosing for site treatment has to take into account the soil oxidant demand in addition to the contaminant demand. The soil oxidant demand is a key parameter, which is usually determined in the permanganate bench tests. An advantage permanganate has over other reagents is its intense purple color, which facilitates detection and monitoring of concentrations. Permanganate is also effective at oxidizing and solubilizing some soil metals and treatments must be monitored for metal mobilization issues.

Persulfate

Persulfate ion ($S_2O_8^{=}$) is a strong oxidant capable of oxidizing most organic compounds to carbon dioxide. The standard reduction potential for the half reaction shown below is +2.08 V, which is about the same as that for ozone and higher than that for permanganate and hydrogen peroxide, but less than the hydroxide radical (Fenton's Reagent intermediate).

$S_2O_8^{-2} + 2e^- \rightarrow 2SO_4^{-2}$ E° = +2.08V

It is believed that persulfate reacts with organic compounds primarily by first splitting into two sulfate radicals, which then undergo reaction with the oxidizable species.

$S_2O_8^{-2}$ or $^-O_4S\text{-}SO_4^- \rightarrow 2 \cdot SO_4^-$

However, in acidic conditions, persulfate can also form peroxomonosulfuric acid (H_2SO_5), and this species may also participate in organic oxidation reactions. This may explain why persulfate reactions are generally faster, and therefore conducted in acidic media where possible.

$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4$

The generation of a reactive intermediate, such as the sulfate radical or peroxomonosulfuric acid, appears to be the rate limiting process as persulfate reactions are not rapid despite the high oxidation/reduction potential for the persulfate to sulfate reaction. Reactions with persulfate to destroy organics in chemical analysis applications are often conducted with a metal catalyst, such as Ag+, and at elevated temperatures of 60 to 80°C to help speed the reaction so it occurs in a matter of minutes. Bench scale treatability tests have shown that persulfate reaction rates are benefited by the presence of Fe^{+2} as a catalyst similar to Fenton's Reagent.

The use of persulfate for in situ chemical oxidation is relatively new compared to Fenton's Reagent and permanganate and has not been used extensively so experience is limited. However testing results show that in situ reactions with persulfate will occur over one to several weeks and persulfate will be effective on recalcitrant organics that are not oxidized by permanganate, in particular.

The reagent is very soluble in water to concentrations above 10% and very stable. These properties allow for optimum delivery and distribution to the subsurface matrix similar to sodium permanganate. In addition, the reagent is similar to permanganate with respect to safety issues, i.e., handling, compatibility, etc.

2.0 TREATABILITY STUDY APPROACH

2.1 Test Objectives And Rationale

The objectives of the chemical oxidation bench-scale treatability study were to provide information to:

- Determine the applicability of chemical oxidation for the treatment of PAH and PCP-contaminated groundwater

- Determine the reduction in PAH and PCP due to the chemical oxidation treatment

- Demonstrate achievement of the groundwater treatment performance criteria,

- Determine the best chemical oxidation reagent based on treatment results, cost, and application considerations, and

- Establish parameters for full-scale chemical oxidation operations.

2.2 Experimental Design and Procedures

While the in-situ application of chemical reagents has been shown to be effective in oxidizing chemical contamination, other species present in site soil and groundwater will consume or decompose the treatment reagent, and thus have a direct impact on the amount of oxidant required and reagent cost. Testing included initial characterization of site soil and groundwater, an oxidant demand test with potassium permanganate on soil and groundwater slurry to define the oxidant-dosing requirement, and batch slurry reaction tests to investigate the rate of reaction of oxidant with the site contaminants. Control samples were prepared along with and identical to the treated slurry to establish baseline concentrations. Soil and groundwater slurries were used in the batch experiments to investigate both oxidant dosing and treatment time requirements. The data from these tests were collected under optimum conditions and this should be considered in interpreting the results obtained, and applying the results for pilot or full-scale implementation. Results for the chemical oxidation technologies investigated are summarized and presented in the data summary tables 3-1 (initial characterization) and tables 3-2, 3-3, 3-4, 3-5 (batch slurry test) of this report. The primary performance goals for the groundwater treated with chemical oxidation are listed below in Table 2-1.

Table 2-1. Chemical Oxidation Treatment Primary Performance Goal for Groundwater

Chemical of Concerns	GW Concentration
Carcinogenic PAH (C-PAH) expresses as BAP equivalent	0.010 mg/L
Total Non-carcinogenic PAH (NC-PAH)	0.150 mg/L
Pentachlorophenol	0.200 mg/L

All water samples collected during batch testing were sent to Microbac Laboratories for PAH and PCP analysis (SVOC 8270). A background soil: groundwater slurry was prepared to determine initial test concentrations for compounds of concern. The control slurry was prepared in the same manner as the treated slurries, equilibrated overnight, and submitted to Microbac for the listed analyses. Measurement of pH and oxidant concentration was done at the TDL and also recorded.

2.2 Equipment and Materials

The equipment utilized for the chemical oxidation testing included:

- 25 quart Hobart mixer
- 12 - 200 mL centrifuge bottles with Teflon lined caps
- 1 - 50 mL burettes with Teflon stopcocks
- 12 - 2.5 L narrow mouth amber sample bottles w/Teflon lined lids
- 12- 1 liter narrow mouth amber sample bottles w/Teflon lined lids
- 12- 15 ml HDPE sample tubes
- pH electrode (w/reference combination) and potentiometric system to obtain readings
- Centrifuge with carousel for 200 mL tubes and refrigeration capability
- Visible spectrophotometer w/ Spectrophotometer tubes or cuvettes
- Whatman #3 filter paper
- 1-5 mL disposable syringes
- 0.2 & 0.45 µm syringe filters for aqueous solutions
- 0.02 – 1.0 mL adjustable pipettes w/disposable pipette tips
- 0.5 – 5.0 mL adjustable pipettes w/disposable pipette tips

The materials utilized in the chemical oxidation testing included:

- Potassium permanganate (Carus Chemical, USP Grade, 99%)
- Ferrous (Fe^{+2}) solution (VWR Ferrous Ammonium Sulfate Solution, 0.250 N)
- Sodium persulfate (J. T. Baker, ACS Reagent, 95% min.)
- Manganese sulfate monohydrate (EM Science, Reagent, 98% min.)
- Sodium thiosulfate 0.1 N standard solution (J. T. Baker, ACS Reagent)
- Potassium iodide (Mallinckrodt, USP Food Grade, 99.0-101.5%)
- Sulfuric acid (EM Science, OmniTrace, 95.5-96.5%)

2.4 Sampling and Analysis

2.4.1 Initial Sample Characterization

The soil was composited and homogenized at the TDL using a 25 quart Hobart mixer and stainless steel mixing bowl. After mixing, the soil composite was placed into (2) one gallon glass sample bottles. The compositing and homogenization process was done in a manner to minimize the amount and time of open exposure for the contaminated soil to avoid loss of SVOCs from the sample.

Portions of the composite groundwater and soil sample material were analyzed for the parameters listed in Table 2-2. Care was taken to minimize sampling bias. The PCP analysis was conducted in triplicate to assess homogeneity.

Table 2-2. Parameters for Characterization of the Treatability Sample

Analysis	Method
Untreated Material Characterization - Site Water	
Total PAHs and PCP	EPA Method 8270
Total TAL Metals	EPA Methods 6010B/7470
Total Organic Carbon (TOC)	EPA Method 5310/9060A
Chemical Oxygen Demand (COD)	EPA Method 410.4
Material pH	EPA Method 9040
Total Suspended Solids	EPA Method 160.2
Total Dissolved Solids	EPA Method 160.1
Untreated Material Characterization - Site Soil	
Total PAHs and PCP	EPA Method 8270
Total TAL Metals	EPA Methods 6010B/7470
Total Organic Carbon (TOC)	EPA Method 5310/9060A
Chemical Oxygen Demand (COD)	EPA Method 410.4
Material pH	EPA Method 9045
Solids Content	ASTM D 2216
Hydraulic Conductivity	ASTM D 5084
Grain Size by Sieve and Hydrometer	ASTM D 422

2.4.2 Oxidant Demand Testing

The oxidant demand test was performed using potassium permanganate to measure the amount of permanganate that will be consumed by oxidizable species in the soil in the course of treatment to destroy the compounds of concern. The oxidant demand test for X-H16-02 was performed using two concentrations of permanganate to investigate demand as a function of treatment concentration. In one test, 0.8 liter of site groundwater and 200 grams of prepared aquifer material was used. The aquifer material/water mixture was treated initially with 1.0 grams of potassium permanganate ($KMnO_4$) to provide an initial permanganate concentration of 1,250 mg/L (0.125%). This concentration is on the lower end of the typical permanganate application concentration range. The second test was performed using 200 grams of prepared aquifer material and 0.2 liter of site groundwater treated initially with 1.4 grams of $KMnO_4$. This treatment had an initial permanganate concentration of 7,000 mg/L (0.7%). The two tests have different aquifer material to water ratios, but this is not anticipated to affect the oxidant demand results, as the critical parameters will be the amount of aquifer material, and the amount and concentration of the permanganate supplied to the aquifer material. The treated slurries will be shaken or tumbled to provide continuous mixing. The solution permanganate concentrations for both tests were monitored as a function of time by removing a small aliquot of the slurry, filtering through a 0.45 um syringe filter and reading the absorbance at 540 nm. The amount of permanganate consumed at each concentration was determined as a function of time, and will be used to define permanganate-dosing requirements. The SOD testing for X-K7-01 was conducted identically to that of X-H16-02 only with higher initial doses of 2500 mg/L (0.25%) and 14,000 mg/L (1.4%), respectively, to account for the higher contaminant concentrations present. Additional permanganate was added as needed during the SOD testing. A graph of g MnO_4^- consumed per kg of soil vs time in hours for all tests was prepared and is included in Appendix A.

2.4.3 Chemical Oxidation Batch Slurry Testing

Results from permanganate chemical oxidant demand testing were used to estimate how much oxidant will be consumed in reaction with oxidizable material in the slurries (stoichiometric oxidant demand). The stoichiometric demand was used along with oxidant concentration requirements for treatment from groundwater tests to establish oxidant doses for permanganate and persulfate.

Testing for sample X-H16-02 consisted of six soil/water slurry tests plus two control tests using a 1:2 ratio by weight of soil to water. This ratio of soil to groundwater is needed to produce sufficient treated groundwater for subsequent testing. Slurries were prepared by weighing 500 g of soil into 2 L reactors and adding 1000 mL of groundwater.

Testing for sample X-K7-01 consisted of four soil/water slurry tests plus one control test using a 1:2 ratio by weight of soil to water. Testing was reduced due to limited groundwater available for testing. This ratio of soil to groundwater is needed to produce sufficient treated groundwater for subsequent testing. Slurries were prepared by weighing 350 g of soil into 1 L reactors and adding 700 mL of groundwater.

After addition of the permanganate or iron catalyzed persulfate, the test bottles were placed on a shaker table to complete distribution. The bottles were inspected periodically and then swirled to redistribute soil and reagents, as appropriate. Test temperatures for each test bottle were also checked periodically. No changes in temperature or color were noted during testing.

Samples were collected from each test bottle at the end of treatment. Each bottle was opened and a 5-10 mL aliquot of the aqueous phase will be decanted into a 15 mL polypropylene tube for pH and residual oxidant measurement. The appropriate quench agent was then added to the bottles to react with and destroy residual oxidant, if required, and the bottles were re-capped. The contents of quenched test bottles were mixed, and the bottles centrifuged to separate solid and aqueous phases. Water samples from each bottle were collected for PAH and PCP analysis. A table of the batch testing conditions is presented in Table 2-2 below.

Table 2-2 Summary of Batch Test Conditions

X-H16-02 (Low Level)				
Test	Oxidant	Concentration	Catalyst	Test Duration
1A Low (75X)	Potassium Permanganate	0.14%	None	7 days
1B Med (150X)		0.28%	None	7 days
1C High (300X)		0.56%	None	7 days
2A Low (75X)	Sodium Persulfate	0.14%	200 ppmFe^{+2}	14 days
2B Med (150X)		0.28%	200 ppmFe^{+2}	14 days
2C High (300X)		0.56%	200 ppmFe^{+2}	14 days
Control	None	None	None	0 days
Control	None	None	None	14 days
X-K7-01 (High Level)				
Test	Oxidant	Concentration	Catalyst	Test Duration
1A Med (100X)	Potassium Permanganate	0.28%	None	7 days
1B High (150X)		0.56%	None	7 days
2A Low (50X)	Sodium Persulfate	0.14%	200 ppmFe^{+2}	14 days
2B High (150X		0.56%	200 ppmFe^{+2}	14 days
Control	None	None	None	14 days

2.5 Data Management

All raw data from the insitu chemical oxidation bench scale Treatability study will reside in bound laboratory notebooks, analytical reports from Shaw's Technology Applications Laboratory or outside analytical laboratories, or computer generated print-outs from computer controlled equipment.

2.5.1 Data in Bound Laboratory Notebooks

All entries in bound laboratory notebooks were made in black ink and will be considered raw data. At the end of each entry, the initials of the laboratory personnel responsible and date were entered. All corrections were initialed and dated at the time of correction and a note explaining the correction included

2.5.2 Analysis Reports

All analytical reports from Shaw's Technology Applications Laboratory or outside analytical laboratories will be maintained as raw data. Any corrections or additions to analytical reports previously received must be accompanied by a written explanation from the analytical laboratory.

2.5.3 Computer Print-outs

Computer printouts from computer-controlled equipment will be maintained as raw data. The initials of the equipment operator and the date of generation were added to each page of all such computer handouts. Regenerated printouts will be identified as such and any corrections noted.

2.5.4 Data Review

Prior to issuing a final report, all pertinent raw data must be reviewed to ensure the data quality. The Treatability Program Manager or the Treatability Laboratory Manager reviewed all relevant laboratory notebook pages, computer printouts, and analytical reports. Any discrepancies in the raw data uncovered in this or any review was immediately brought to the attention of the appropriate laboratory personnel and corrected.

2.6 Deviations from Workplan

The initial workplan only provided for the insitu chemical oxidation treatability study of a soil outside of the DNAPL impacted site (H-16-02) with low level PAH contamination. However after evaluation of the effectiveness of the treatment at this site, it was decided to evaluate chemical oxidation treatment at a more highly zone on the site (X-K7-O1). This study was conducted similar to the first with revisions in the number of conditions due to limited site groundwater available for testing. The two oxidants were tested at two concentrations instead of three. Treated soil was also collected at the end of the batch treatment from the highest oxidant condition in order to evaluate the effectiveness of the oxidants on the PAH levels in the soil as well as in the groundwater.

3.0 RESULTS AND DISCUSSION

3.1 Characterization

The characterization results are summarized in Table 3-1. The composite soil sample from outside of the NAPL-impacted area, XH-16-02, contained low concentrastions of total PAHs. PCP was not detected in the total analysis at the laboratory reporting limit (<5 mg/kg). The PAHs most notably present in the sample were phenanthrene (2.20 mg/kg), pyrene (0.83 mg/kg), acenaphthene (1.06 mg/kg), flouranthene (1.10 mg/kg), and flourene (0.73 mg/kg).

The composite soil sample, K-07 (10 to 16'), contained higher concentrations of total PAH from the contaminated zone. PCP was only detected in the total analysis at the laboratory reporting limit of 5 mg/kg for one sample of the triplicate analysis. The PAHs most notably present in the sample were phenanthrene (336 mg/kg), naphthalene (716 mg/kg), acenaphthene (154 mg/kg) flouranthene (106 mg/kg), and flourene (110 mg/kg).

The site groundwater identified as XH-16-02 was non-detect at <0.01 mg/L for all PAH compounds.

3.2 Soil Oxidant Demand

Oxidant dose requirements for the batch slurry test were based on the results from the soil oxidant demand test. The permanganate oxidant demand for sample XH-16-02 was 3.25 g per kg wet soil. Persulfate demand is typically 1 to 2 times that of permanganate and is consumed much slower and is harder to determine due to its stability. This is considered a low demand and well within the typical permanganate or persulfate chemical oxidation application range of 1-15 g oxidant per kg soil.

The permanganate oxidant demand for sample X-K7-01 was 60 g per kg wet soil. This is considered a very high demand. However, chemical oxidation may be an economical treatment option depending on the size of the treatment area, and may be very effective in treatment of "hot spots".

Table 3.1 Initial Characterization Summary Table

Parameter	Units	TDL5221 GW XH-16-02	TDL5226 SOIL XH-16-02	TDL5225 SOIL X-K7-01
pH	Std Units	6.90	7.38	7.05
TOC	g/cc	4.7	314	1,100
COD	mg/L or mg/kg	25.2	1183	27,700
TSS	mg/L	<1.0	NA	NA
TDS	mg/L	271	NA	NA
Solids Content	%	NA	88.9	87.2
Total PCP[1]	mg/L or mg/kg	<0.05 /<0.05/ <0.05	<1.66 /<5.0/ <5.0	<5.0/<5.0/5.0
PAHs				
Acenaphthene	mg/L or mg/kg	<0.01	1.06	154
Acenaphthylene	mg/L or mg/kg	<0.01	<0.33	<5.0
Anthracene	mg/L or mg/kg	<0.01	<0.33	56
Benzo(a)anthracene (cPAH)	mg/L or mg/kg	<0.01	<0.33	<5.0
Benzo(a)pyrene (cPAH)	mg/L or mg/kg	<0.01	<0.33	<5.0
Benzo(b)flouranthene (cPAH)	mg/L or mg/kg	<0.01	<0.33	<5.0
Benzo(ghi)perylene	mg/L or mg/kg	<0.01	<0.33	<5.0
Benzo(k)flouranthene (cPAH)	mg/L or mg/kg	<0.01	<0.33	<5.0
Chrysene (cPAH)	mg/L or mg/kg	<0.01	<0.33	<5.0
Dibenz(a,h)anthracene (cPAH)	mg/L or mg/kg	<0.01	<0.33	<5.0
Flouranthene	mg/L or mg/kg	<0.01	1.10	106
Flourene	mg/L or mg/kg	<0.01	0.73	110
Indeno(1,2,3-cd)pyrene (cPAH)	mg/L or mg/kg	<0.01	<0.33	<5.0
Naphthalene	mg/L or mg/kg	<0.01	<0.33	716
Phenanthrene	mg/L or mg/kg	<0.01	2.20	336
Pyrene	mg/L or mg/kg	<0.01	0.83	<5.0
Metals				
Aluminum	mg/kg	--	2595	3592
Antimony	mg/kg	--	<14.0	<41.0
Arsenic	mg/kg	--	<8.27	<17.6
Barium	mg/kg	--	15.7	13.7
Beryllium	mg/kg	--	0.141	<0.20
Cadmium	mg/kg	--	<0.90	<2.76
Calcium	mg/kg	--	228	188
Chromium	mg/kg	--	4.10	5.17
Cobalt	mg/kg	--	<1.53	<4.5
Copper	mg/kg	--	0.94	<1.7
Iron	mg/kg	--	1920	2780
Lead	mg/kg	--	<8.41	<24.8
Magnesium	mg/kg	--	165	170
Manganese	mg/kg	--	22.6	22.5
Nickel	mg/kg	--	<1.75	<5.8
Potassium	mg/kg	--	203	208
Selenium	mg/kg	--	<15.1	<44.4
Silver	mg/kg	--	<0.94	<2.76
Sodium	mg/kg	--	24.1	39.0
Thallium	mg/kg	--	<9.24	<27.2
Vanadium	mg/kg	--	6.46	7.13
Zinc	mg/kg	--	7.33	5.74

3.3 Soil/Water Test Results

Soil/water slurry tests were conducted to evaluate the impact of soil on the ability of permanganate and persulfate reagents to treat PCP and PAHs in site groundwater. The results are summarized in Tables 3-2, 3-3, 3-4 and 3-5.

Permanganate

Low impacted site: PCP was not detected in any of the site soil or groundwater samples in testing the low impacted site XH-16-02 and could not be evaluated. Groundwater PAH concentrations were effectively reduced below detectable levels of 0.01 mg/l and below the treatment primary performance goals with an initial aqueous permanganate concentration of 1800 mg/L in 7 days treatment time.

Highly impacted site: Soil/water batch slurry tests verified the ability of permanganate reagent at a 4-6% aqueous concentration to effectively treat the 1.21 mg/l PCP and 14.3 mg/L PAH concentration in the groundwater, to below detectable levels of <0.020mg/l PCP and <0.20 mg/l NC-PAHs a >99% reduction. The 1478 mg/kg PAHs in the site soil were treated to 29.3 mg/kg, a 98% reduction, in 7 days treatment time. PAH concentrations were reduced to below detectable levels for all compounds in the site groundwater and all except flouranthene in the soil (72% reduction). The residual flouranthene concentration may be reduced further with increased treatment time. The residual oxidant concentration of 1.6% after seven days treatment time is sufficient to continue the reduction for several weeks.

Persulfate

Sodium persulfate with 200 mg/L Fe^{+2} catalyst was not as effective for treating the PAHs as permanganate in the presence of site soil.

Low impacted site: Groundwater PAH concentrations were effectively reduced below detectable levels and below the treatment primary performance goal with an initial aqueous persulfate concentration of 3500 mg/L in 14 days treatment time.

Highly impacted site: Aqueous PAH concentrations showed an increase with only 59% reduction of total PAHs in the site soil at a 5.6% aqueous persulfate concentration. The reason for the increase in aqueous PAH concentrations was not clear.

Table 3.2 Permanganate Batch Test Summary Table

Texarkana X-H16-02 soil

500 g soil:1000 g water		**Groundwater Concentrations**				
Parameter	**Units**	**Control Initial**	**Control Final**	**Permanganate 1.1 X[a]**	**Permanganate 1.9 X[a]**	**Permanganate 3.8 X[a]**
Initial Aqueous Oxidant Concentration	mg/L	**--**		1800	3500	6900
Final Aqueous Oxidant Concentration	mg/L	**--**		374	1670	4520
Soil Oxidant Dose	g/kg			1.75	3.47	6.94
Test duration	Days	0	14	7	7	7
pH	Std Units	7.20	7.20	7.37	7.52	7.57
PAH's						
Acenaphthene	mg/L	<0.01	**0.26**	<0.01	<0.01	<0.01
Acenaphthylene	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Anthracene	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(a)anthracene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(a)pyrene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(b)flouranthene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(ghi)perylene	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(k)flouranthene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Chrysene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Dibenzo(a,h)anthracene(cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Flouranthene	mg/L	**0.011**	**0.032**	<0.01	<0.01	<0.01
Flourene	mg/L	**0.22**	<0.01	<0.01	<0.01	<0.01
Indeno(1,2,3-cd)pyrene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Naphthalene	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Phenanthrene	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Pyrene	mg/L	<0.01	**0.019**	<0.01	<0.01	<0.01
Total PAH Reduction	mg/L	**0.231**	**0.311**	**<0.01**	**<0.01**	**<0.01**

[a] oxidant stoichiometry factor based on SOD and PAH concentrations

Table 3.3 Sodium Persulfate Batch Test Summary Table

Texarkana X-H16-02 soil

500 g soil:1000 g water		**Groundwater Concentrations**				
Parameter	**Units**	**Control Initial**	**Control Final**	**Persulfate 1.1 X[a]**	**Persulfate 1.9 X[a]**	**Persulfate 3.8 X[a]**
Initial Aqueous Oxidant Concentration	mg/L	**--**		1500	3500	8000
Final Aqueous Oxidant Concentration	mg/L	**--**				
Soil Oxidant Dose	g/kg					
Test duration	Days	0	14	14	14	14
pH	Std Units	7.20	7.20	7.37	7.52	7.57
PAH's						
Acenaphthene	mg/L	<0.01	**0.26**	<0.01	<0.01	<0.01
Acenaphthylene	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Anthracene	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(a)anthracene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(a)pyrene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(b)flouranthene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(ghi)perylene	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Benzo(k)flouranthene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Chrysene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Dibenzo(a,h)anthracene(cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Flouranthene	mg/L	**0.011**	**0.032**	<0.01	<0.01	<0.01
Flourene	mg/L	**0.22**	<0.01	**0.022**	<0.01	<0.01
Indeno(1,2,3-cd)pyrene (cPAH)	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Naphthalene	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Phenanthrene	mg/L	<0.01	<0.01	**0.016**	<0.01	<0.01
Pyrene	mg/L	<0.01	**0.019**	<0.01	<0.01	<0.01
Total PAH Reduction	mg/L	**0.231**	**0.311**	**.038**	**<0.01**	**<0.01**

[a] oxidant stoichiometry factor based on SOD and PAH concentrations

Table 3.4 Permanganate Batch Test Summary Table

Texarkana X-K7-01 soil

Media **2:1 GroundWater:Soil slurry**		**Groundwater**				**Soil**		
Parameter	**Units**	**Control**	**$KMnO_4$ 1 X[a]**	**$KMnO_4$ 1.5 X**	**% Reduction**	**Untreated**	**Treated Permanganate 1.5X**	**% Reduction**
Initial Aqueous Oxidant Concentration	mg/L	**--**	37500	56250	--	--		
Final Aqueous Oxidant Concentration	mg/L	**--**	2930	15900	--	--		
Soil Oxidant Dose	g/kg		75	113			113	
Test duration	Days		7	7	--	--	7	
pH	Std Units	7.31	8.81	8.75	--	7.05		
PCP	mg/L or mg/kg	1.21	<0.020	<0.020	**>98%**	<5.0/<5.0/5.0	<3.3	**>50%**
PAH's								
Acenaphthene	mg/L or mg/kg	**1.26**	<0.20	<0.20	**>84%**	**154**	<3.3	**>98%**
Acenaphthylene	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<3.3	--
Anthracene	mg/L or mg/kg	**0.42**	<0.20	<0.20	**>52%**	**56**	<3.3	**>94%**
Benzo(a)anthracene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<3.3	--
Benzo(a)pyrene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<3.3	--
Benzo(b)flouranthene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<3.3	--
Benzo(ghi)perylene	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<3.3	--
Benzo(k)flouranthene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<3.3	--
Chrysene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<3.3	--
Dibenzo(a,h)anthracene(cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<3.3	--
Flouranthene	mg/L or mg/kg	**1.04**	<0.20	<0.20	**>81%**	**106**	**29.3**	**72%**
Flourene	mg/L or mg/kg	**1.16**	<0.20	<0.20	**>83%**	**110**	<3.3	**>97%**
Indeno(1,2,3-cd)pyrene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20		<5.0	<3.3	--
Naphthalene	mg/L or mg/kg	**7.40**	<0.20	<0.20	**>97%**	**716**	<3.3	**>99%**
Phenanthrene	mg/L or mg/kg	**2.30**	<0.20	<0.20	**>91%**	**336**	<3.3	**>99%**
Pyrene	mg/L or mg/kg	**0.67**	<0.20	<0.20	**>70%**	<5.0	<3.3	**--**
Total PAH Reduction	mg/L or mg/kg	**14.3**	**<0.20**	**<0.20**	**>99%**	**1478**	**29.3**	**>98%**

[a] oxidant stoichiometry factor based on SOD and PAH concentrations

Table 3.5 Sodium Persulfate Batch Test Summary Table

Texarkana X-K7-01 soil

Media **2:1 GroundWater:Soil slurry**		**Groundwater**				**Soil**		
Parameter	**Units**	**Control**	**Persulfate 0.5 X[a]**	**Persulfate 1.5 X**	**% Reduction**	**Untreated**	**Treated Persulfate 1.5X**	**% Reduction**
Initial Aqueous Oxidant Concentration	mg/L	**--**	19000	56250	--	--		
Final Aqueous Oxidant Concentration	mg/L	**--**	14411	46687	--	--		
Soil Oxidant Dose	g/kg		37.5	113			113	
Test duration	Days		14	14	--	--	14	
pH	Std Units	7.31	1.97	1.81	--	7.05		
PCP	mg/L or mg/kg	1.21	<0.020	<0.020	>98%	<5.0/<5.0/5.0	<3.3	>50%
PAHs								
Acenaphthene	mg/L or mg/kg	**1.26**	<0.20	**30.2**		**154**	<33	**>79%**
Acenaphthylene	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<33	--
Anthracene	mg/L or mg/kg	**0.42**	<0.20	<0.20		**56**	<33	**>41%**
Benzo(a)anthracene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<33	--
Benzo(a)pyrene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<33	--
Benzo(b)flouranthene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<33	--
Benzo(ghi)perylene	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<33	--
Benzo(k)flouranthene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<33	--
Chrysene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<33	--
Dibenzo(a,h)anthracene(cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20	--	<5.0	<33	--
Flouranthene	mg/L or mg/kg	**1.04**	<0.20	**14.6**		**106**	**70**	**34%**
Flourene	mg/L or mg/kg	**1.16**	<0.20	**15.6**		**110**	**65**	**41%**
Indeno(1,2,3-cd)pyrene (cPAH)	mg/L or mg/kg	<0.20	<0.20	<0.20		<5.0	<33	--
Naphthalene	mg/L or mg/kg	**7.40**	**2.82**	**84**		**716**	**290**	**59%**
Phenanthrene	mg/L or mg/kg	**2.30**	**0.49**	**45.8**		**336**	**180**	**46%**
Pyrene	mg/L or mg/kg	**0.67**	<0.20	**3.01**		<5.0	<33	--
Total PAH Reduction	mg/L or mg/kg	**14.3**	**3.31**	**163**		**1478**	**605**	**59%**

[a] oxidant stoichiometric factor based on SOD and PAH concentrations

4.0 Conclusions and Recommendations

4.1 Conclusions

The composite soil sample, X-H16-02, from outside the impacted area contained a low-level amount of total PAH for the site. Pentachlorophenol was not detected in the totals analysis (<5.0 mg/kg) or in the control batch slurry extract. The PAHs most notably present in the sample were phenanthrene (2.20 mg/kg), acenaphthene (1.06 mg/kg), flouranthene (1.10 mg/kg), pyrene (0.83) and flourene (0.73 mg/kg). Based on the aqueous concentrations in the control test, the equilibrium PAH concentrations for groundwater in contact with the soil were <0.01, 0.26, 0.032, 0.019, and <0.010 mg/L, respectively, and the PAHs were 0.311 mg/L. Permanganate oxidation at an initial concentration of 1,800 mg/L effectively reduced groundwater concentrations to less than the MDL of<0.01mg/l (less than the 0.15 mg/l treatment goal). Persulfate oxidation also effectively reduced concentrations to less than the MDL of<0.01mg/l (less than the 0.15 mg/l treatment goal), but an an initial concentration of at least 3,500 mg/L was required. Persulfate was nearly as effective as permanganate for PAH treatment.

The composite soil sample, K-07 (10 to 16'), from inside the impacted area contained a mid-level amount of total PAH for the site. Like the previous sample, pentachlorophenol was not detected in the totals analysis above the 5.0 mg/kg MDL, but was found in the control batch slurry extract at 1.21 mg/L. The PAHs most notably present in the sample were phenanthrene (336 mg/kg), naphthalene (716 mg/kg), acenaphthene (154 mg/kg), flouranthene (106 mg/kg), and flourene (110 mg/kg). Based on the aqueous concentrations in the control test, the equilibrium PAH concentrations for groundwater in contact with the soil were 2.30, 7.40, 1.26, 1.04, and 1.16 mg/L, respectively, and the ncPAHs were 14.3mg/L. Permanganate oxidation effectively reduced concentrations to less than the MDL of<0.20mg/l (slightly above the 0.15 mg/l treatment goal). The PAH concentration MDL (<0.20 mg/L) was slightly above the treatment criterion of 0.15 mg/L, due to the reduced volume of sample available. Detection limits in the PAH analysis can be improved if more than 1 liter of extract is submitted for PAH analysis. The treated soil PAH concentrations in the 1.5x stoichiometry test were reduced below the soil MDL of <3.3 mg/kg for all of the PAHs except for fluoranthene, which had a residual PAH concentration of 29.3 mg/kg.

For the persulfate treated tests residual groundwater and soil PAH concentrations remained in the range of 0.49 to 84 mg/L for the treated groundwater and 65 to 290 mg/kg in the treated soil. Persulfate was not as effective as permanganate for PAH treatment.

The solids content and pH for the two samples were within expected ranges for sandy subsurface soils.

4.2 Recommendations

- Testing results support consideration of permanganate reagent for the treatment of site PCP and PAH groundwater contaminants outside the impacted area.
- Inside the impacted area permanganate treatment can be effective, but depending on the amount of soil exposed to the reagent in the process of treating the groundwater, reagent costs may be prohibitively high.
- Treatment with permanganate in soil/water slurry was demonstrated to be capable of reducing PAH contaminant concentrations in site groundwater to below the 0.20 mg/L detection limit, which is just above the treatment criteria.
- Potassium permanganate reagent, which is cheaper than sodium permanganate but less soluble should be used, since results showed that treatment with a saturated potassium permanganate solution (~3% by weight) was sufficient to provide treatment.
- Due to the high oxidant demand for soil inside the impacted area, multiple injections may be required to meet the demand and provide enough permanganate for groundwater treatment.
- Permanganate dosing should be based on the volume of soil to be treated in the process of treating the contaminated zone groundwater and the contaminated soil's oxidant demand. Measurements from these tests put the soil oxidant demand (SOD) at 3.3 g $KMnO_4$ per kilogram of soil (wet) for the soil, X-H16-02, from outside the impacted area and 60 g $KMnO_4$ per kilogram of soil (wet) for the soil, K-07 (10 to 16'), from inside the impacted area. These demands include that for the PAH contamination on the soil, which is approximately 0.1 g $KMnO_4$ per kilogram of soil (theoretical) for the soil from outside the impacted area and approximately 26 g $KMnO_4$ per kilogram of soil (theoretical) for the soil from inside the impacted area.
- The SOD measurements can be used for initial site estimates, but values can vary widely over an area and at different soil depths, so several additional measurements should be made to better characterize for the soil zone to be treated before proceeding.

Based on the soil oxidant demand measurements, reagent costs for treatment of groundwater outside of the impacted area will be \$8/ton of soil exposed to the reagent and total costs would be in the range of \$20-\$30/ton of soil treated in the process.

The costs for treatment of groundwater inside of the impacted area will be $140/ton of soil exposed to the reagent and total costs would be in the range of $160-$170/ton of soil treated in the process.