CHEMICAL OXIDATION TREATABILITY STUDY

RADIO MATERIALS CORPORATION
ATTICA, INDIANA

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1.0 INTRODUCTION

1.1 BACKGROUND

Conestoga-Rovers & Associates (CRA) is conducting a Phase IIB Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) at the Radio Materials Corporation (RMC) facility located in Attica, Indiana (Site). This work is being conducted in compliance with the U.S. Environmental Protection Agency (U.S. EPA) Region 5 RCRA 3008(h) Consent Order No. IND 005 477 021. The Site is located in west-central Indiana at 1095 East Summit Street in the eastern portion of the City of Attica, in Fountain County, Section 5, Township 21 North, Range 7 West (Figure 1.1). The purpose of the Phase IIB RFI is to delineate the vertical and horizontal extent of potential contamination from five Solid Waste Management Units (SWMUs) and three Areas of Concern (AOCs) at the Site. The SWMUs and AOCs are depicted in Figure 1.2

In July 2006, CRA submitted an Interim Corrective Measures (ICM) Work Plan to the U.S. EPA that described the work to be completed to evaluate and implement interim corrective measures for soil in several areas that are amenable to implementation of such measures. The ICM Work Plan identifies the areas of the Site that are amenable to ICMs, the stabilization technologies selected for these areas, the rationale for selection, and the activities required to investigate the technologies, and obtain the data and information required to design and implement the stabilization technologies. In a letter dated August 27, 2006, the U.S. EPA issued a letter stating that the pilot studies were a necessary step in the implementation of the remedy and approved the proposed work plan on the design of the pilot studies.

1.2 PURPOSE

Among the stabilization technologies selected in the ICM Work Plan was in-situ chemical oxidation (ISCO). The ICM Work Plan identified further studies that were required to assess ISCO technology at the Site including a Natural Oxidant Demand (NOD) study and a microcosm study to be completed in order to evaluate the effectiveness of potassium permanganate and Fenton's Reagent for the treatment of VOCs in soils at the Site. This purpose of this report is to summarize the work completed and the results of the NOD and microcosm study completed to evaluate the use of ISCO at the Site.

2.0 DESCRIPTION OF ISCO

ISCO is an effective technology for treating a wide range of VOCs. The technology is based on the use of strong oxidizing agents to completely oxidize the VOCs within relatively short periods. In a chemical oxidation reaction, the oxidizing agent breaks the carbon bonds in VOCs within hours to generate non-toxic compounds, primarily carbon dioxide and water.

The oxidizing agents commonly used in ISCO include:

- potassium permanganate ($KMnO_4$);
- Fenton's reagent (a solution of hydrogen peroxide and ferrous sulfate);
- ozone; and
- sodium persulfate ($Na_2S_2O_8$).

$KMnO_4$, Fenton's reagent, and ozone are the most commonly used oxidants. $KMnO_4$ is easier to handle than Fenton's reagent, which is pH-dependent and requires the use of ferrous salt as a catalyst for optimum performance. ISCO application involves simple methods and does not require sophisticated equipment, except for ozone treatment. $KMnO_4$ is effective against VOCs that have carbon-carbon double bonds including tetrachloroethene (PCE), trichloroethene (TCE) and related degradation products including cis-1,2-dichloroethene (cis-1,2-DCE) and vinyl chloride. Fenton's reagent is a strong enough oxidant to oxidize single carbon bonds. Fenton's is also more effective in clay soils where $KMnO_4$ does not always penetrate the clay matrix.

ISCO is site-specific, and successful treatment is typically a function of the effectiveness of the delivery system (being able to deliver sufficient amounts of oxidant to the impacted soil and making sufficient "contact") and subsequent transport of the oxidant within the soil matrix. The treatment performance is dependent to a great extent on the soil and groundwater chemistry.

For the RMC Site, $KMnO_4$ is likely the best oxidant since it if effective against the chemicals of concern at the Site. However, in case properties of the soil matrix make $KMnO_4$ ineffective, Fenton's reagent was also tested in this study.

3.0 TREATABILITY STUDY OBJECTIVES

The primary objectives of this laboratory study were to gather the data necessary to determine:

i) the effectiveness of ISCO for treatment of the VOCs in representative soil and groundwater samples from the Site;

ii) the most effective oxidant for treatment of Site soils; and

iii) the effective concentration/dosage of oxidant required to complete treatment as expeditiously as possible.

The NOD is a critical factor in the evaluation of ISCO treatment in determining the dosages of oxidant that are required to effectively oxidize the contaminants present (referred to as stoichiometric demand) as well as the competing reactions. The competing reactions are typically caused by the presence of natural organic materials such as humates and fulvates, as well as reduced metal species. The consumption of oxidants by these non-target compounds is defined as the NOD. In order to determine the optimum oxidant dosage, treatability studies to determine the NOD of the soil must be conducted.

A series of microcosm tests were conducted to assess the effectiveness of selected chemical oxidizing agents for treatment of VOCs in the soils and to determine the optimum concentration range of the chemical oxidizing agents' solution to be used for implementation.

4.0 LABORATORY TREATABILITY STUDIES

4.1 ISCO TARGET AREAS

If the application of ISCO technology encompasses too large of an area, it would rapidly become expensive and difficult to implement due to the volume of oxidant required, and would be of limited effectiveness; particularly where lower VOC concentrations are present in soil. Therefore, ISCO was selected to address isolated areas within SWMU 5 and SWMU 11/AOC 2, where elevated levels of VOCs and evidence of free product were observed during prior soil investigations, to rapidly reduce VOC concentrations and minimize ongoing releases to soil vapor and groundwater from source areas.

In SWMU 5, ISCO injections are proposed in the area around borings B-512, B-518, B-522, and B-524 at depth intervals where free product was indicated by visual observation, photoionization detector (PID) readings, or where VOC concentrations in soils exceeding 200 mg/kg were observed. The VOC concentrations exceeding 200 mg/kg are limited to depths of between approximately 15 and 30 feet below ground surface (bgs), which will be the target depth interval for ISCO injections. The conceptual SWMU 5 ISCO deployment areas are depicted on Figure 4.1.

In SWMU 11/AOC 2, ISCO injections are targeted in the area around boring B-1117 and the former vapor degreaser where free product was observed at the 22 to 24-foot below grade depth interval (see Figure 4.2).

4.2 WORK COMPLETED

4.2.1 SAMPLE ACQUISITION AND INITIAL CHARACTERIZATION

CRA obtained a 5-gallon soil sample from the area near boring B-518 in SWMU 5. The soil samples were obtained from the target depth interval of 18 to 22 feet bgs. The soil was shipped from the Site to CRA's Treatability Study Laboratory, Niagara Falls, New York on May 23, 2006. Due to the similar nature of the geology and soil contaminants as well as close proximity, the sample from SWMU 5 also was determined to be adequate for evaluation of oxidants and NOD in the SWMU 11/AOC 2 area.

The soil sample obtained from SWMU 5 was analyzed for VOCs. The results of the analyses are shown in Table 4.1. The soil sample contained 2,520 mg/kg TCE. It also contained 665 mg/kg PCE, 125 mg/kg toluene, 14 mg/kg cis-1,2-DCE, 11 mg/kg

xylenes, 2 mg/kg ethylbenzene, 0.3 mg/kg 1,1,2-TCE, and less than 0.1 mg/kg 1,1-DCE and trans-1,2-DCE.

4.2.2 CHEMICAL OXIDATION MICROCOSM TESTS

In order to evaluate the effectiveness of $KMnO_4$ and Fenton's reagent in the treatment of VOCs at the Site, a series of microcosm tests were conducted. The soil microcosm tests were set up using 100 gram (g) samples of homogenized Site soil. The soil microcosm tests consisted of placing 100 g of soil in 4-ounce (oz) glass jars and mixing with 25 milliliters (mL) of oxidant solutions at varying concentrations (5 percent, 10 percent, and 15 percent for hydrogen peroxide and 1 percent, 2 percent, and 3 percent for $KMnO_4$). The jars treated with hydrogen peroxide also received ferrous sulfate at 200 parts per million (ppm) iron (Fe) as a catalyst. Control tests were prepared similarly but without the use of an oxidizing agent solution.

The jars were sealed immediately to prevent losses by volatilization and incubated in the dark at laboratory temperature for two weeks. After one week, it was observed that the purple color had disappeared from all of the jars treated with $KMnO_4$, indicating that all of the oxidant had been consumed. Therefore the lowest treatments for each oxidant were re-dosed such that their final dose was twice as high as the original highest dose. Therefore, for the treatments with $KMnO_4$, the new dose was equivalent to two doses of 3 percent $KMnO_4$ and for Fenton's Reagent the new dose was equivalent to two doses of 15 percent hydrogen peroxide (H_2O_2).

At the end of the incubation period, the microcosms were sampled and analyzed for residual VOCs. The results of these analyses are shown in Tables 4.2 and 4.3.

A loading rate of 15 g/kg $KMnO_4$, which was the highest concentration tested, removed greater than 93 percent of TCE and PCE, greater than 70 percent of the toluene, and ethylbenzene, and greater than 50 percent of 1,1,2-TCE and xylenes (see Figure 4.3). A loading rate of 75 g/kg H_2O_2, which was the highest concentration tested, removed greater than 90 percent of the toluene, greater than 80 percent of TCE and cis-1,2-DCE, greater than 70 percent of PCE and xylenes, and greater than 50 percent of 1,1,2-TCE and ethylbenzene (see Figure 4.4).

4.2.3 EVALUATION OF NATURAL OXIDANT DEMAND

The natural oxidant demand of the soil sample was assessed by placing 50 g of soil in an 8-oz jar and adding 100 mL of 3 percent potassium permanganate. The initial $KMnO_4$ concentration was recorded by measuring the absorbance at 525 nanometers (nm) and comparing to a standard curve. Each week the jar was sampled and the potassium permanganate concentration recorded.

After four weeks, the soil sample had consumed 47.5 g of $KMnO_4$ per kg soil. These data are shown in Table 4.4.

5.0 RECOMMENDATIONS

The results of the pilot studies demonstrate that chemical oxidation treatment of the soil was effective. Treatment with $KMnO_4$ reduced Site-related contaminant concentrations by between 90 percent and 95 percent. Therefore, chemical oxidation treatment would be effective for its intended use at the Site. The $KMnO_4$ treatment would be focused on the most contaminated soil where free product could be present to reduce the initial concentrations and eliminate source material in a short time frame.

The target for concentration reduction of the highly concentrated source material using ISCO is approximately 75 percent. The recommended dose to achieve an approximately 75 percent reduction in the levels of the chemicals of concern is 15 g $KMnO_4$ per kg of soil. In SWMU 5, based on the treatment areas, the thickness of the treatment zone (15 feet), and the anticipated number of injection points based on a radius of influence of 15 feet, it is estimated that approximately 3,720 pounds of $KMnO_4$ will be required per injection event. In SWMU 11, it is estimated that approximately 500 pounds of $KMnO_4$ will be required per event.

The injection pilot study will need to be completed to evaluate the effectiveness of injecting $KMnO_4$ into the subsurface using direct-push technology (DPT). This field test is planned for the near future. Assuming the $KMnO_4$ can be effectively delivered to the treatment zone, six bi-monthly injections of 5.5 percent $KMnO_4$ are recommended to achieve the target VOC reduction. In order to achieve a 5.5 percent solution of $KMnO_4$, the water that will be used to dissolve the $KMnO_4$ must be heated. Either an in-line heater or a submersible heater may be used. From our experience and also from information provided by the $KMnO_4$ supplier, it will be necessary to heat the water to approximately 20°Centigrade (C) or 68°Fahrenheit (F) to achieve a 5.5 percent solution of $KMnO_4$.

6.0 SUMMARY AND CONCLUSIONS

ISCO is an effective technology for treating a wide range of VOCs. The technology is based on the use of strong oxidizing agents to completely oxidize the VOCs within relatively short periods. ISCO was selected to address isolated areas within SWMU 5 and SWMU 11/AOC 2 where elevated levels of VOCs and evidence of free product were observed.

Laboratory studies completed included a NOD study and microcosm studies. Laboratory treatability studies were performed to gather the data necessary to determine:

i) the effectiveness of ISCO for treatment of the VOCs in representative soil and groundwater samples from the Site;

ii) the most effective oxidant for treatment of the Site; and

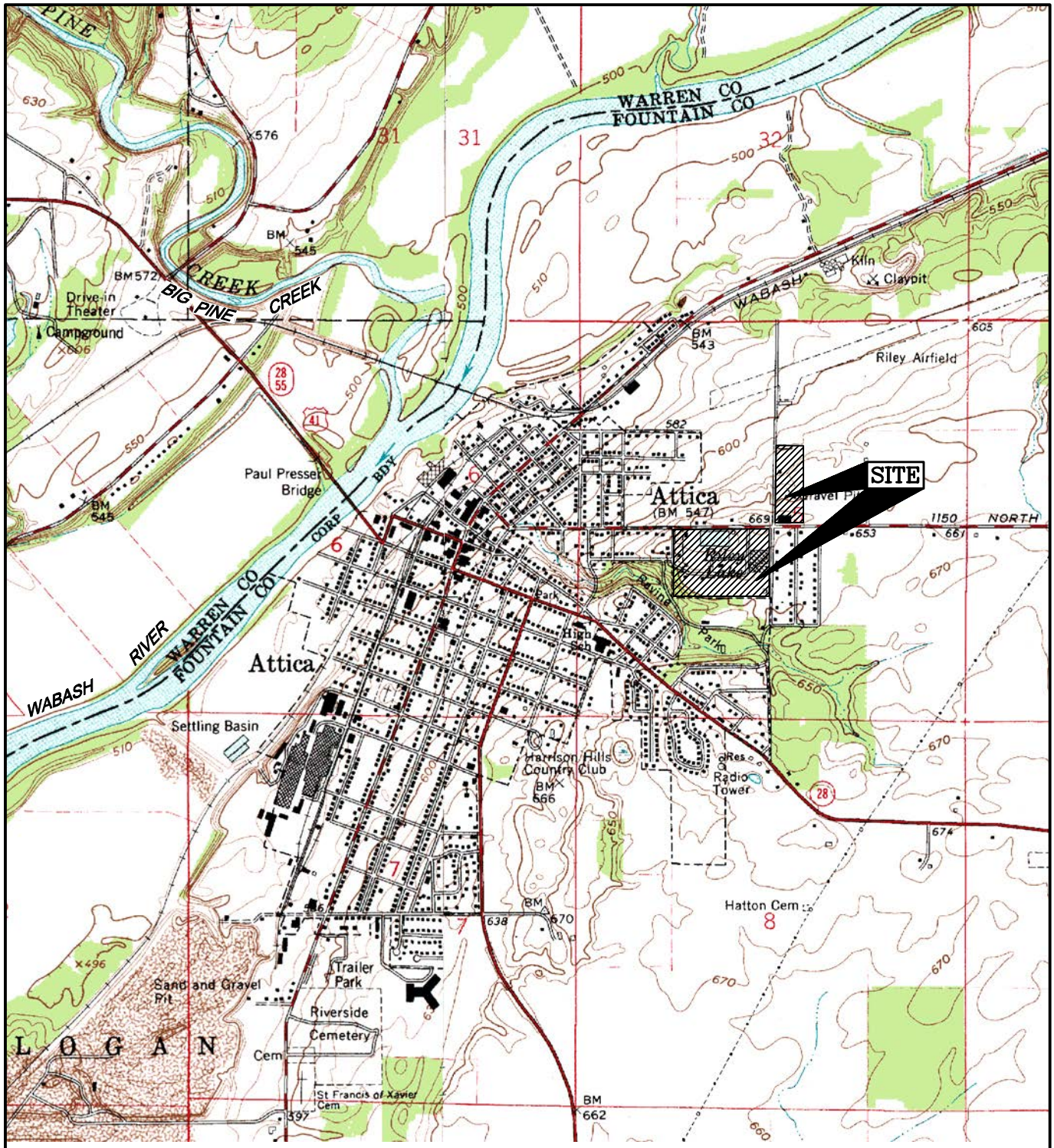
iii) the effective concentration/dosage of oxidant required to complete treatment as expeditiously as possible.

The results of the pilot studies demonstrate that chemical oxidation treatment of the soil was effective. Treatment with $KMnO_4$ reduced Site-related contaminant concentrations by between 90 percent and 95 percent. Therefore, chemical oxidation treatment would be effective for its intended use at the Site.

The following summarizes the significant conclusions of the laboratory studies:

- $KMnO_4$ removed greater than 90 percent of TCE and PCE, which were the compounds present at the highest concentrations in the soil, and 95 percent of the toluene which was the next most concentrated compound present;
- Fenton's reagent, while also effective in removing the chemicals present in high concentrations in the soil, achieved lower removal rates than the $KMnO_4$;
- the NOD of the soil was 47.5 g $KMnO_4$ per kg of soil;
- the recommended dose to achieve an approximately 75 percent reduction in the levels of the chemicals of concern is 15 g $KMnO_4$ per kg of soil;
- it is estimated that approximately 3,720 pounds of $KMnO_4$ will be required per injection event in SWMU 5 and approximately 500 pounds of $KMnO_4$ will be required per injection event in SWMU 11; and
- six bi-monthly injections of 5.5 percent $KMnO_4$ solution are recommended in both treatment areas to achieve the target VOC reduction.

The injection pilot study will need to be completed to evaluate the effectiveness of injecting $KMnO_4$ into the subsurface using DPT. This field test is planned for the near future.



SOURCE: ATTICA AND WILLIAMSPORT, INDIANA
U.S.G.S. TOPOGRAPIC MAPS

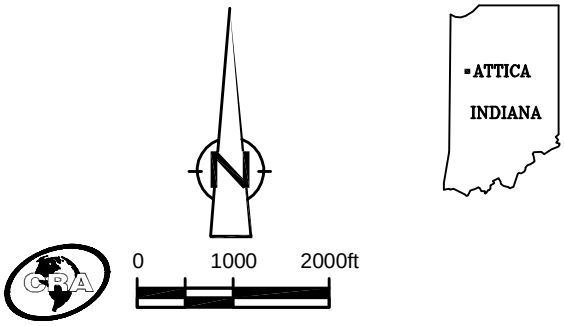


figure 1.1

SITE LOCATION
RADIO MATERIALS CORPORATION
Attica, Indiana

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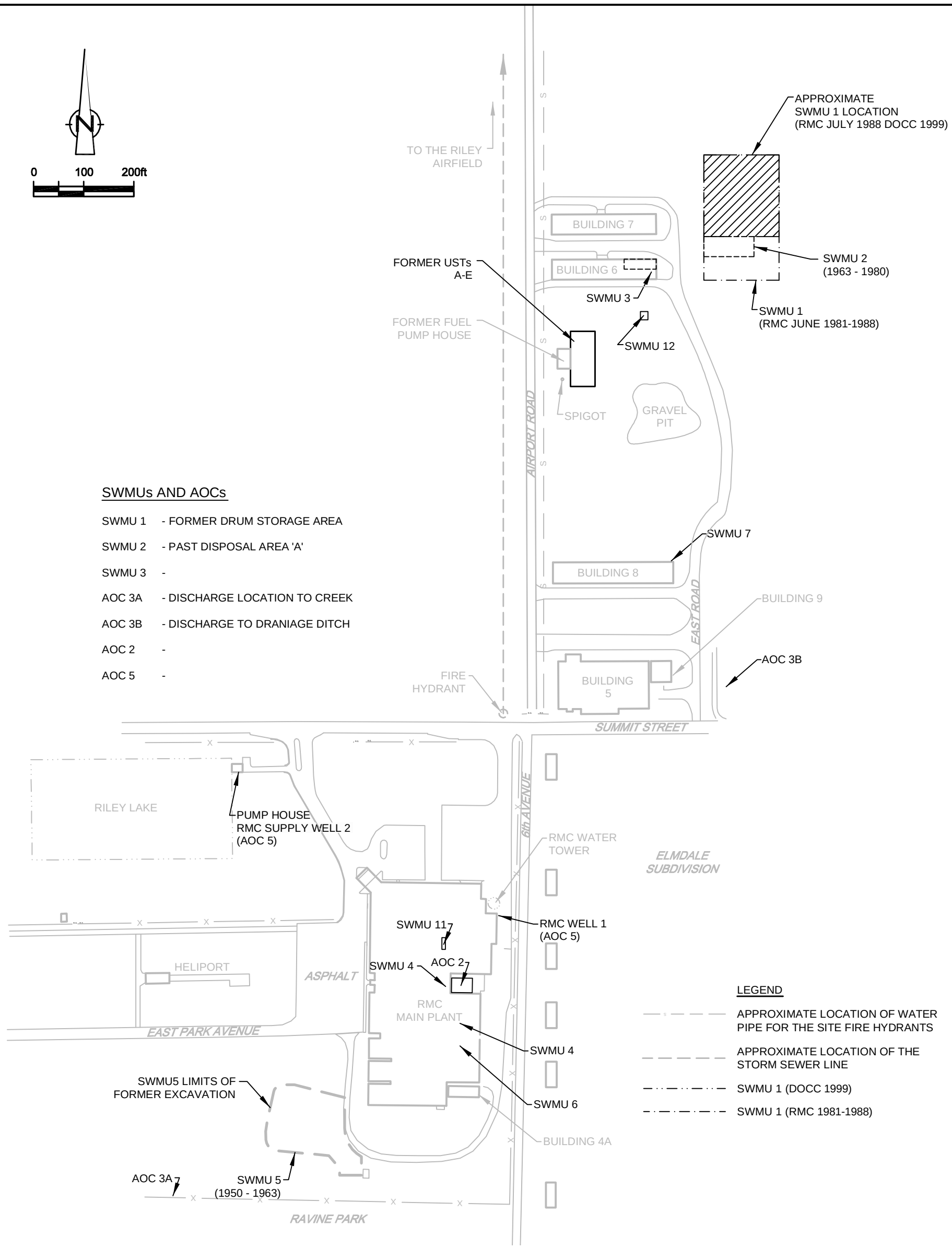

SWMUs AND AOCs

SWMU 1 - FORMER DRUM STORAGE AREA

SWMU 2 - PAST DISPOSAL AREA 'A'

SWMU 3 -

AOC 3A - DISCHARGE LOCATION TO CREEK

AOC 3B - DISCHARGE TO DRANIAGE DITCH

AOC 2 -

AOC 5 -

NOTE:

SWMU 1 APPEARS TO HAVE VARIED IN SIZE FROM THE EXTENTS SHOWN IN RMC DRAWINGS (1981 TO 1988) TO THE DOCC REPORT (1999)

figure 1.2

SITE PLAN WITH SWMUs AND AOCs
RADIO MATERIALS CORPORATION
Attica, Indiana

SOURCE: PHASE I RFI (2000)

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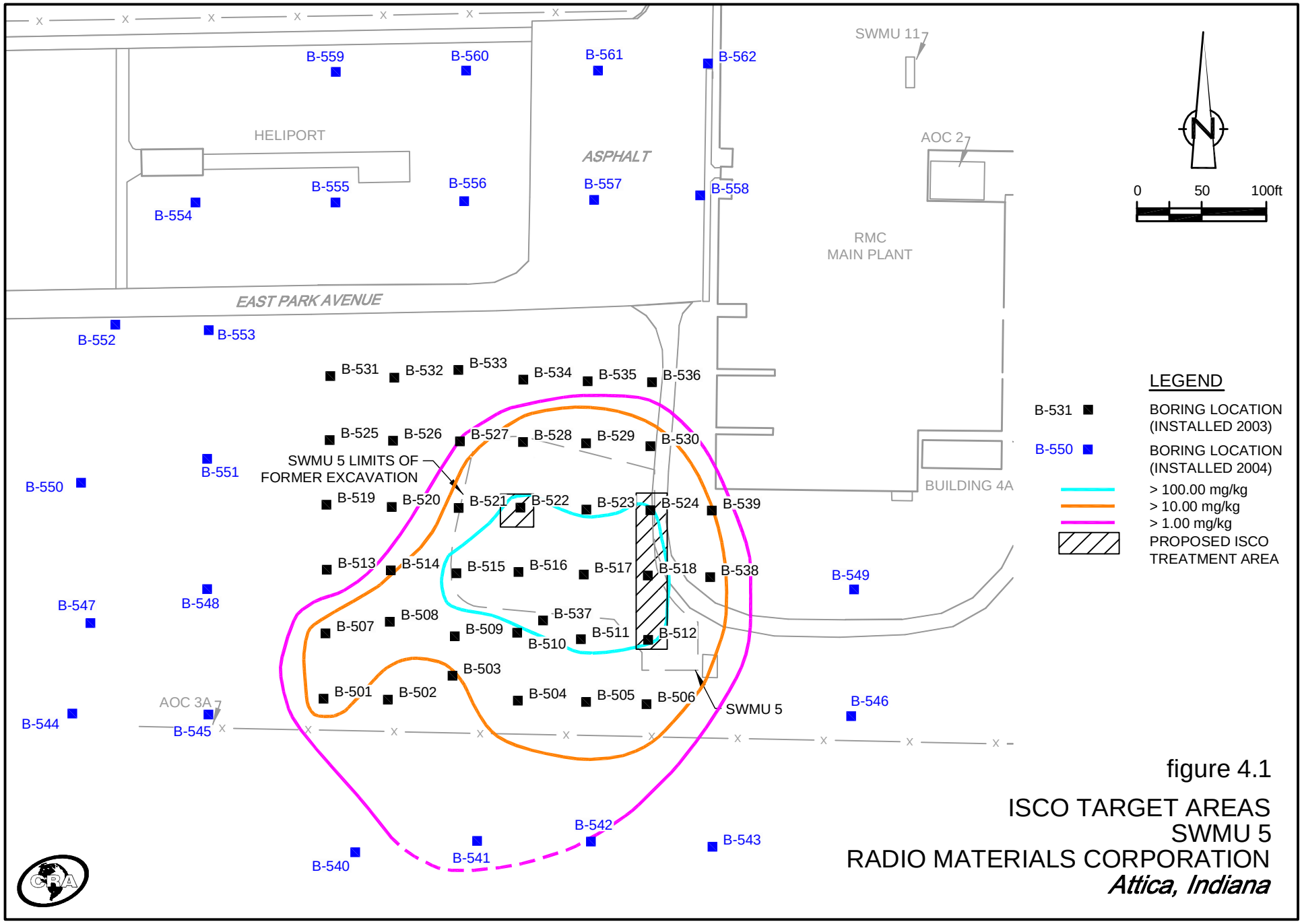

figure 4.1

ISCO TARGET AREAS
SWMU 5
RADIO MATERIALS CORPORATION
Attica, Indiana

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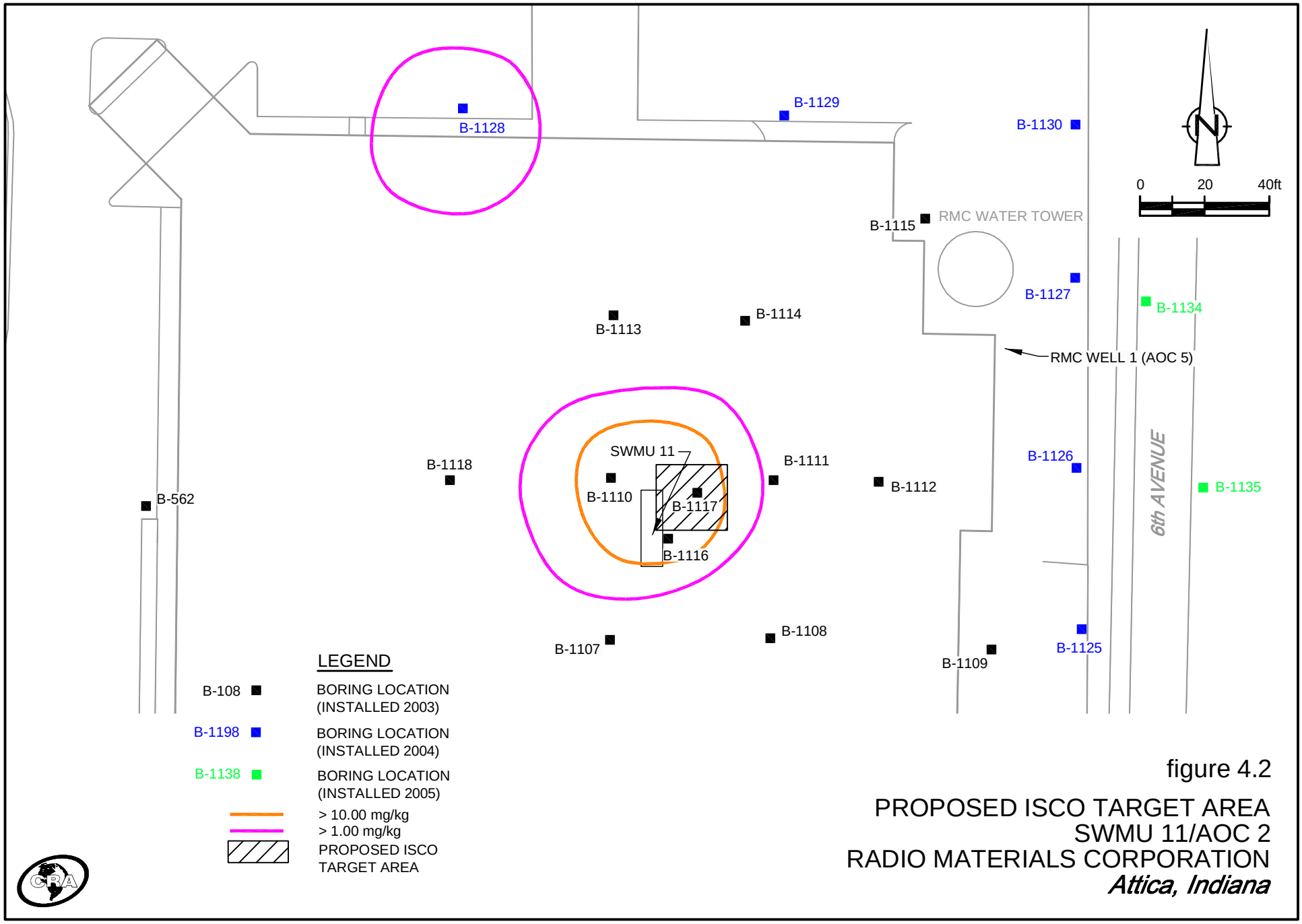

figure 4.2

PROPOSED ISCO TARGET AREA
SWMU 11/AOC 2
RADIO MATERIALS CORPORATION
Attica, Indiana

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Figure 4.3
Percent Removal of VOCs by $KMnO_4$

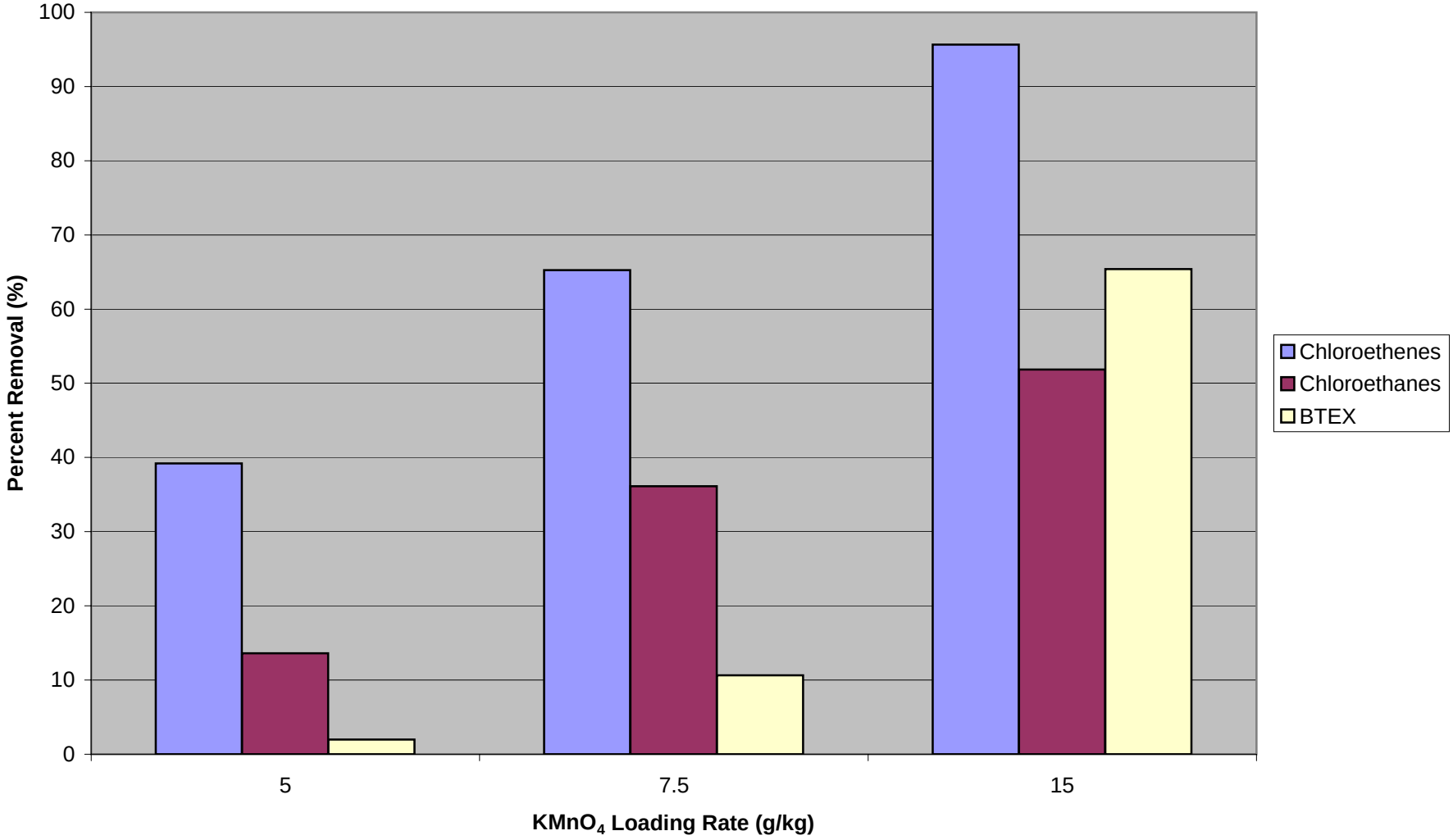

Figure 4.4
Percent Removal of VOCs by Fenton's Reagent

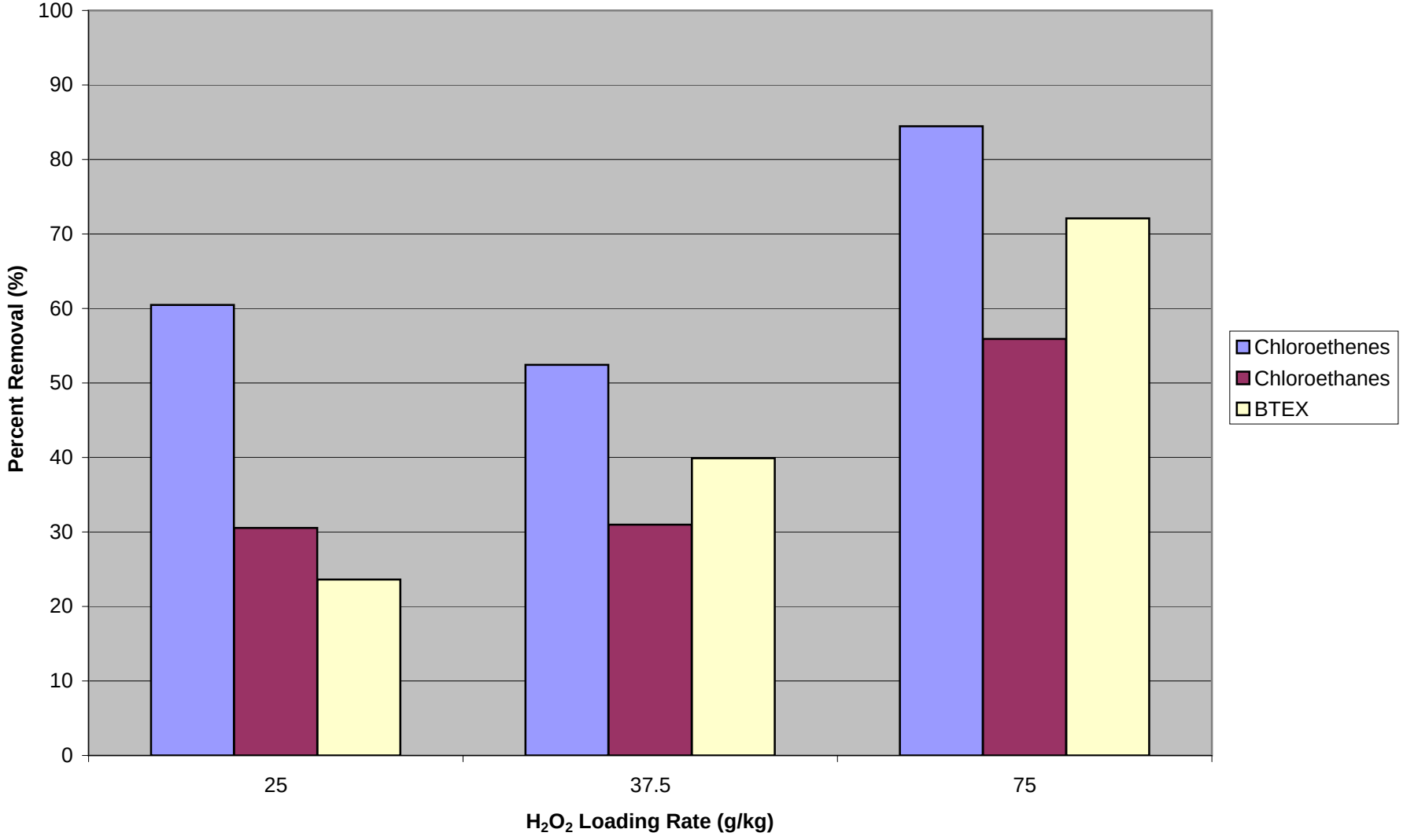

TABLE 4.1

INITIAL ANALYSIS OF SOIL SAMPLE
RADIO MATERIALS CORPORATION
ATTICA, INDIANA

	Units	*S-TS-052306-MG-001*
1,1-dichloroethene	mg/kg	0.087
trans-1,2-dichloroethene	mg/kg	0.0883
cis-1,2-dichloroethene	mg/kg	14.4
trichloroethylene	mg/kg	2520
1,1,2-trichloroethane	mg/kg	0.302
tetrachloroethylene	mg/kg	665
toluene	mg/kg	125
ethylbenzene	mg/kg	1.99
m/p-xylenes	mg/kg	8.03
o-xylene	mg/kg	3.13

TABLE 4.2

CHEMICAL OXIDATION OF SOIL SAMPLE USING $KMnO_4$
RADIO MATERIALS CORPORATION
ATTICA, INDIANA

Treatment	***Units***	***Control***	***2%KMnO $_4$***	***3%KMnO $_4$***	***2x3%KMnO $_4$***
Loading Rate	g/kg	0	5	7.5	15
1,1-dichloroethene	mg/kg	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)
trans-1,2-dichloroethene	mg/kg	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)
cis-1,2-dichloroethene	mg/kg	0.769/0.876	0.578/0.397	0.388/0.167	0.0558/0.0539
trichloroethylene	mg/kg	341/370	92.6/92.2	66.6/31.7	2.97/1.97
1,1,2-trichloroethane	mg/kg	0.159/0.195	0.163/0.143	0.110/0.116	0.0906/0.0796
tetrachloroethylene	mg/kg	151/164	183/123	90.3/88.3	11/6.90
toluene	mg/kg	26.2/29.5	29.2/22.1	17.7/16.6	9.59/5.93
ethylbenzene	mg/kg	0.335/0.349	0.551/0.399	0.331/0.324	0.0525/0.0481
m/p-xylenes	mg/kg	1.70/1.76	2.63/1.80	1.86/1.80	1.050/0.842
o-xylene	mg/kg	0.685/0.707	1.06/0.595	0.753/0.751	0.320/0.253
% 1,1-dichloroethene removal	%	-	n/a	n/a	n/a
% trans-1,2-dichloroethene removal	%	-	n/a	n/a	n/a
% cis-1,2-dichloroethene removal	%	-	40.7	66.3	93.3
% trichloroethylene removal	%	-	74.0	86.2	99.3
% 1,1,2-trichloroethane removal	%	-	13.6	36.1	51.9
% tetrachloroethylene removal	%	-	2.9	43.3	94.3
% toluene removal	%	-	7.9	38.4	72.1
% ethylbenzene removal	%	-	<1	4.2	85.3
% m/p-xylenes removal	%	-	<1	<1	45.4
% o-xylene removal	%	-	<1	<1	58.8

TABLE 4.3

CHEMICAL OXIDATION OF SOIL SAMPLE USING FENTON'S REAGENT
RADIO MATERIALS CORPORATION
ATTICA, INDIANA

Treatment	*Units*	*Control*	*10%H2O2*	*15%H2O2*	*2x15%H2O2*
Loading Rate	g/kg	0	25	37.5	75
1,1-dichloroethene	mg/kg	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)
trans-1,2-dichloroethene	mg/kg	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)	ND (0.05)/ND (0.05)
cis-1,2-dichloroethene	mg/kg	0.769/0.876	0.246/0.504	0.341/0.584	0.183/0.133
trichloroethylene	mg/kg	341/370	152/22.5	115/193	73.1/53.7
1,1,2-trichloroethane	mg/kg	0.159/0.195	0.119/0.126	0.0983/0.146	0.0904/0.0655
tetrachloroethylene	mg/kg	151/164	11.1/15.9	10.1/13.9	3.25/2.10
toluene	mg/kg	26.2/29.5	90.5/117	61/94.5	41.6/35.1
ethylbenzene	mg/kg	0.335/0.349	0.234/0.326	0.168/0.280	0.121/0.0964
m/p-xylenes	mg/kg	1.70/1.76	1.18/1.61	0.761/1.37	0.552/0.408
o-xylene	mg/kg	0.685/0.707	0.437/0.640	0.317/0.575	0.223/0.164
% 1,1-dichloroethene removal	%	-	n/a	n/a	n/a
% trans-1,2-dichloroethene removal	%	-	n/a	n/a	n/a
% cis-1,2-dichloroethene removal	%	-	54.4	43.7	80.8
% trichloroethylene removal	%	-	75.5	56.7	82.2
% 1,1,2-trichloroethane removal	%	-	30.5	31.0	55.9
% tetrachloroethylene removal	%	-	51.5	56.9	90.4
% toluene removal	%	-	34.1	50.6	75.7
% ethylbenzene removal	%	-	18.1	34.5	68.2
% m/p-xylenes removal	%	-	19.6	38.5	72.3
% o-xylene removal	%	-	22.6	36.0	72.2

TABLE 4.4

ANALYSIS OF NATURAL OXIDANT DEMAND
RADIO MATERIALS CORPORATION
ATTICA, INDIANA

	Units	*Soil*
Permanganate concentration at T=0	%	3.56
Permanganate concentration at T=1 week	%	2.31
Permanganate concentration at T=2 weeks	%	0.93
Permanganate concentration at T=3 weeks	%	0.77
Permanganate concentration at T=4 weeks	%	0.74
Amount of permanganate consumed by NOD per kg of soil after 4 weeks	g/kg	47.5