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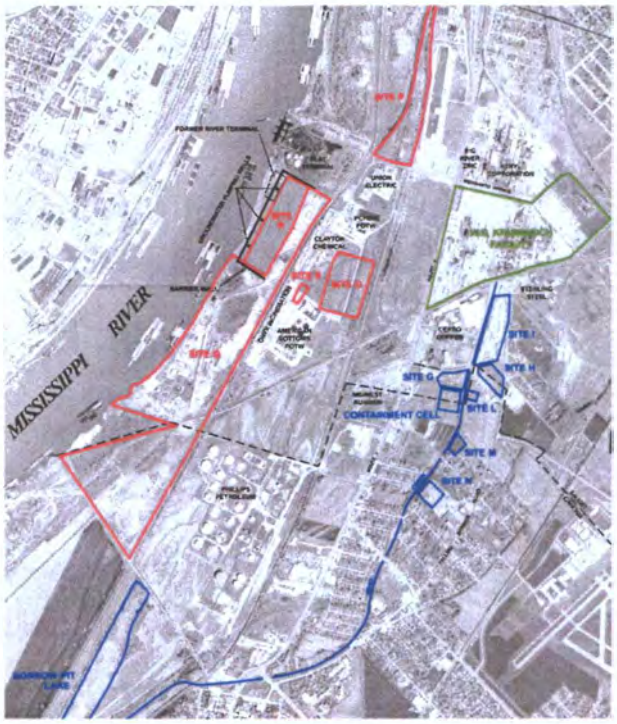
IN-SITU THERMAL DESORPTION WORK PLAN

MASS REMOVAL TREATABILITY STUDY

SOLUTIA INC. W.G. KRUMMRICH FACILITY SAUGET, ILLINOIS



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GROUNDWATER SERVICES, INC.

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IN-SITU THERMAL DESORPTION
WORK PLAN
MASS REMOVAL TREATABILITY TEST

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May 27, 2005

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1.0 INTRODUCTION

On May 3, 2000, USEPA executed a Resource Conservation and Recovery Act (RCRA) 3008(h) Administrative Order on Consent for Solutia Inc.'s W.G. Krummrich facility in Sauget, Illinois (**Figure 1.1**). Solutia Inc. signed the Administrative Order on Consent, Docket No. R8H-5-00-003, on May 26, 2000. Sections VI.1a, 1b, 2, 3 and 5, respectively, required Solutia to submit a Description of Current Conditions Report, investigate the nature and extent of any releases at or from the W.G. Krummrich facility, stabilize groundwater migration and show that any discharge of groundwater to surface water is either insignificant or currently acceptable, control completed pathway human exposures to contamination and propose final corrective measures for the site.

To fulfill the requirements of the AOC Solutia submitted a Description of Current Conditions Report, performed site investigations for air, soil, DNAPL and groundwater, completed Environmental Indicator Determinations for Migration of Contaminated Groundwater under Control (CA750) and Current Human Exposure Under Control (CA725) and submitted a Final Corrective Measures Study as summarized in the following table:

Summary of Work Performed to Fulfill the Requirements of the W.G. Krummrich RCRA AOC (Docket No. R8H-5-00-003)

• Description of Current Conditions Report	August 1, 2000
• Sediment, Surface Water and Fish Tissue Sampling	October and November 2000
• Ecological Risk Assessment	June 1, 2001
• CA750 Migration of Contaminated Groundwater Under Control Environmental Indicator Determination	May 26, 2004
• CA725 Current Human Exposure Under Control Environmental Indicator Determination	May 26, 2004
• Air, Soil, DNAPL and Groundwater Investigation	2003 and 2004
• Corrective Measures Study	August 27, 2004

In addition to these actions, Solutia implemented or planned a number of removal and remedial actions at Sauget Area 1, Sauget Area 2 and the W.G. Krummrich Facility prior to and after the May 26, 2000 RCRA AOC. A time line of the various removal actions and remedial actions and estimated expenditures for each action are given below:

Time Line of Sauget Area 1, Sauget Area 2 and W.G. Krummrich Removal/Remedial Actions and Estimated Expenditures

Sauget Area 1	2001	Dead Creek Culvert Replacement Removal Action	$750,000
	2002	Dead Creek Time Critical Sediment Removal Action	12,300,000
	2004	Dead Creek Segment B, D and F Soil Removal Action Plan	
Sauget Area 2	1979	Site R Capping	
	1985	Site R Riverbank Stabilization	750,000
	2003/4	Groundwater Migration Control System	25,400,000
W.G. Krummrich	1987	Route 3 Drum Site Impermeable Cap	
	2000	Sewer System Improvements	17,100,000
	2001	Chlorobenzene Process Area Spill	
	2003	Plant Process Area Permeable Covers	310,000
		Estimated Total Expenditure	$56,610,000

On November 18, 2004, USEPA issued 51 pages of comments on Volumes I, II and III of the August 27,

2004 W.G. Krummrich RCRA Corrective Measures Study, including 21 general comments and 71 specific comments. In partial response to USEPA's November 18, 2004 comments, Solutia will undertake bench-scale treatability tests to determine whether or not mass removal at the Former PCB Manufacturing Area and the Former Chlorobenzene Process Area is technically practicable. These bench-scale treatability tests are designed to provide a yes/no answer as to whether or not it is technically **feasible** to remove contaminant mass in the Former PCB Manufacturing Area and the Former Chlorobenzene Process Area.

In-situ thermal desorption (ISTD) was identified as the best treatment technology for performing bench-scale PCB and Chlorobenzene (MCB) and Dichlorobenzene (DCB) mass removal treatability tests on unsaturated soil samples from the Shallow Hydrogeologic Unit (SHU) at the Former PCB Manufacturing Area and the Former Chlorobenzene Process Area (**Figures 1.1 and 1.2**). As directed by USEPA, bench-scale thermal treatability tests will also be conducted on saturated SHU soils from the Former Chlorobenzene Process Area.

Unsaturated soils containing PCBs were selected for bench-scale treatability testing because USEPA believes the Former PCB Manufacturing Area presents a potential risk for migration of PCBs via the groundwater pathway. Unsaturated and saturated soils containing MCB and DCB were selected for bench-scale testing because these two constituents are the principal components of the groundwater plume migrating from the W.G. Krummrich facility to the Mississippi River.

This ISTD Work Plan includes the following sections:

Section 1.0	**Introduction**
Section 2.0	**PCB Mass Removal Treatability Test**
Section 3.0	**MCB/DCB Mass Removal Treatability Test**

2.0 PCB MASS REMOVAL ISTD TREATABILITY TEST

2.1 Technology Evaluation

A literature search was conducted to identify technologies tested at bench-scale, pilot-scale or full-scale for their potential to treat unsaturated zone source areas with elevated concentrations of PCBs. The literature search included technical journals, conference proceedings, technical presentations, and Internet databases, such as the EPA Clu-In website. Key findings of the three studies located by this literature search are summarized on **Table 2.1** and the three studies are included in **Appendix A**. Thermal treatment and chemical oxidation were tested in these studies for their potential in addressing unsaturated zone source areas with elevated concentrations of PCBs. These technologies were evaluated for their potential applicability at the W.G. Krummrich Facility based on performance and implementability.

2.1.1 Thermal Treatment

Performance - Thermal treatment is a general term for a variety of approaches designed to destroy or mobilize organic constituent mass *in situ*. High temperature thermal treatment (i.e., in-situ thermal desorption, ISTD) is applicable at sites with PCB contamination in the unsaturated zone if soil temperatures can be raised to the point where soil moisture boils off and the reported distillation range of 275°C to 420°C for PCB mixtures can be reached. Further heating (often > 500°C) will desorb and volatilize PCBs and, when higher temperatures are employed, they can be completely oxidized or pyrolyzed.

Treatment by high-temperature ISTD involves injection of heat into the soil by thermal conduction from a network of heater/vacuum wells. Heat is conducted away from the heater/vacuum wells, raising soil temperatures, while vaporized constituents are drawn back toward the heater/vacuum wells by applied suction. Zones of very high temperature are created between the heater/vacuum wells, which can volatilize, oxidize and/or pyrolize PCBs. Heater/vacuum wells, which are connected to a vapor treatment process system, collect volatilized PCBs, water and carbon dioxide, which are the primary gaseous products of high-temperature ISTD. A ring of heater-only wells, installed around the perimeter of the treatment area outside of the contaminated zone, is used to prevent condensation of contaminant vapors outside the treatment area. This technology is applicable in both fine-grained and coarse-grained soils under a wide range of soil moisture conditions.

Vinegar et al. (1997) reported that a pilot test of high-temperature ISTD decreased PCB soil concentrations from approximately 20,000 mg/kg to less than 1 mg/kg over a 42-day treatment period. Temperatures exceeded 500°C in the interwell regions. Of 94 soil samples collected in the treatment zone after completion of ISTD treatment, 81 samples did not contain PCBs above the detection limit of

0.033 mg/kg. Based on the favorable results of this demonstration, high-temperature ISTD was applied at approximately four additional PCB sites (Ralph Baker, TerraTherm, personal communication, January 31, 2005).

Implementation - Surface and subsurface obstacles, such as buildings, process equipment, and utility corridors could make the application of thermal technologies difficult in some locations.

2.1.2 Chemical Oxidation

Performance - In-situ chemical oxidation (ISCO) acts to deplete source mass via a chemical reaction between a strong oxidant and a chlorinated organic compound with the goal of directly converting the organic compound to CO_2. Mass destruction occurs through a thermodynamically favorable chemical oxidation in which the contaminant accepts electrons generated from the reduction of the added oxidant. The by-products of this reaction are carbon dioxide, water, and chloride. Common chemicals used for this purpose include, in order of decreasing oxidation potential, Fenton's Reagent, ozone, hydrogen peroxide and potassium permanganate ($KMnO_4$).

Cassidy et al. (2002) compared the PCB destruction performance of two oxidants, Chemox (a proprietary solid phase oxidant) and ozone gas, in bench-scale tests. Both oxidants achieved greater than 92% removal of PCBs. In another bench-scale test, Balba et al. (2002) reported a 79% reduction in PCB soil concentrations using potassium permanganate as the oxidant. The authors reported that chemical oxidation was not carried forward for pilot testing because mass removal rates were lower than required to meet remediation objectives.

Implementation - Implementation of in-situ chemical oxidation would require a large network of injection and recovery wells, as well as extensive characterization of the subsurface flow patterns before and after the placement of wells, in order to achieve uniform distribution of oxidant due to heterogeneities within the unsaturated zone.

2.1.3 Selected Technology

Thermal treatment using high-temperature ISTD was selected for treatability testing to determine whether or not source control in the Former PCB Manufacturing Area is technically feasible and cost effective. ISTD is more likely to be successful in treating PCBs in unsaturated source area soils than ISCO and it is easier to implement.

2.2 Soil Sample Location

Environmental Visualization System software (EVS, Version 7.92) was used to define the distribution of PCB mass within the W.G. Krummrich plant process area, identify high mass areas, determine the

geometry of these areas and quantify the amount of PCB mass present in them using existing data. The goal of this modeling was to define a high mass area where soil samples should be collected to perform bench-scale treatability studies.

Table 2.2 presents the EVS modeled PCBs mass and volume in unsaturated soils (0 to 15 ft. bgs.) in the plant process area and in the area with the highest PCB mass (**Appendix B**). **Figure 2.1** is a plan view depiction of PCB concentrations in plant process area unsaturated soils made by flattening the Z-axis (depth axis) of the three-dimensional plot to show the highest concentration in the 0 to 15 foot deep unsaturated zone. Color-coded zones of increasing order of magnitude (1 to 10, 10 to 100, 100 to 1000, 1000 to 10,000 and greater than 10,000 ppm) were created to clearly depict areas of increasing mass.

The Former PCB Manufacturing Area has the highest PCB concentrations within the plant process area (**Figure 2.2**) and contains 3.5 times more PCB mass per cubic yard of soil than in the overall site (0.19 Kg/cy vs. 0.054 Kg/cy):

Area	Volume of PCB-Containing Soil (cubic yards)	Mass of PCBs (Kg)	Percent of Total PCB Volume	Percent of Total PCB Mass	PCB Density Kg /cy
Former PCB Manufacturing Area	24,055	4,478	9.6	38.8	0.19
Overall Plant Process Area	250,710	13,550	100	100	0.054

Notes: 1) Modeled soil volume corresponds to total PCB concentrations greater than 1 mg/kg
2) The confidence of the model ranges from 66 to 100%, which is the key indicator on the confidence of the volume estimates

The PCB ISTD bench-scale treatability test sample will be collected from unsaturated soils in the Former PCB Manufacturing Area from the target depth of 7.5 to 11.5 ft bgs at the location shown on **Figure 2.3** because it is the highest concentration/highest mass location (sample location S0825 at a depth of 9.5 ft bgs) within the plant process area. Sample collection will not be performed until USEPA approves the selected sampling location.

2.3 Soil Sample Collection

Soil samples will be collected as described in the Field Sampling Plan (**Appendix C**). To provide baseline sample characterization information, a soil sample will be collected from the target depth at the approved sampling location, placed in appropriate containers, cooled and shipped at 4°C to Severn Trent Laboratories in Savannah, Georgia for chemical and geotechnical analyses.

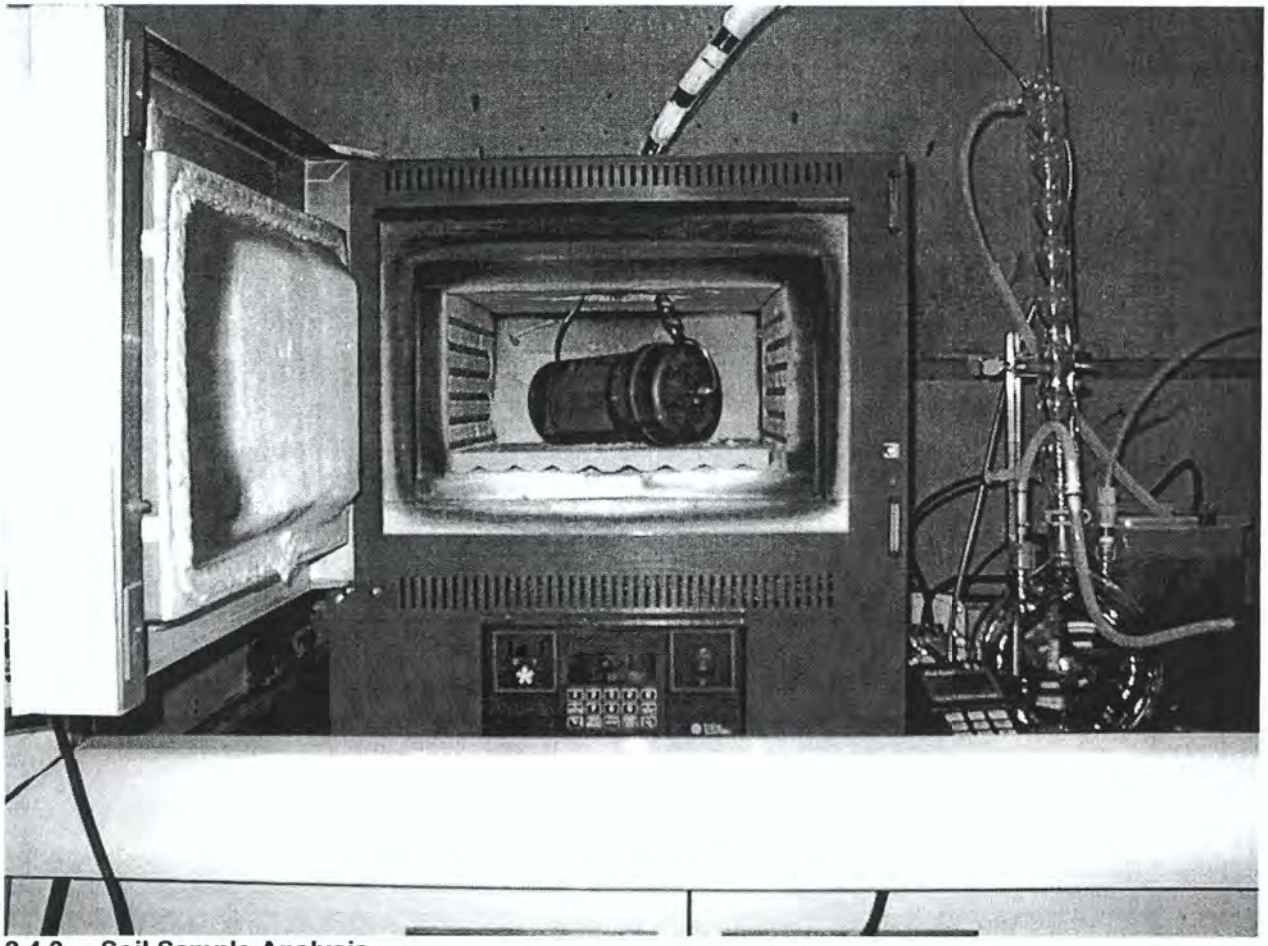
After collection of the baseline sample, approximately 30 kg (66 lbs) of soil will be collected from the target depth at the approved sampling location. The soil sample will be divided into six even sections and each section will be split evenly among six one-gallon containers. After filling the six one-gallon

containers, they will be cooled and shipped at 4°C to Kemron Environmental Services in Atlanta, Georgia for homogenization and separation into bench-test aliquots.

2.4 Treatability Test

2.4.1 Objective and Approach

The objective of the Former PCB Manufacturing Area ISTD treatability test is to determine if PCB mass removal can be achieved through volatilization, oxidation and/or pyrolysis in unsaturated soil from this source area. TerraTherm, the technology vendor, will conduct the treatability tests via a supervised subcontract to a specialty laboratory, Kemron Environmental Services, Inc., Atlanta, Georgia. Target treatment temperatures of 300, 350, and 425°C target temperatures will be maintained for 72 hours on aliquots of the unsaturated SHU soil sample to determine the extent of PCB removal at each temperature. An aliquot of the target depth soil sample will be placed in a cylindrical metal tube and air will be passed through the sample, to simulate vacuum extraction, while heating the assembly within a muffle furnace as shown below. The temperature of the muffle furnace will be set at a target temperature and a thermocouple in the soil sample will allow the soil temperature to be monitored.



2.4.2 Soil Sample Analysis

The baseline soil sample will be analyzed for PCBs, Moisture Content, Particle Size and Permeability by Severn Trent Laboratories using the following methods:

PCB Treatability Test Soil Sample Characterization

Parameter	Analytical Method
Total PCBs	USEPA Method 680
VOCs	USEPA Method 8260B
SVOCs	USEPA Method 8270C
Extractable Organic Halides (EOX)	USEPA Method 9023
Moisture Content	ASTM D 2216
Particle Size	ASTM D 422
Permeability	ASTM D 2434 (Granular Soil) ASTM D 5084 (Fine-Grained Soil)

As directed by USEPA, VOCs, SVOCs and EOX were added to the analytical parameter list. Samples will be analyzed as described in the Field Sampling Plan-Quality Assurance Project Plan (**Appendix C**).

Upon receipt of the soil sample, Kemron will log in the six, one-gallon, untreated soil sample containers and place them in refrigerated storage at a temperature of 4°C. The cooled soil sample will be

homogenized by emptying the six sample containers into a large mixing pan and blending until visually homogeneous using stainless steel utensils. As a part of the homogenization process, any large and/or agglomerated particles will be broken into smaller, more manageable sizes. Kemron will then divide the soil sample into six equal aliquots as shown below:

Bench-Scale PCB Thermal Treatability Test Homogenized Untreated Soil Sample Aliquots

Aliquot	Purpose	Description
• Aliquot 1	Sample Chemical Characterization	PCB, VOC, SVOC and EOX Analysis
• Aliquot 2	Verification of Sample Homogenization	PCB, VOC, SVOC and EOX Analysis
• Aliquot 3	Sample Geotechnical Characterization	Moisture Content and Particle Size Analysis
• Aliquot 4	Treatability Test Sample	300°C Target Temperature
• Aliquot 5	Treatability Test Sample	350°C Target Temperature
• Aliquot 6	Treatability Test Sample	425°C Target Temperature

Aliquots 1, 2 and 3 will be placed in appropriate containers, cooled and shipped at 4°C to Severn Trent Laboratories in Savannah, Georgia for chemical and geotechnical analyses as described above. Results of the baseline and homogenized untreated soil sample analyses will be sent to USEPA. Treatability tests will proceed once the Agency confirms that the PCB concentrations in the treatability study aliquots are representative of site conditions and that the treatability study soil sample is adequately homogenized.

2.4.3 Treatability Test

Thermal treatability tests will be conducted on homogenized soil sample Aliquots 4, 5 and 6 at temperatures of 300, 350, and 425°C, respectively. Bench-scale thermal testing will be conducted using a Fisher Scientific Series 750 muffle furnace (or equivalent) capable of reaching temperatures as high as 2,100°F (1158°C). Temperatures will be recorded with a data logger while the furnace heats up to the target treatment temperature, throughout the duration of treatment and while the testing residuals cool to ambient conditions.

A homogenized soil sample aliquot will be placed into a stainless steel cylinder measuring approximately 6 inches in length and 3 inches in diameter. Cylinder and soil weight will be measured separately and recorded before initiating each thermal treatability test. The cylinder will be placed in the furnace and a temperature probe will be placed through an opening in the roof of the furnace and into the soil for monitoring soil temperature during the testing process. Furnace temperature will then be gradually increased from ambient temperature to the target soil treatment temperature. Once the thermocouple reaches the target treatment temperature, the soil sample will be thermally treated for 72 hours. A 72-hour treatment period (at target temperature) simulates the minimum length of time that the coolest location in a pilot or full-scale treatment zone will be at the target treatment temperature.

At the end of the treatment period, the cylinder will be removed from the furnace and allowed to cool to

room temperature under a fume hood. The final weight of the cylinder and testing residuals will then be measured and recorded prior to post-test sampling and analysis. Each treated aliquot will be analyzed for Total PCBs, VOCs, SVOCs and EOX using the methods described above.

Upon completion laboratory analyses and data validation, a treatability study report that describes testing protocols, treatability test results, and includes all data collected during the study including laboratory notes and reports, will be prepared and submitted to USEPA. Total project duration is expected to be 90 days.

3.0 MCB/DCB MASS REMOVAL ISTD TREATABILITY TEST

3.1 Technology Evaluation

A literature search was conducted to identify technologies with bench-scale, pilot-scale or full-scale treatability tests of unsaturated zone source areas with elevated concentrations of MCB and/or DCB. The literature search included technical journals, conference proceedings, technical presentations, and Internet databases, such as the EPA Clu-In website. Key findings of the two studies located by this literature search are summarized on **Table 3.1** and the two studies are included in **Appendix D**. Thermal treatment and chemical oxidation were tested in these two studies for treating unsaturated zone source areas with elevated concentrations of MCB and/or DCB. These technologies were evaluated for their potential applicability at the W.G. Krummrich Facility based on performance and implementation. Attempts to recover MCB from the unsaturated zone after a 10,000 gallon release at the Former Chlorobenzene Process Area in 2001 demonstrated that dual-phase vapor extraction (DPVE) and pooled product recovery were not effective source control technologies.

3.1.1 Thermal Treatment

Performance - Thermal treatment is a general term for a variety of approaches designed to destroy or mobilize constituent mass *in situ*. Low-temperature in-situ thermal treatment methods involve heating unsaturated soils using electrical resistance heating, steam heating or microwave heating to vaporize and strip low-boiling point volatile organic compounds (B.P. < 100°C) from source area soils. Vacuum wells are necessary to capture and recover the vapor phase constituents. In-situ treatment of unsaturated soils containing high boiling-point volatile and semivolatile organic compounds (B.P. > 100°C), such as MCB and DCB, requires higher temperatures. Higher temperature applications can use thermal conduction to completely boil off all water within the treatment zone, followed by further heating (often > 500°C) to desorb and volatilize semivolatile compounds. When higher temperatures are employed, constituents can be completely oxidized or pyrolyzed. MCB has a boiling point of 132°C; boiling points for the DCB isomers range from 173 to 180°C. This data indicates that high temperature thermal treatment (i.e., in-situ thermal desorption, ISTD) would be needed at sites with MCB/DCB in unsaturated zone source area soils. At sites with MCB/DCB in source area soils, soil moisture would have to be boiled off before volatilization of MCB and DCB could occur.

Treatment by ISTD involves injection of heat into the soil by thermal conduction from a network of heater/vacuum wells. Heat radiates away from the heater/vacuum wells while vaporized constituents are drawn toward the heater/vacuum wells by applied suction from a vapor treatment system. A zone of very high temperatures is created near the heater/vacuum wells, which can oxidize or pyrolize MCB/DCB. The primary gaseous products are volatilized organics, water and carbon dioxide. A ring of heater-only wells is installed around the perimeter of the treatment area, outside of the contaminated zone, to prevent

condensation of contaminant vapors outside the treatment area. This technology is applicable in both fine-grained and coarse-grained soils under a wide range of soil moisture conditions.

Baker et al. (2002) reported that a bench-scale test of ISTD decreased MCB/DCB mass by more than 94%. MCB had the highest mass removal (99.8%), and removal of the three DCB isomers ranged from 94.8% to 97.3%. The authors concluded that ISTD was a viable remedial technology for treatment of MCB and DCB in unsaturated soil.

Implementation - Surface and subsurface obstacles, such as buildings, process equipment, and utility corridors could make the application of thermal technologies difficult in some locations.

3.1.2 Chemical Oxidation

Performance - In-situ chemical oxidation (ISCO) acts to deplete source mass via a chemical reaction between a strong oxidant and a chlorinated organic compound with the goal of directly converting the organic compound to CO_2. Mass destruction occurs through a thermodynamically favorable chemical oxidation in which the contaminant accepts electrons generated from the reduction of the added oxidant. The by-products of this reaction are carbon dioxide, water, and chloride. Common chemicals used for this purpose include, in order of decreasing oxidation potential, Fenton's Reagent, ozone, hydrogen peroxide and potassium permanganate ($KMnO_4$).

Based on the literature search, one site reported the use of chemical oxidation for treatment of soil phase MCB/DCB (**Table 3.1**). Horst et al. (2002) investigated the use of potassium permanganate to treat MCB and 1,2-DCB in bench-scale tests. They observed greater than 99% concentration reduction for both MCB and 1,2-DCB. In a subsequent pilot-test, the authors reported that the oxidant was unable to sustain reaction with the target compounds.

Implementation - Implementation of in-situ chemical oxidation would require a large network of injection and recovery wells, as well as extensive characterization of the subsurface flow patterns before and after the placement of wells, in order to achieve uniform distribution of oxidant due to heterogeneities within the unsaturated zone.

3.1.3 Selected Technology

Thermal treatment using high-temperature ISTD was selected for treatability testing to determine whether or not source control in the Former Chlorobenzene Process Area is technically feasible. ISTD is more likely to be successful in treating unsaturated zone MCB/DCB source areas that ISCO and is easier to implement.

3.2 Soil Sample Location

Environmental Visualization System software (EVS, Version 7.92) was used to identify the highest concentrations of monochlorobenzene (MCB) and total dichlorobenzene (DCB) in unsaturated soils in the plant process area, define the geometry of high mass areas and to quantify the MCB/DCB mass present in unsaturated soils at the site using existing data (**Appendix E**). The goal of this modeling was to define a high mass area where soil samples should be collected to perform bench-scale treatability studies.

Table 3.2 presents the EVS modeled MCB and DCB mass and volume in the unsaturated zone soils over the plant process area and in the area of highest MCB/DCB mass. **Figures 3.1 and 3.2** are plan view depictions, respectively, of maximum MCB and DCB concentrations in the plant process area. In these depictions, the concentrations of MCB and DCB in unsaturated soils (0 to 15 ft. bgs.) are projected to the surface. Color-coded zones of increasing MCB and DCB concentration (1 to 10, 10 to 100, 100 to 250, 250 to 500 and greater that 500 ppm) were created to clearly depict areas of increasing mass.

While several smaller high mass areas are present in the plant process area at the North Tank Farm, the Former Chlorobenzene Storage Area and along a pipe corridor, the Former Chlorobenzene Process Area has the highest MCB/DCB concentrations in the plant process area (**Figures 3.3 and 3.4**). This portion of the plant process area contains roughly 40 percent more MCB mass per cubic yard of soil than the overall site (0.15 Kg/cy vs. 0.11 Kg/cy).

Area	Volume of MCB-Containing Soil (cubic yards)	Mass of MCB (Kg)	Percent of MCB Volume	Percent of MCB Mass	MCB Density Kg /cy
Chlorobenzene Process Area	56,184	8,647	40.7	56.3	0.15
Overall Plant Process Area	138,010	15,350	100	100	0.11

NOTE: 1) Modeled soil volume corresponds to MCB concentrations greater than 1 mg/kg
2) DCB mass is contained within MCB mass, so the volume of the former is not included in table
3) The confidence of the model ranges from 67 to 100%, which is the key indicator on the confidence of the volume estimates

For these reasons, the Former Chlorobenzene Process Area was selected as the location to sample for the MCB/DCB unsaturated and saturated soil thermal treatability tests.

The MCB/DCB ISTD bench-scale unsaturated soil treatability test sample will be a composite of soil collected from near two former borings in the Former Chlorobenzene Process Area. The two borings SCTB67 and K-4 exhibited the highest concentrations/highest mass locations within the plant process area of MCB and DCB, respectively. The MCB portion of the composite sample will be collected from the target depth of 9 to 13 ft bgs at the location shown on **Figure 3.5** (sample location SCTB67 at a depth of

11 ft bgs). The DCB portion of the composite sample will be collected from the target depth of 7 to 11 ft bgs at the location shown on **Figure 3.5** (sample location K-4 at a depth of 9 ft bgs).

The saturated soil treatability test sample will be collected from a target depth of 14.5 to 16.5 ft bgs at the location shown on **Figure 3.6** (sample location K-4 at a depth of 16.5 ft bgs), which is the highest concentration/highest mass location within the plant process area. Sample collection will not be performed until USEPA approves the selected sampling locations.

3.3 Soil Sample Collection

Soil samples will be collected as described in the Field Sampling Plan (**Appendix C**). To provide baseline sample characterization information, a soil sample will be collected from the unsaturated and saturated soil target depths at the approved sampling location, placed in appropriate containers, cooled and shipped at 4°C directly from the site to Severn Trent Laboratories in Savannah, Georgia for chemical and geotechnical analyses.

After collection of the baseline sample, approximately 30 kg (66 lbs) of soil will be collected from the unsaturated soil target depth at the approved sampling location. The unsaturated soil samples will be divided into six even sections and each section will be split evenly among six one-gallon containers. After filling the six one-gallon containers, they will be cooled and shipped at 4°C to Kemron Environmental Services in Atlanta, Georgia for homogenization and separation into bench-test aliquots.

The same procedure will be used to collect the saturated soil target depth sample. Only four one-gallon containers of soil will be required for the saturated SHU treatability test.

3.4 Treatability Test

3.4.1 Objective and Approach

The objective of the Former Chlorobenzene Process Area ISTD treatability test is to determine if MCB/DCB mass removal can be achieved through volatilization, oxidation and/or pyrolysis in unsaturated and saturated soil from this source area. TerraTherm, the technology vendor, will conduct the treatability tests via a supervised subcontract to a specialty laboratory, Kemron Environmental Services, Inc., Atlanta, Georgia. The temperature of the aliquots of the unsaturated SHU soil will be raised to 100, 132, and 200°C to determine the extent of MCB/DCB removal at each temperature. The aliquots of saturated SHU soil will be tested at a target temperature of 100°C until all soil moisture has been removed. For the treatability tests, an aliquot of the target depth soil sample will be placed in a cylindrical metal tube and air will be passed through the sample, to simulate vacuum extraction, while heating the assembly within a

muffle furnace as shown below. The temperature of the muffle furnace will be set at a target temperature and a thermocouple in the soil sample will allow the soil temperature to be monitored.

3.4.2 Soil Sample Analysis

The unsaturated and saturated baseline soil samples will be analyzed for MCB, DCB, VOCs, SVOCs, EOX, Moisture Content, Particle Size and Permeability by Severn Trent Laboratories using the following methods:

MCB/DCB Treatability Test Soil Sample Characterization

Parameter	Analytical Method
MCB/DCB	USEPA Method 8260B
VOCs	USEPA Method 8260B
SVOCs	USEPA Method 8270C
Extractable Organic Halides (EOX)	USEPA Method 9023
Moisture Content	ASTM D 2216
Particle Size	ASTM D 422
Permeability	ASTM D 2434 (Granular Soil) ASTM D 5084 (Fine-Grained Soil)

As directed by USEPA, VOCs, SVOCs and EOX were added to the analytical parameter list. Samples will be analyzed as described in the Field Sampling Plan-Quality Assurance Project Plan (**Appendix C**).

Unsaturated Soil Sample - Upon receipt of the unsaturated soil sample, Kemron will log in the six, one-gallon, untreated soil sample containers and place them in refrigerated storage at a temperature of 4°C. The cooled soil sample will be homogenized by emptying the six sample containers into a large mixing pan and blending until visually homogeneous using stainless steel utensils. As a part of the homogenization process, any large and/or agglomerated particles will be broken into smaller, more manageable sizes. Kemron will then divide the soil sample into six equal aliquots as shown below:

Bench-Scale MCB/DCB Thermal Treatability Test Homogenized Untreated Unsaturated Soil Sample Aliquots

Aliquot	Purpose	Description
• Aliquot 1	Sample Chemical Characterization	MCB/DCB, VOC, SVOC and EOX Analysis
• Aliquot 2	Verification of Sample Homogenization	MCB/DCB, VOC, SVOC and EOX Analysis
• Aliquot 3	Sample Geotechnical Characterization	Moisture Content and Particle Size Analysis
• Aliquot 4	Treatability Test Sample	100°C Target Temperature
• Aliquot 5	Treatability Test Sample	132°C Target Temperature
• Aliquot 6	Treatability Test Sample	200°C Target Temperature

Aliquots 1, 2 and 3 will be placed in appropriate containers, cooled and shipped at 4°C to Severn Trent Laboratories in Savannah, Georgia for chemical and geotechnical analyses as described above. Results of the baseline and homogenized untreated soil sample analyses will be sent to USEPA. Treatability tests will proceed once the Agency confirms that the PCB concentrations in the treatability study aliquots are representative of site conditions and that the treatability study soil sample is adequately homogenized.

Saturated Soil Sample - Upon receipt of the saturated soil sample, Kemron will log in the six, one-gallon, untreated soil sample containers and place them in refrigerated storage at a temperature of 4°C. The cooled soil sample will be homogenized by emptying the six sample containers into a large mixing pan and blending until visually homogeneous using stainless steel utensils. As a part of the homogenization process, any large and/or agglomerated particles will be broken into smaller, more manageable sizes. Kemron will then divide the soil sample into four equal aliquots as shown below:

Bench-Scale MCB/DCB Thermal Treatability Test Homogenized Untreated Saturated Soil Sample Aliquots

Aliquot	Purpose	Description
• Aliquot 1	Sample Chemical Characterization	MCB/DCB, VOC, SVOC and EOX Analysis
• Aliquot 2	Verification of Sample Homogenization	MCB/DCB, VOC, SVOC and EOX Analysis
• Aliquot 3	Sample Geotechnical Characterization	Moisture Content and Particle Size Analysis
• Aliquot 4	Treatability Test Sample	100°C Target Temperature

Aliquots 1, 2 and 3 will be placed in appropriate containers, cooled and shipped at 4°C to Severn Trent Laboratories in Savannah, Georgia for chemical and geotechnical analyses as described above. Results of the baseline and homogenized untreated soil sample analyses will be sent to USEPA. Treatability tests will proceed once the Agency confirms that the PCB concentrations in the treatability study aliquots are representative of site conditions and that the treatability study soil sample is adequately homogenized.

3.4.3 Treatability Test

Unsaturated Soil Sample - Thermal treatability tests will be conducted on the unsaturated homogenized soil sample Aliquots 4, 5, and 6 at temperatures of 100, 132, and 200°C, respectively. Bench-scale thermal testing will be conducted using a Fisher Scientific Series 750 muffle furnace (or equivalent) capable of reaching temperatures as high as 2,100°F (1158°C). Temperatures will be recorded with a data logger while the furnace heats up to the target treatment temperature, throughout the duration of treatment and while the testing residuals cool to ambient conditions.

Each homogenized soil sample aliquot submitted for treatability testing (4, 5, and 6) will be placed into a stainless steel cylinder measuring approximately 6 inches in length and 3 inches in diameter. Cylinder and soil weight will be measured separately and recorded before initiating each thermal treatability test.

The cylinder containing the unsaturated soil sample will be placed in the furnace and a temperature probe will be placed through an opening in the roof of the furnace and into the soil for monitoring soil temperature during the testing process. Furnace temperature will then be gradually increased from ambient temperature to the target soil treatment temperature. Once the thermocouple reaches the target treatment temperature, the soil sample will be thermally treated for 72 hours. A 72-hour treatment period

(at target temperature) simulates the minimum length of time that the coolest location in a pilot or full-scale treatment zone will be at the target treatment temperature.

Saturated Soil Sample - Thermal treatability tests will be conducted on the saturated homogenized soil sample Aliquot 4 at a temperature of 100°C. Bench-scale thermal testing will be conducted using a Fisher Scientific Series 750 muffle furnace (or equivalent) capable of reaching temperatures as high as 2,100°F (1158°C). Temperatures will be recorded with a data logger while the furnace heats up to the target treatment temperature, throughout the duration of treatment and while the testing residuals cool to ambient conditions.

The homogenized soil sample aliquot submitted for treatability testing (Aliquot 4) will be divided and placed into two identical stainless steel cylinders measuring approximately 6 inches in length and 3 inches in diameter. Cylinder and soil weight will be measured separately and recorded before initiating the thermal treatability test. The soil within the cylinders will then be saturated with water and weighed again. This will ensure that any water lost during homogenation and handling is replaced. The difference between the weight of the cylinder and soil following and prior to saturation will determine how much water was added to each sample. One cylinder and soil sample will be dried to determine the saturated moisture content. The second cylinder and soil sample will be submitted for the thermal treatment study.

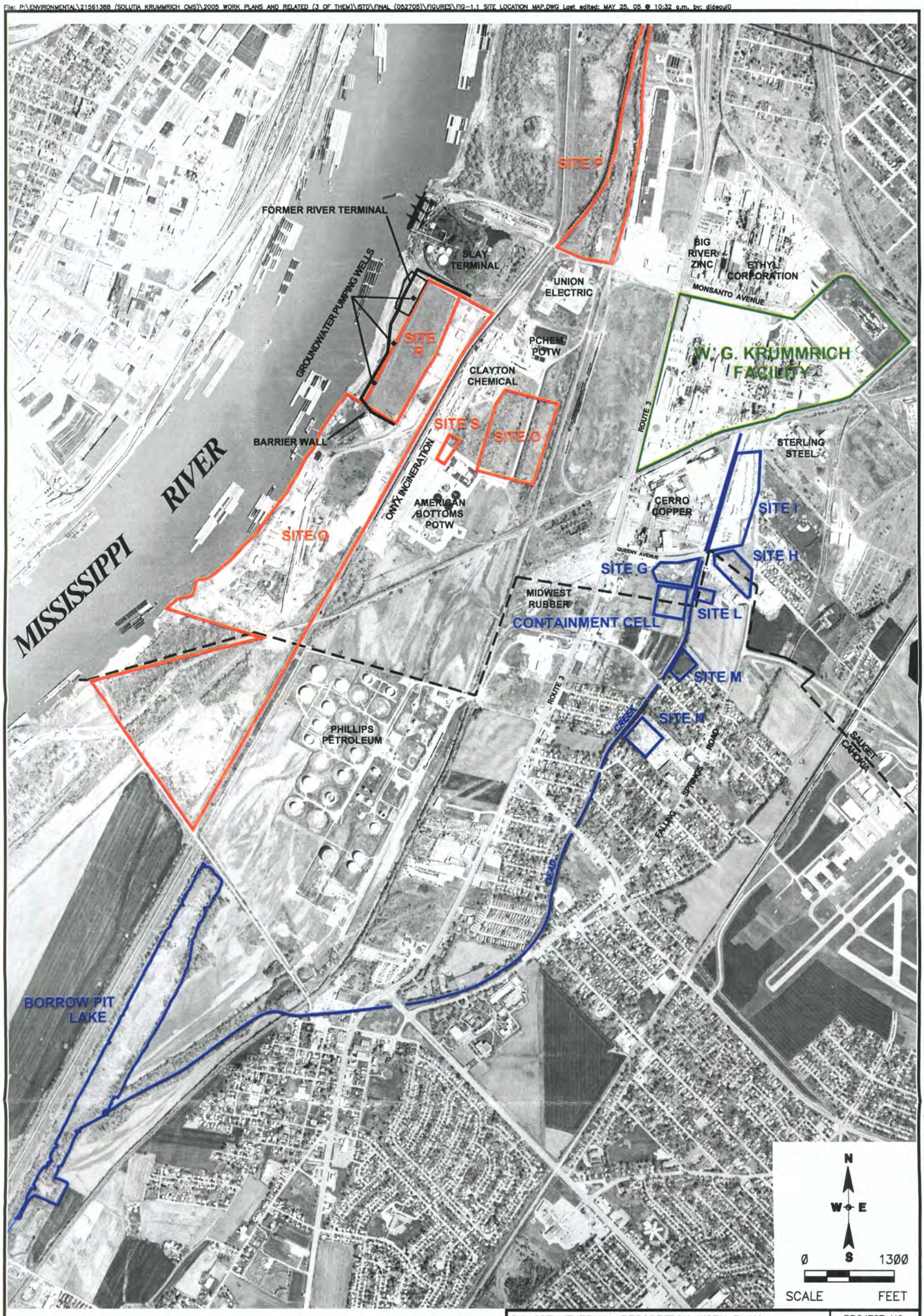
The cylinder containing the saturated soil will be placed in the furnace and a temperature probe will be placed through an opening in the roof of the furnace and into the soil for monitoring soil temperature during the testing process. Furnace temperature will then be gradually increased from ambient temperature to the target soil treatment temperature. Aliquot 4 will be heated until the thermocouple within the soil begins to increase above 100 °C. This will correspond to the point at which all of the water within the sample core has been removed. Aliquot 4 will mimic conditions below the water table and at the edges of the treatment zone where the target treatment temperature may not exceed 100 °C.

At the end of the treatment period, the cylinder will be removed from the furnace and allowed to cool to room temperature under a fume hood. The final weight of the cylinder and testing residuals will then be measured and recorded prior to post-test sampling and analysis. The treated aliquot will be analyzed for MCB/DCB, VOCs, SVOCs and EOX using the methods described above.

Upon completion laboratory analyses and data validation, a treatability study report that describes testing protocols, treatability test results, and includes all data collected during the study including laboratory notes and reports, will be prepared and submitted to USEPA. Total project duration is expected to be 90 days.

Figures

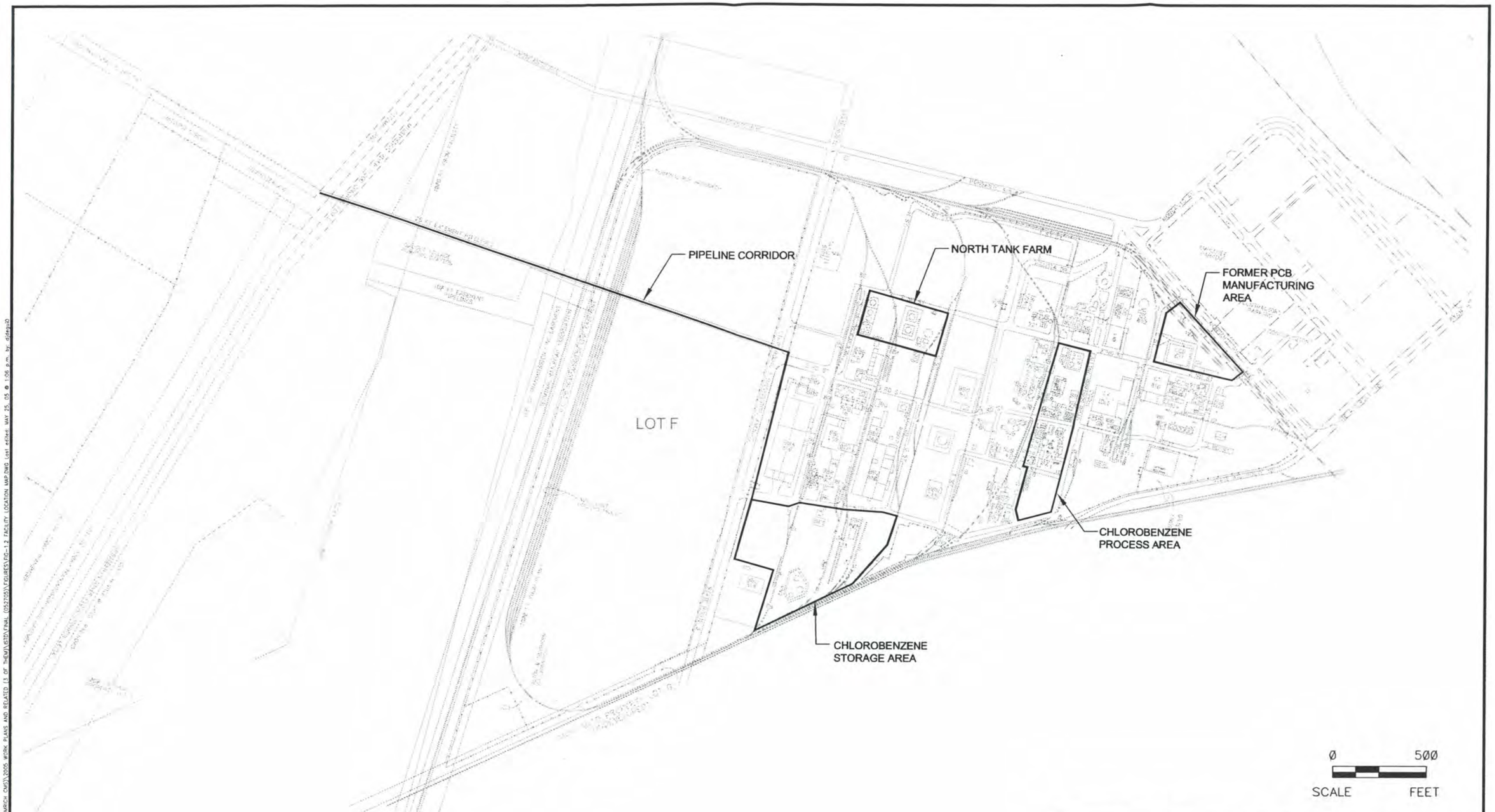
File: P:\ENVIRONMENTAL\21561388 (SOLUTIA KRUMMRICH CMS)\2005 WORK PLANS AND RELATED (3 OF THEM)\ISTD\FINAL (052705)\FIGURES\FIG-1.1 SITE LOCATION MAP.DWG Last edited: MAY 25, 05 @ 10:32 a.m. by: didequi0



LEGEND

- W.G. KRUMMRICH FACILITY
- SAUGET AREA #1
- SAUGET AREA #2

IN-SITU THERMAL DESORPTION WORK PLAN MASS REMOVAL TREATABILITY TESTS W.G. KRUMMRICH FACILITY, SAUGET, ILLINOIS	PROJECT NO. 21561388.00000
URS	
DRN. BY: 2/9/05 DSGN. BY: tja CHKD. BY:	Site Location Map — FIG. NO. 1.1



IN-SITU THERMAL DESORPTION WORK PLAN MASS REMOVAL TREATABILITY TESTS W.G. KRUMMRICH FACILITY, SAUGET, ILLINOIS	PROJECT NO. 21561388.00000

URS

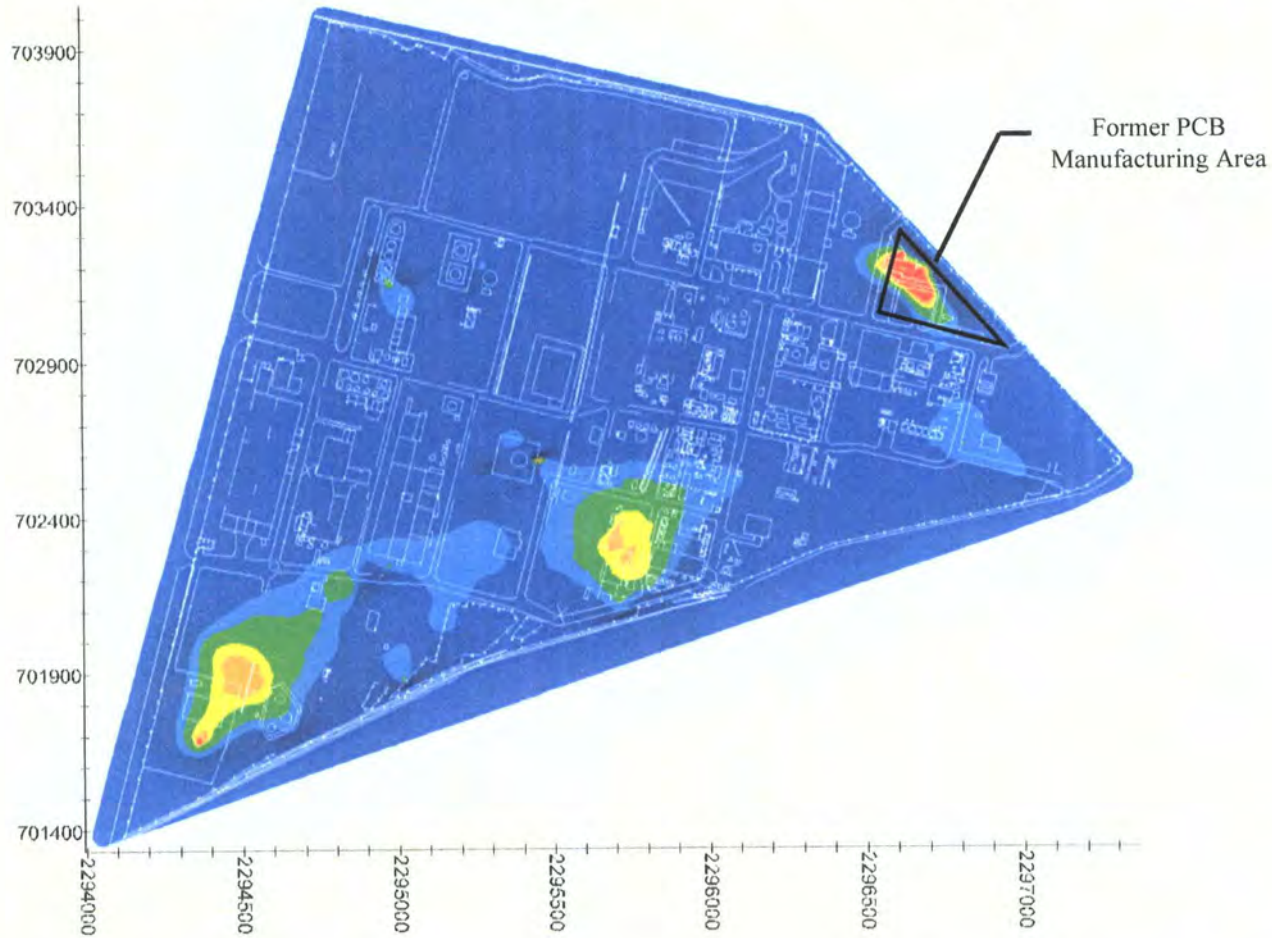
DRN. BY: 4/9/05 DSGN. BY: cm CHKD. BY:	Facility Location Map	FIG. NO. 1.2

File: P:\ENVIRONMENTAL\21561388 (SOLUTIA KRUMMRICH OMS)\2005 WORK PLANS AND RELATED (1 OF THEM)\STDY\FINAL (052705)\FIGURES\FIG-1.2 FACILITY LOCATION MAP.DWG Last edited: MAY 25, 05 @ 1:06 p.m. by: ddeja20

Plan View

URS

PCB Distribution in Unsaturated Soils
[0-15 feet below ground surface (bgs)]



- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

Date:	02/03/05
Figure Number:	2.1
Project Number:	21561573.00000

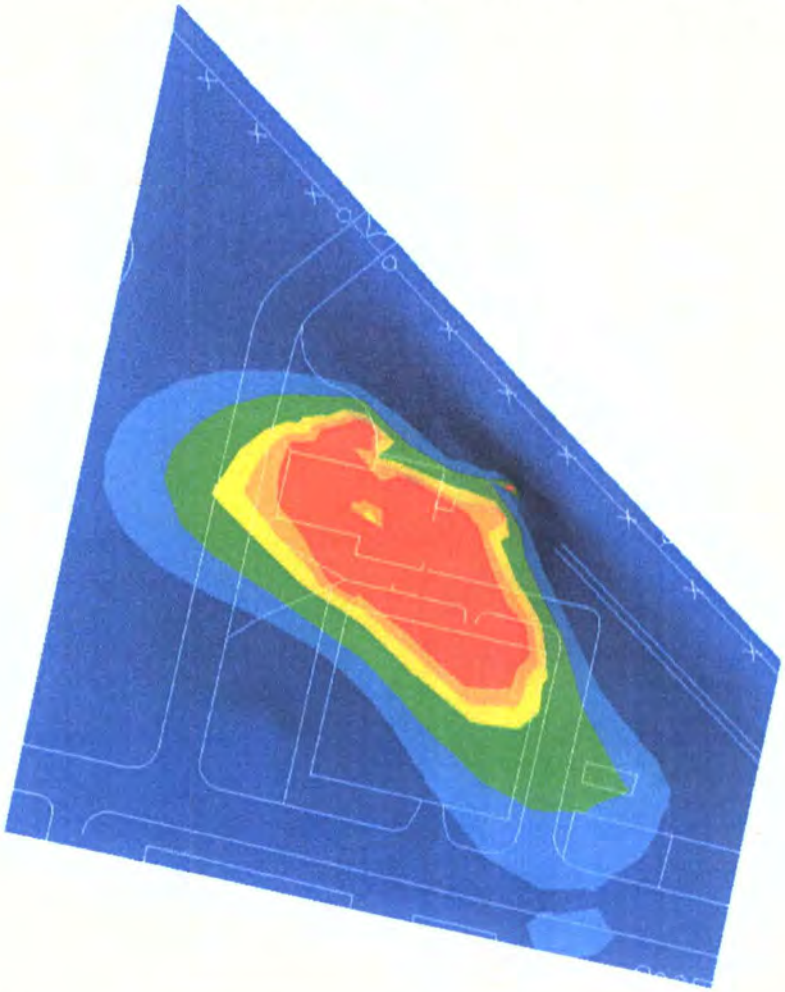
In-Situ Thermal Desorption Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

Plan View

PCB Distribution in Former PCB Manufacturing Area
Unsaturated Soils (0-15 feet bgs)

URS

N



0' 100'

SCALE FEET

- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

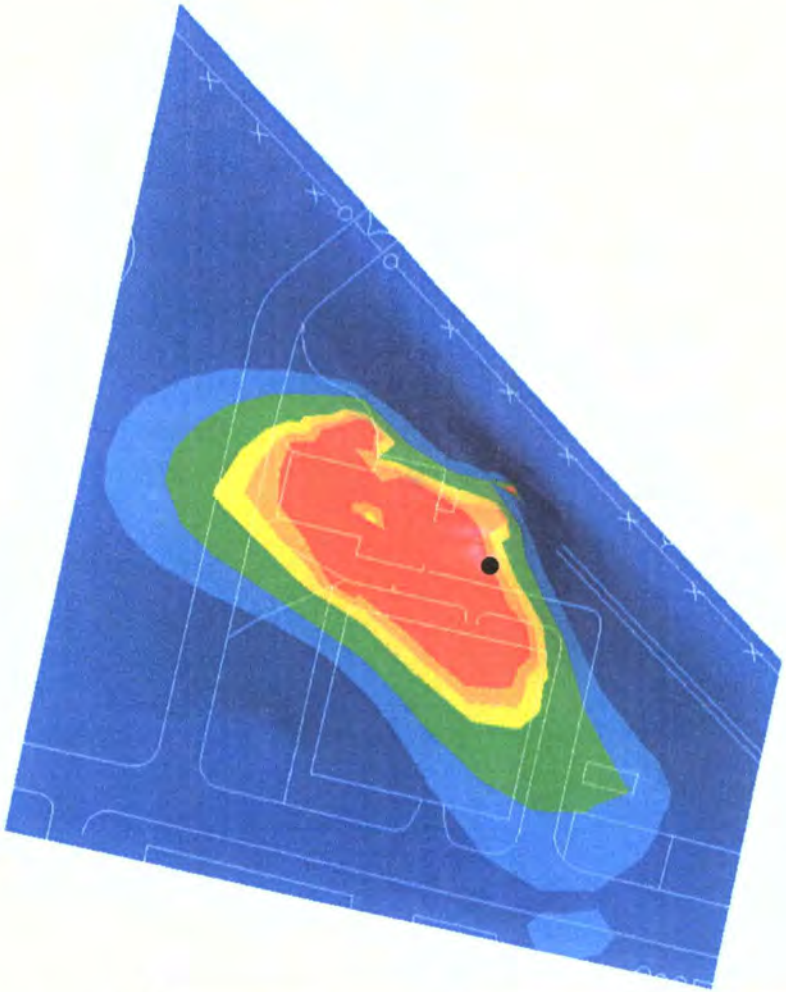
Date:	02/03/05
Figure Number:	2.2
Project Number:	21561573.00000

In-Situ Thermal Desorption Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

Plan View

PCB ISTD Treatability Test Sample Location

URS



N

0' 100'

SCALE FEET

● Sample Location (Near S0825)

<1 ppm	100 to 250 ppm
1 to 10 ppm	250 to 500 ppm
10 to 100 ppm	>500 ppm

SOLUTIA

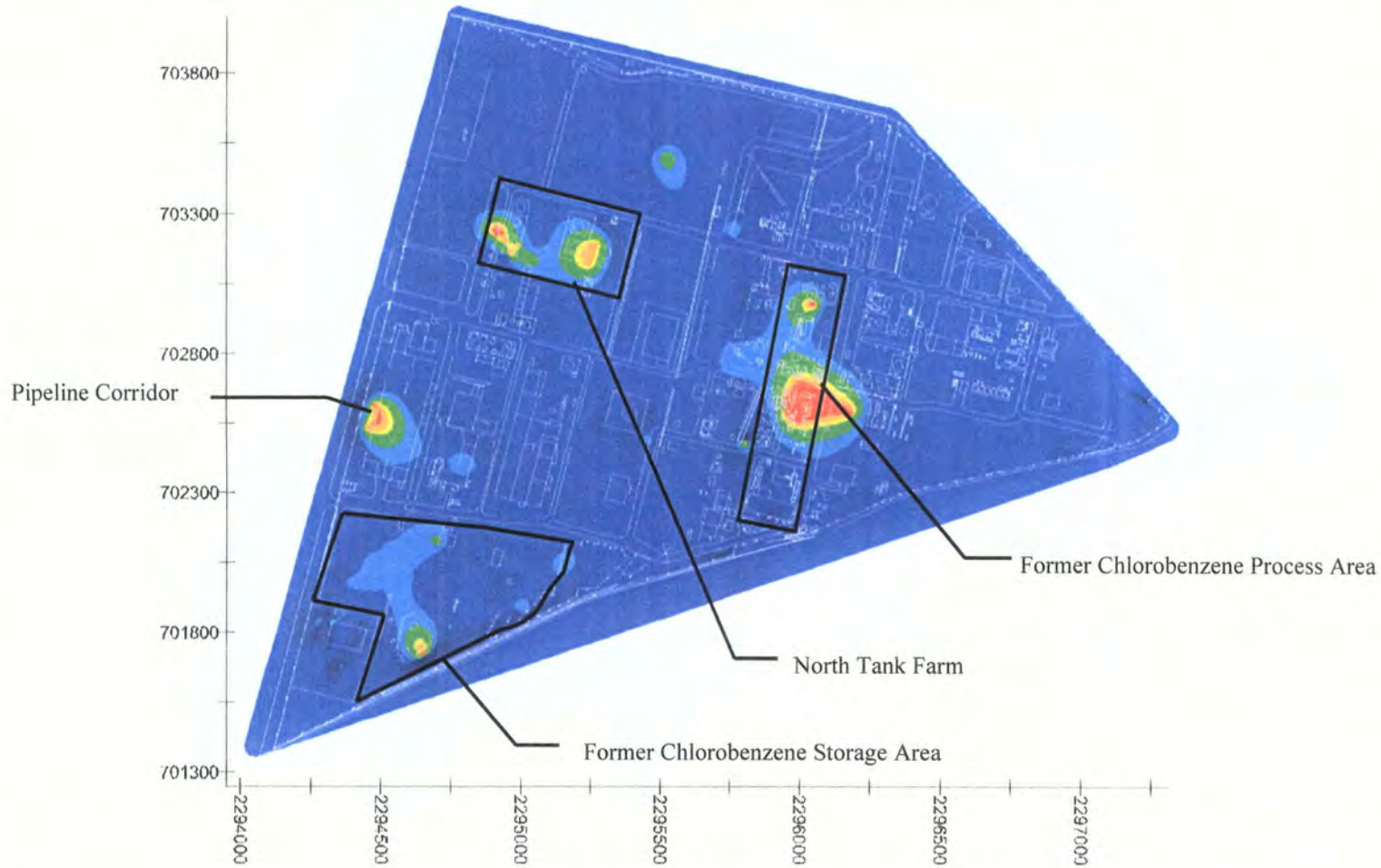
Date:	02/03/05
Figure Number:	2.3
Project Number:	21561573.00000

In-Situ Thermal Desorption Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

Plan View

URS

MCB Distribution in Unsaturated Soils (0-15 feet bgs)



<1 ppm	100 to 250 ppm
1 to 10 ppm	250 to 500 ppm
10 to 100 ppm	>500 ppm

SOLUTIA

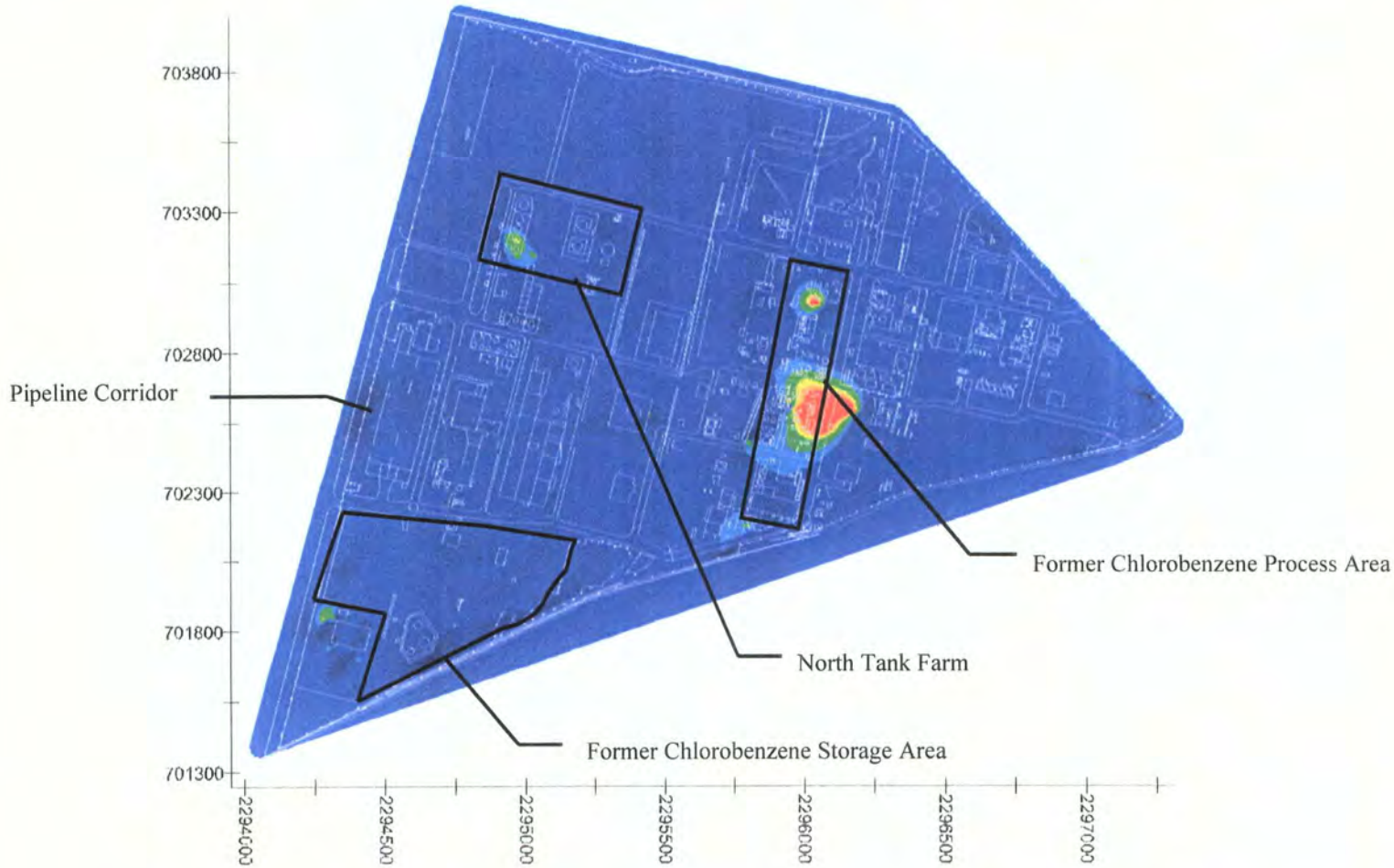
Date:	02/03/05
Figure Number:	3.1
Project Number:	21561573.00000

In-Situ Thermal Desorption Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

Plan View

URS

DCB Distribution in Unsaturated Soils (0-15 feet bgs)



- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

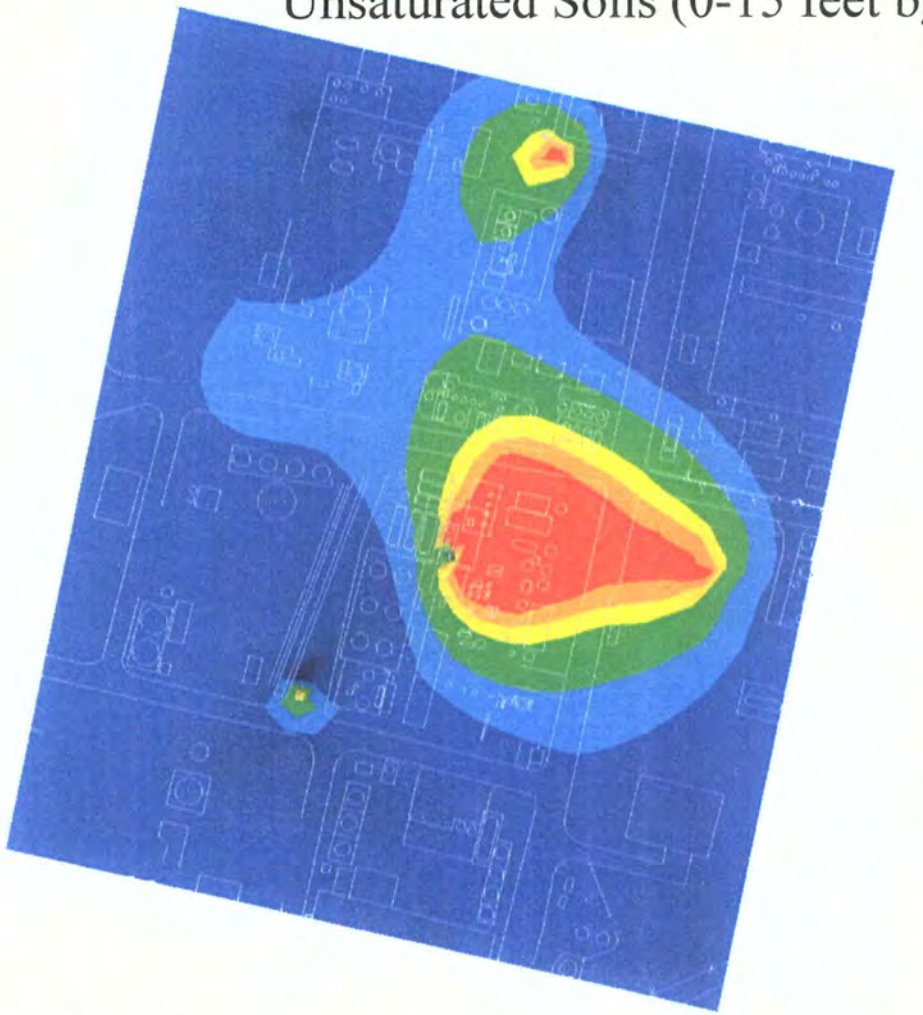
Date:	02/03/05
Figure Number:	3.2
Project Number:	21561573.00000

In-Situ Thermal Desorption Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

Plan View

MCB Distribution in Former Chlorobenzene Process Area
Unsaturated Soils (0-15 feet bgs)

URS



N

0' 100'

SCALE FEET

- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

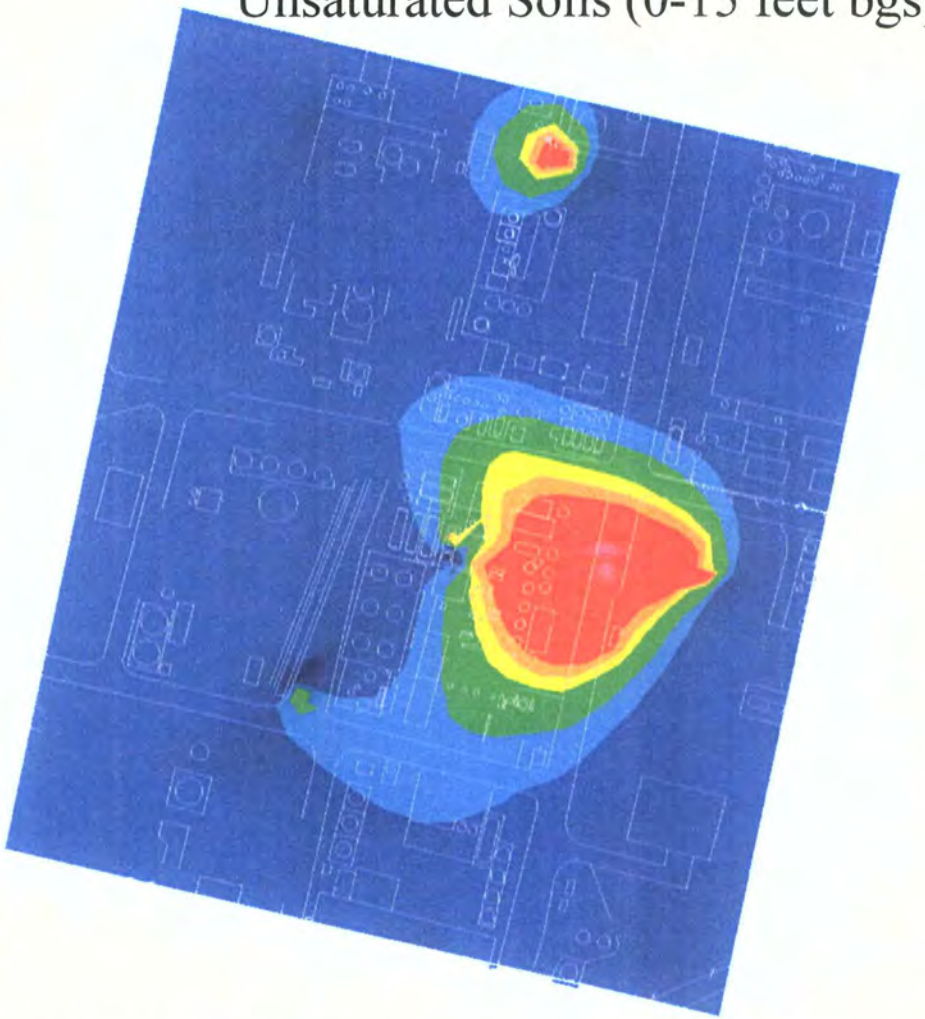
Date:	02/03/05
Figure Number:	3.3
Project Number:	21561573.00000

In-Situ Thermal Desorption Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

Plan View

DCB Distribution in Former Chlorobenzene Process Area
Unsaturated Soils (0-15 feet bgs)

URS



N

0' 100'

SCALE FEET

- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

Date:	02/03/05
Figure Number:	3.4
Project Number:	21561573.00000

In-Situ Thermal Desorption Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

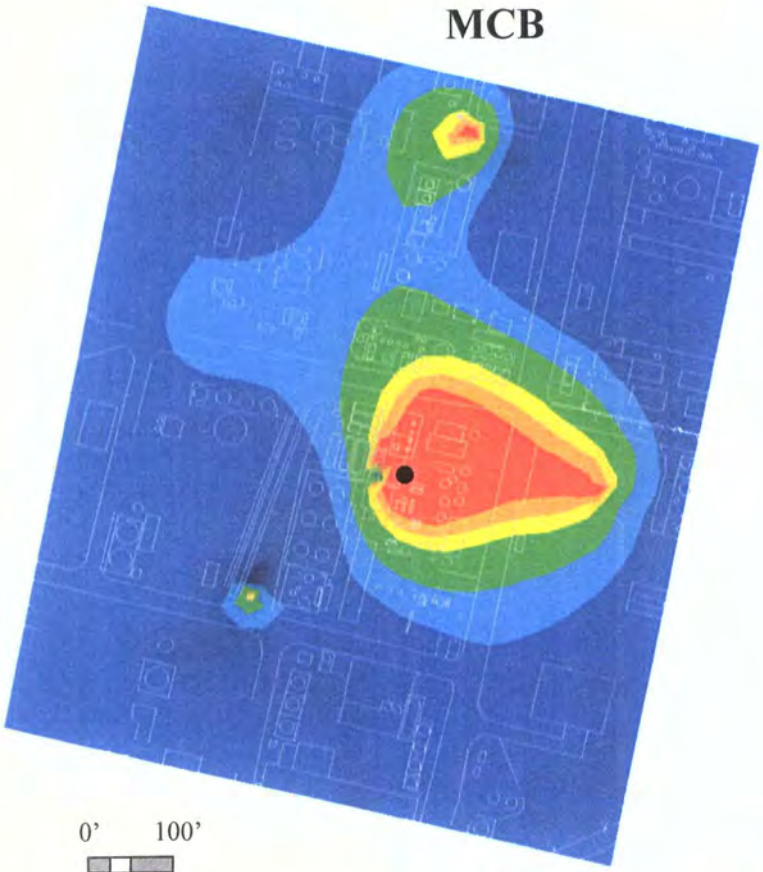
Plan View

MCB/DCB ISTD Unsaturated Soil Treatability Test
Sample Location

URS

N

MCB

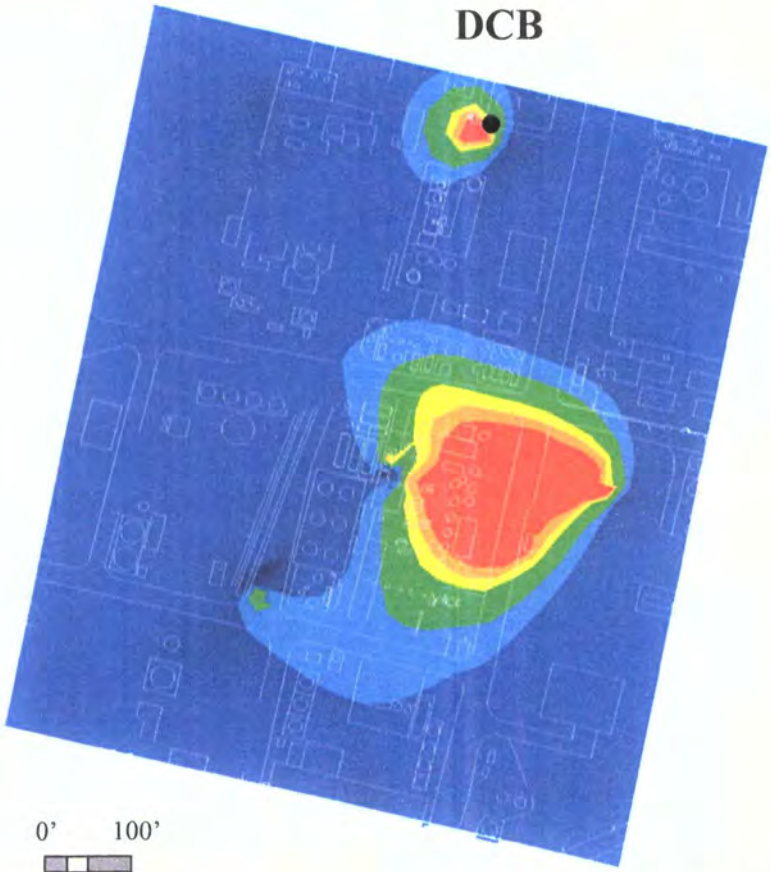


0' 100'

SCALE FEET

● Sample Location (Near SCTB-67)

DCB



0' 100'

SCALE FEET

● Sample Location (Near K-4)

- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

Date:	02/03/05
Figure Number:	3.5
Project Number:	21561573.00000

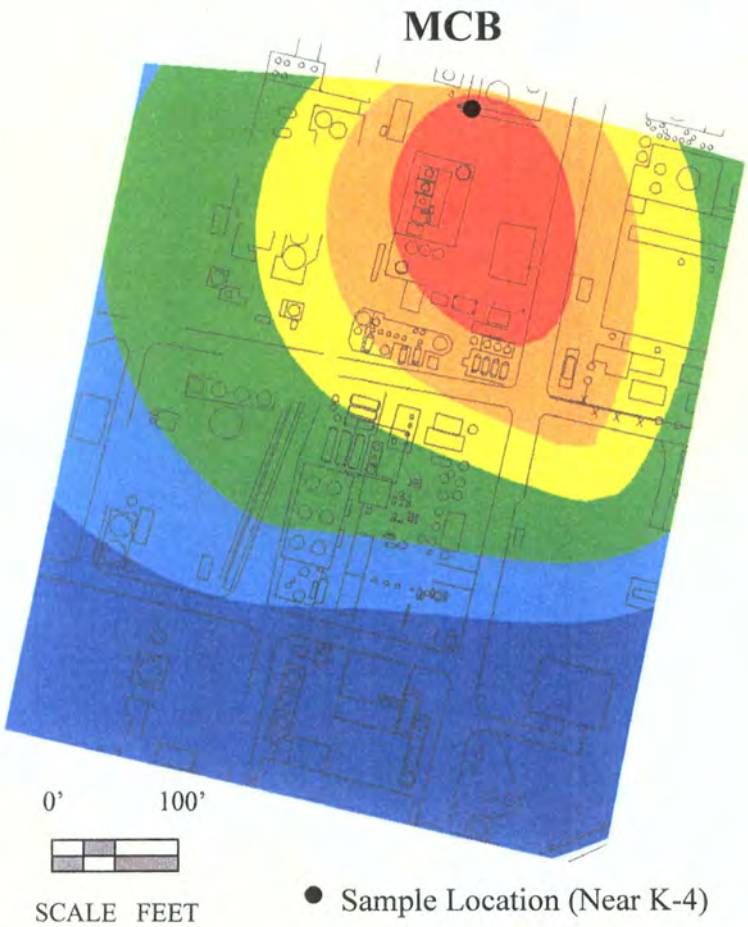
In-Situ Thermal Desorption Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

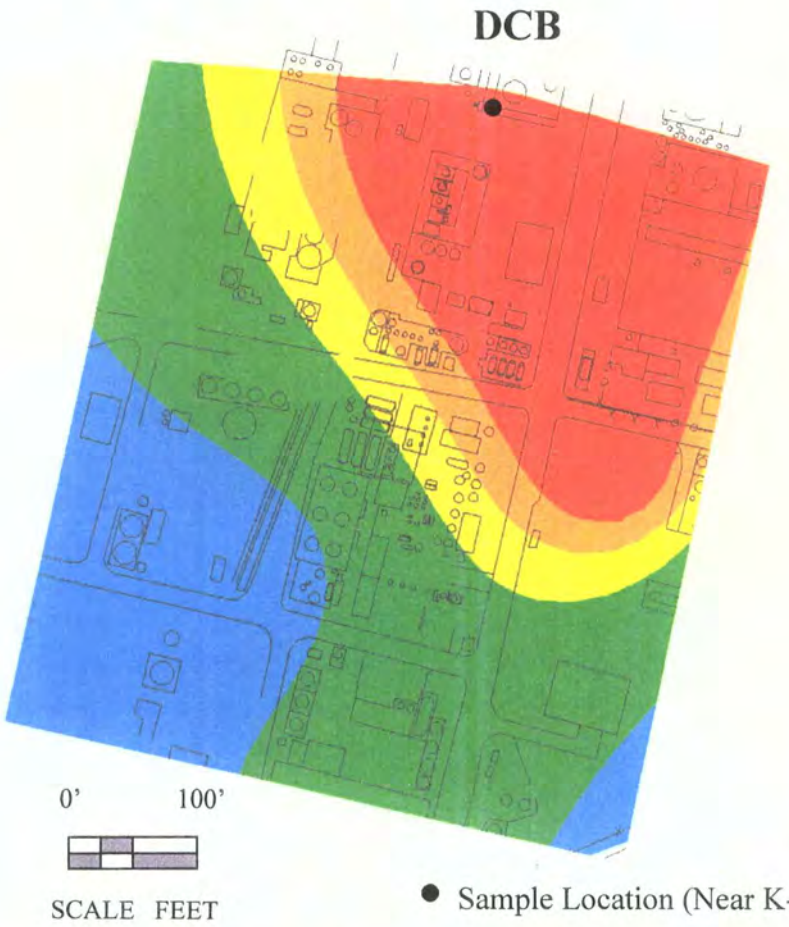
Plan View

MCB/DCB ISTD Saturated Soil Treatability Test
Sample Location

URS

N





- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

Date:	02/03/05
Figure Number:	3.6
Project Number:	21561573.00000

In-Situ Thermal Desorption Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

TABLE 2.1
KEY FINDINGS OF IN-SITU PCB TREATABILITY STUDIES

Solutia Inc., W.G. Krummrich Facility
Sauget, Illinois

Reference	Treatment Scale	Constituent(s)	Initial Conc. (mg/kg)	Conc. Reduction	Treatment Duration	Comments
Chemical Oxidation						
Cassidy et al., 2002	Bench	2-,2'-DCB HCB	1,000 1,000	Chemox: DCB = 99% HCB = 95% Ozone: DCB = 97% HCB = 92%	30 days	• Two oxidants tested: Chemox and ozone gas • Chemox is a solid phase oxidant that requires mixing with affected soil • Ozone sparged continuously at a fixed concentration of 0.5% (v/v) • Final DCB and HCB concentrations were 20 to 40 mg/kg
Balba et al., 2002	Bench	PCBs	202 – 239	79%	1 week	• $KMnO_4$ used in conjunction with ultrasound • $KMnO_4$ resulted in 69% reduction in PCB, and ultrasound increased percentage removal to 79% • Technology not implemented for field testing due low mass removal
Thermal Treatment						
Vinegar et al., 1997	Pilot	PCBs	19,900	100%	42 days	• In-situ thermal desorption (ISTD) • Temperatures above 1000 F achieved within the treatment zone • Post-treatment concentrations of all constituents were below 1 mg/kg

Note:
DCB = 2-,2'-dichlorobiphenyl; HCB = 2-,3-,4-,2'-3'-4'-hexachlorobiphenyl; PCBs = polychlorinated biphenyls; $KMnO_4$ = potassium permanganate

TABLE 2.2
PCB MASS AND VOLUME IN UNSATURATED SOILS
(0-15 FT BGS)

	Soil		Chemical	
	Volume (Cubic Yards)	Mass (Kilograms)	Volume (Cubic Yards)	Mass (Kilograms)
PCB - Plant Process Area				
>1ppm	250,710	354,610,000	12.693	13550
>10ppm	84,522	119,550,000	11.907	12711
>100ppm	20,833	29,467,000	8.9988	9606.6
>250ppm	10,142	14,345,000	6.6683	7118.8
>500ppm	4,585	6,485,300	4.134	4413.3
PCB - Former PCB Manufacturing Area				
>1ppm	24,055	34,024,000	4.1941	4477.5
>10ppm	14,939	21,131,000	4.1066	4384
>100ppm	6,790	9,603,300	3.5205	3758.3
>250ppm	4,039	5,712,500	2.8124	3002.4
>500ppm	2,208	3,123,200	1.9868	2121

Note:

1) ft bgs = feet below ground surface

2) Volume and mass determined with Environmental Visualization Software (Version 7.92)

TABLE 3.1
KEY FINDINGS OF IN-SITU MCB/DCB TREATABILITY STUDIES

Solutia Inc., W.G. Krummrich Facility
Sauget, Illinois

Reference	Treatment Scale	Constituent(s)	Initial Conc. (mg/kg)	Conc. Reduction	Treatment Duration	Comments
Chemical Oxidation						
Horst et al., 2002	Bench	MCB 1,2-DCB	34,333 30,333	99.9% 99.5%	Not reported	• $KMnO_4$ as oxidant • Pilot-scale field testing indicated $KMnO_4$ was unable to sustain reaction with the target compounds
Thermal Treatment						
Baker et al., 2002	Bench	MCB 1,2-DCB 1,3-DCB 1,4-DCB	32 140 6.6 65	99.8% 97.2% 97.3% 94.8%	3 days	• In-situ thermal desorption (ISTD) technology • Tests carried out in 55-gallon drums filled with excavated soil • Results indicated ISTD is a viable remedial approach for remediation of MCB and DCBs

Note:
MCB = monochlorobenzene; DCB = dichlorobenzene; $KMnO_4$ = potassium permanganate

TABLE 3.2
MCB AND DCB MASS AND VOLUME IN UNSATURATED SOILS
(0-15 FT BGS)

	Soil		Chemical	
	Volume (Cubic Yards)	Mass (Kilograms)	Volume (Cubic Yards)	Mass (Kilograms)
MCB - Plant Process Area				
>1ppm	152,630	215,880,000	21.584	18262
>10ppm	61,556	87,066,000	20.962	17735
>100ppm	24,540	34,709,000	18.215	15411
>250ppm	14,777	20,901,000	15.428	13053
>500ppm	9,479	13,407,000	12.288	10396
MCB - Former Chlorobenzene Process Area				
>1ppm	68,293	96,595,000	13.632	11534
>10ppm	32,803	46,397,000	13.404	11340
>100ppm	14,719	20,819,000	12.156	10285
>250ppm	9,497	13,432,000	10.647	9007.9
>500ppm	6,388	9,034,700	8.7048	7364.8
DCB - Plant Process Area				
>1ppm	63,500	89,817,000	9.4896	9276.7
>10ppm	32,471	45,927,000	9.2645	9056.6
>100ppm	12,468	17,635,000	8.1886	8004.9
>250ppm	7,956	11,253,000	7.0928	6933.7
>500ppm	4,885	6,909,600	5.4836	5360.5
DCB - Former Chlorobenzene Process Area				
>1ppm	53,507	75,681,000	9.2821	9073.8
>10ppm	29,189	41,286,000	9.1042	8899.9
>100ppm	12,132	17,160,000	8.1418	7959.1
>250ppm	7,935	11,224,000	7.0891	6930
>500ppm	4,885	6,909,500	5.4836	5360.5

Note:

1) ft bgs = feet below ground surface
2) Volume and mass determine with Environmental Visualization Software (Version 7.92)

IN-SITU PCB TREATABILITY STUDIES

Paper 2C-27, in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds—2002*. Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2002). ISBN 1-57477-132-9, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

COMPARATIVE STUDY OF CHEMICAL OXIDATION AND BIODEGRADATION OF PCBs IN SEDIMENTS

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(Western Michigan University, Kalamazoo, MI, USA)
H. Eric Nuttall (University of New Mexico, Albuquerque, NM , USA)
William L. Lundy (billlundy@msn.com), (BMS, Inc., Tinley Park, IL, USA)

ABSTRACT: Laboratory experiments were done to test the feasibility of ozone and a newly developed solid chemical oxidation reagent *(chemox)* to oxidize PCBs in sediments, and to determine the nature and biodegradability of the oxidation products. Two PCBs were tested; 2-,2'-dichlorobiphenyl (DCB) and 2-,3-,4-,2'-,3'-,4'-hexachlorobiphenyl (HCB). DCB and HCB were allowed to adsorb onto kaolinite. Concentrations of PCBs, Cl^-, and chemical oxygen demand (COD) were measured during 30 days of oxidation with ozone and a newly developed solid chemical oxidation reagent *(chemox)*. Gas chromatography/mass spectrometry (GC/MS) was used to identify the organic acids produced from reaction of both oxidants with DCB and HCB. After chemical oxidation, the liquid was treated for 20 days in bioreactors with inoculum from a domestic wastewater treatment plant. A newly developed solid chemical oxidation reagent *(chemox)* removed 99% of DCB and 95% of HCB. Removal of DCB and HCB with ozone was 97% and 92%, respectively. Oxidation products were identical with both oxidants. Formic and oxalic acid were oxidation products of both PCBs. Specific oxidation products of DCB and HCB were 2-hydroxybenzoic acid and 2,3,4-trihydroxybenzoic acid, respectively. The results show that ozone and a newly developed solid chemical oxidation reagent *(chemox)* caused ring cleavage of PCBs and quantitative removal of Cl. In excess of 93% of the soluble COD remaining after chemical oxidation with both oxidants was biodegradable within 20 days.

INTRODUCTION

Remediation of sediments contaminated with polychlorinated biphenyls (PCBs) is among the more intractable environmental problems. Dredging is the most common remedial method, but is problematic because it suspends sediments in the water column and cannot remove all of the sediments. For example, two years after dredging 147,000 cubic meters of sediment in Lake Jarnsjon, Sweden, the PCB concentration in one-year old fish was twice the pre-remediation value (Bremle, 1997). Post-dredging PCB levels in carp at Waukegan Harbor, Illinois, were five times greater than pre-remediation values (U.S. EPA, 1994). Moreover, the two most common disposal methods for PCB-contaminated sediments, landfilling and incineration, pose tremendous permitting problems and are very expensive. Maintenance dredging is required in many waterways, and if dredged material is contaminated a suitable ex situ remediation strategy is needed. One approach is a to combine of chemical and biological oxidation of contaminants.

Fenton's reagent, a commonly used oxidant consisting of H_2O_2 and Fe^{2+}, produces free radicals that oxidize organic compounds. Aronstein and Rice (1995) reported that adding Fenton's reagent to PCB-contaminated soil increased the overall

extent of PCB biodegradation by over 7 times relative to not adding the oxidant. However, there are several problems associated with Fenton's reagent. It works best at a pH below 3 (Carberry and Yang, 1994), which would require subsequent pH adjustment to encourage biological activity. Fenton's reagent also releases considerable heat upon reaction, which can volatilize contaminants and kill biota. A newly developed solid chemical oxidation reagent *(chemox)* uses Fenton-like chemistry but contains proprietary stabilizers that reduce the exothermic nature of the reactions, allow it to work at pH values between 7 and 8, and increase the residence time of the oxidant. A newly developed solid chemical oxidation reagent *(chemox)* can be added in dissolved or solid form, and has been shown to be effective at oxidizing chlorinated solvents (Nauta and Lundy, 1999) and pesticides (Holish, Lundy and Nuttall, 2000).

Ozone produces hydroxyl free radicals, but does so at a neutral pH and without releasing heat to a degree that interferes with biological activity (Narkis and Schneider-Rotel, 1980). Ozone also dissolves readily in water (ozone is 13 times more soluble than oxygen). Ozone sparging has proven effective at oxidizing polycyclic aromatic hydrocarbons (PAH) in sediments (Clayton, 1998; Brown et al., 1997; Nelson et al., 1997). Ozone increased the biodegradability of heavily chlorinated guaiacol (2-methoxy phenol) 10 times by replacing chlorine atoms with hydroxyl groups (Heinzle et al., 1995).

The goals of this study were to test the effectiveness of ozone and a newly developed solid chemical oxidation reagent *(chemox)* as chemical oxidants of PCBs, and to characterize the oxidation products and their potential to be degraded by common environmental microorganisms.

MATERIALS AND METHODS

Materials. All chemicals were obtained from Aldrich (Milwaukee, Wisconsin), except a newly developed solid chemical oxidation reagent *(chemox)*, which was obtained from BMS, Incorporated (Tinley Park, Illinois). The concentration of hydrogen peroxide in the a newly developed solid chemical oxidation reagent *(chemox)* formulation was 28.5%. Kaolinite was obtained from Fisher Scientific (Chicago, Illinois).

Slurry Preparation. Separate kaolinite slurries were spiked with DCB and HCB (1000 mg/kg) and were mixed for 4 months to promote adsorption. Slurries were then thickened a solids concentration of approximately 1800 kg/m^3.

Oxidation Reactors. The triplicate ozone reactors consisted of 1.5 L glass columns with 1 L of thickened slurry and fritted-glass openings at the bottom to allow gas sparging upward through the sediment. Control reactors were sparged continuously with laboratory air. Ozone reactors were sparged continuously with a laboratory ozone generator (Ozone Services Model OL-100, Burton, British Columbia, Canada), supplying ozone at a fixed concentration of 0.5% (v/v). The triplicate reactors were maintained at 20°C. For a newly developed solid chemical oxidation reagent *(chemox)* tests, a newly developed solid chemical oxidation reagent *(chemox)* was placed in the slurry at a mass ratio of 1:10 (a newly developed solid chemical oxidation reagent *(chemox)*/soil). A newly developed solid chemical oxidation reagent *(chemox)* was mixed into the slurry by sparging with nitrogen gas for an hour every 5 days. A newly developed solid chemical

oxidation reagent *(chemox)* control reactors received no a newly developed solid chemical oxidation reagent *(chemox)*. Effluent gas was passed through activated carbon to quantify stripping of DCB and HCB. The reactors were buffered at a pH 8. Samples were taken as described by Cassidy et al. (2002).

Bioreactors. After 30 days of chemical oxidation, the remaining contents from each reactor were separated from the solids by centrifuging. The liquid fraction (approximately 200 mL) was placed in closed, 500 mL glass bottles. Nitrogen and phosphorus were added to the ozone-treated liquid but not to the newly developed solid chemical oxidation reagent *(chemox)*-treated liquid, since a newly developed solid chemical oxidation reagent *(chemox)* contains these nutrients in its formulation. Inoculum (20 mL) from the aeration tank of a domestic WWTP was added to the active reactors and the controls received none. All bottles were attached to a Hach BODTrak® to monitor O_2 consumption. Periodically, pH was measured with a probe and samples were taken to measure COD.

Analytical Methods. DCB and HCB were quantified with gas chromatography with electron capture detection (GC/ECD), organic acids were quantified with GC/mass spectrometry (GC/MS), and Cl^- was quantified with ion chromatography (IC), as described in detail by Cassidy et al. (2002).

RESULTS AND DISCUSSION

Figures 1 through 3 show time profiles of removal of DCB and HCB from a newly developed solid chemical oxidation reagent *(chemox)* treatment, accompanying production of COD and Cl^-, and biodegradation of the residual COD. Error bars show standard deviation. Similar time profiles were obtained for ozone treatment (Cassidy et al., 2002). Reactors without a newly developed solid chemical oxidation reagent *(chemox)* maintained their initial DCB and HCB levels of 1000 mg/kg throughout the 30-day period, showing no measurable PCB removal (Figure 1). In contrast, both DCB and HCB showed a considerable decrease in concentration in the reactors sparged with a newly developed solid chemical oxidation reagent *(chemox)*. Final concentrations of DCB and HCB were approximately 20 mg/kg and 40 mg/kg, respectively. The results from Figure 1 show that the loss of DCB and HCB in the reactors was due to reaction with a newly developed solid chemical oxidation reagent *(chemox)*. No stripping of DCB or HCB was observed, which is consistent with the low volatility of PCBs.

Figure 2 shows the production of soluble COD and Cl^- resulting from the reaction of DCB and HCB with a newly developed solid chemical oxidation reagent *(chemox)*. The increase in COD with time observed with a newly developed solid chemical oxidation reagent *(chemox)* treatment represents a conversion of DCB and HCB to soluble organic compounds due to reaction with a newly developed solid chemical oxidation reagent *(chemox)*. Aronstein and Rice (1995) reported the production of soluble products from ozone treatment of PCBs in sediments, but they did not identify the products. COD reached peak values between days 14 and 16 of near 9000 mg/L for DCB and over 5000 mg/L for HCB. The decrease in COD during the last 14 days indicates that the constituents of the soluble COD were being further oxidized at a greater rate than they were being replenished by oxidation of remaining DCB and HCB. Formate and oxalate

were products of oxidation of DCB and HCB with ozone and a newly developed solid chemical oxidation reagent *(chemox)*. Specific oxidation products of DCB and HCB were 2-hydroxybenzoic acid and 2,3,4-trihydroxybenzoic acid, respectively, showing that ring cleavage of the PCBs occurred. Concentrations of Cl^- increased steadily during a newly developed solid chemical oxidation reagent *(chemox)* treatment, indicating that Cl atoms were removed from DCB and HCB. Dechlorination increases the aerobic biodegradability and decreases the toxicity of PCBs. (Abramowicz, 1990). Heinzle et al. (1995) reported release of Cl^- from chlorinated guaiacols with Fenton's reagent.

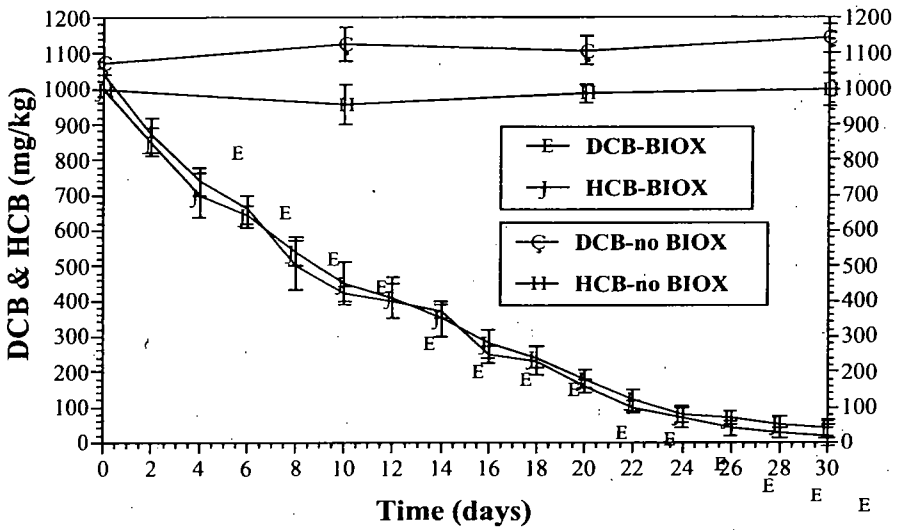

FIGURE 1. DCB and HCB removal with time during a newly developed solid chemical oxidation reagent *(chemox)* treatment.

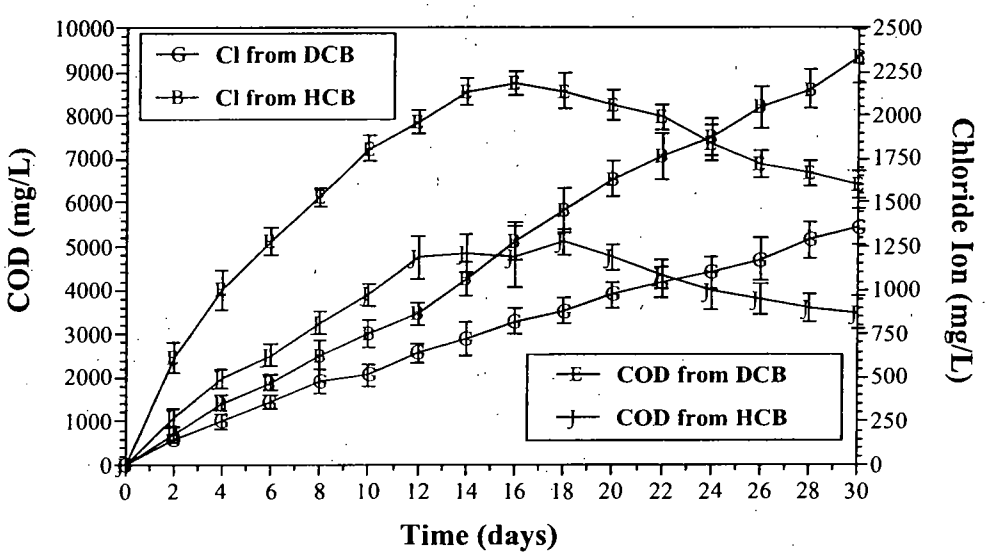

FIGURE 2. Production of COD and Cl^- with time during a newly developed solid chemical oxidation reagent *(chemox)* treatment. No COD or Cl^- was measured in reactors without a newly developed solid chemical oxidation reagent *(chemox)* (data not shown).

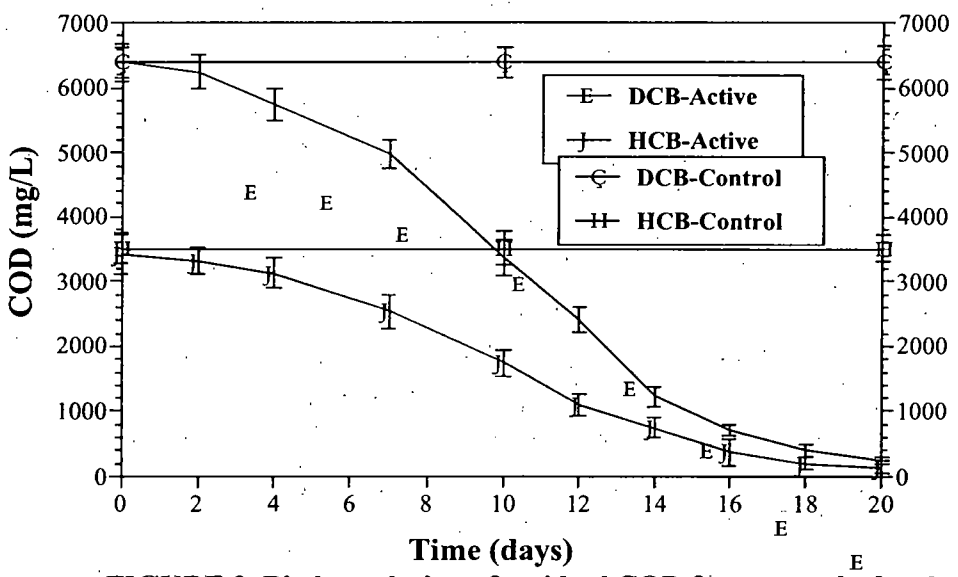

FIGURE 3. Biodegradation of residual COD from a newly developed solid chemical oxidation reagent *(chemox)* treatment of PCBs.

Figure 3 shows the removal of residual COD from a newly developed solid chemical oxidation reagent *(chemox)* treatment via biodegradation. Control reactors showed no decrease in COD in the bioreactors, indicating that no measurable biodegradation took place. In contrast, active bioreactors showed a considerable decrease in COD during 2 days. Since the bioreactors were closed, except when sampling took place, the observed COD removal cannot be attributed to stripping. Moreover, oxygen consumption (data not shown) was nearly identical to COD removal. These results show that the partial oxidation products from a newly developed solid chemical oxidation reagent *(chemox)* treatment of DCB and HCB were readily biodegradable under aerobic conditions by common environmental microorganisms. This is not surprising, since all the organic acids positively and tentatively identified with GC/MS are known to be readily biodegradable.

Ozone and a newly developed solid chemical oxidation reagent *(chemox)* treatment followed by biodegradation of the residual COD is compared in Table 1. Treatment with both oxidants resulted in greater than 90% removal of both DCB and HCB. Chemical oxidation was somewhat greater with a newly developed solid chemical oxidation reagent *(chemox)* than with ozone, and was more effective on DCB than on HCB. Measured release of Cl^- from treatment with ozone and a newly developed solid chemical oxidation reagent *(chemox)* was nearly identical to the percent removal of DCB and HCB. Moreover, the molar ratio of Cl^- released to DCB and HCB removed was approximately equal to the number of moles of Cl on the respective PCB (i.e., 2 Cl replaced per mole of DCB, and 6 Cl replaced per mole of HCB). The results show that Cl removal was stoichiometric. The oxidation products formed indicate that Cl atoms on the PCBs were replaced with OH groups. The ozone dose was approximately 19 g and 30 g per g of DCB and HCB, respectively. Dose was not measured for a newly developed solid chemical oxidation reagent *(chemox)* because there was no way to measure reactant concentrations, as they are proprietary. Microbes from a WWTP were able to degrade

more than 90% of the residual COD from treatment with ozone and a newly developed solid chemical oxidation reagent *(chemox)*, though values were higher for a newly developed solid chemical oxidation reagent *(chemox)* treatment.

The effect of native organic matter (NOM) on ozone doses for oxidation of DCB and HCB and is reported by Cassidy et al. (2002). Ozone doses increased approximately 15 times in the presence of 2% NOM relative to the NOM-free kaolinite. NOM scavenges all chemical oxidants, and would be expected to increase doses of a newly developed solid chemical oxidation reagent *(chemox)* required to achieve PCB oxidation by a similar degree.

TABLE 1. Summary of results for 30 days of treatment of dichlorobiphenyl (DCB) and hexachlorobiphenyl (HCB) adsorbed to kaolinite with ozone and a newly developed solid chemical oxidation reagent *(chemox)*, followed by 20 days of biodegradation.

Parameter	Ozone	BIOX®
Dichlorobiphenyl (DCB)		
DCB Removed with Oxidants (%)	97 ± 4 (9)[a]	99 ± 4 (9)
Cl^- Released with Oxidants (%)	95 ± 3 (9)	97 ± 5 (9)
Cl^- Released/DCB Removed (mol/mol)	1.9 ± 0.5 (43)	2.1 ± 0.7 (38)
Oxidant Dose (g oxidant/g DCB removed)	18.6 ± 2.7 (43)	NM[b]
COD Removed by Biodegradation (%)	92 ± 5 (9)	97 ± 4 (9)
Hexachlorobiphenyl (HCB)		
HCB Removed with Oxidants (%)	92 ± 6 (9)	95 ± 5 (9)
Cl^- Released with Oxidants (%)	93 ± 4 (9)	96 ± 7 (9)
Cl^- Released/HCB Removed (mol/mol)	6.2 ± 0.9 (43)	6.1 ± 0.7 (43)
Oxidant Dose (g oxidant/g HCB removed)	30.0 ± 3.9 (43)	NM
COD Removed by Biodegradation (%)	91 ± 4 (9)	98 ± 3 (9)

[a] average ± standard deviation (number of measurements).
[b] NM=not measured, because the reactants in a newly developed solid chemical oxidation reagent *(chemox)* are proprietary.

CONCLUSIONS

The following conclusions can be drawn from the experimental data:

1. Ozone and a newly developed solid chemical oxidation reagent *(chemox)* effectively oxidize PCBs in sediments and soils.
2. Reaction of PCBs with ozone and a newly developed solid chemical oxidation reagent *(chemox)* results in replacement of Cl atoms with OH groups, causes ring cleavage, and produces formic, oxalic and hydroxylated benzoic acids.
3. The residual organic carbon that accumulates in the aqueous phase from ozone and a newly developed solid chemical oxidation reagent *(chemox)* treatment of PCBs is readily biodegradable by common microorganisms.

ACKNOWLEDGMENTS

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SOIL REMEDIATION BY POTASSIUM PERMANGANATE: BENCH-SCALE TO FIELD APPLICATION

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ABSTRACT: The soil at a former manufacturing plant in Indiana had been impacted with elevated concentrations of trichloroethene (TCE). The shallow soils at certain locations were also impacted with polychlorinated biphenyl compounds (PCBs). Potential site remediation technologies were reviewed and chemical oxidation was selected as the most cost-effective alternative. A bench-scale treatability study was conducted to assess the effectiveness of potassium permanganate ($KMnO_4$) for the remediation of the impacted soil. Ultrasound treatment in conjunction with potassium permanganate to enhance the oxidation of PCBs in the Site soils was also tested. The treatability study results showed that $KMnO_4$ treatment was very effective in reducing TCE concentrations in soil and up to 95 percent removal was observed. $KMnO_4$ was also effective in treating the PCBs in the soil. The treatment resulted in destroying 69 percent of the PCBs within a period of one week. PCBs are extremely hydrophobic and tend to adsorb tightly to soil particles. The use of ultrasound in conjunction with chemical oxidation enhanced the solubilization and degradation by approximately 10 percent. However, the residual PCB concentrations after the treatment remained above the cleanup criteria. Based on these results, chemical oxidation using $KMnO_4$ was selected for the remediation of TCE-impacted soil. The PCB-impacted soils were excavated and disposed of off-Site at a hazardous waste landfill. The treatment strategy developed in the laboratory was demonstrated in a pilot test. Based on the successful results of the pilot test, full-scale application proceeded and the impacted soil has been successfully remediated.

INTRODUCTION

Soil at a former manufacturing plant in Indiana had been impacted with elevated concentrations of TCE and PCBs. Shallow unsaturated soils contained up to 10,000 mg/Kg of TCE. PCBs were also detected in the surface soils at several areas of the Site.

Chemical oxidation was identified as a cost-effective potential remedial alternative for the TCE-impacted soil at the Site. Therefore, CRA, Inc. conducted bench-scale laboratory studies to assess the feasibility potential of using $KMnO_4$ to treat the contaminants in the soil.

Ultrasound in conjunction with $KMnO_4$ was also tested to improve the solubilization of PCBs so oxidation by potassium permanganate can be optimized. Ultrasound is known to affect the physical surface of particles and enhances the solubilization of hydrophobic chemicals. Additionally, ultrasound has been shown to destroy a wide range of compounds (Drijvers et al., 1996; Olson and Barbier, 1994; Hua et al., 1996). The formation and collapse of cavitation bubbles, generating extremely high pressure and temperatures in the center of the cavitation bubbles, is considered the

main mechanism through which chemical reaction occurs in sonochemistry (Lu and Weavers, 2002.)

BENCH-SCALE TREATABILITY STUDIES

Initial Characterization. The TCE-impacted soil consisted of primarily sand and silt with some clay and gravel, while the PCB-impacted soil consisted of primarily sandy soil. TCE concentrations in the soil varied between 40 and 51 mg/Kg (wet weight basis). The soil pH was in the alkali range (7.6-8.9). Soils impacted with PCBs showed concentrations between 202-239 mg/kg.

Chemical Oxidation Tests. Laboratory studies were conducted to assess the feasibility of chemical oxidation using $KMnO_4$ for the remediation of the TCE, its daughter compounds, and PCBs in representative soil from the Site. The effectiveness of using ultrasound in conjunction with $KMnO_4$ treatment of the PCB-impacted soils was also tested.

The laboratory studies involved three types of tests:

i) *Soil column tests*: Intact soil cores were used to conduct column tests to determine the effect of infiltrating $KMnO_4$ solution by gravity through the soil column. At the end of the tests, samples were collected from the columns and analyzed for TCE.

ii) *Batch tests*: A series of batch tests was conducted using a homogenized representative soil sample. In these tests, the soil samples were placed in glass jars and mixed with of varying concentrations of $KMnO_4$ solution. The jars were sealed, and visual observations of reactivity, changes in color, etc. were made immediately after the addition of the $KMnO_4$. The jars were maintained in the dark at laboratory temperature for two weeks. At the end of the two-week period, the soil was analyzed for residual volatile organic compounds (VOCs).

iii) *Ultrasound-enhanced chemical oxidation tests*: Known concentrations of $KMnO_4$ solutions were mixed with the PCB-impacted soil as described above under (ii). These tests were conducted with and without ultrasound to examine potential enhancement affects of ultrasound on the degradation of PCBs. Each test was conducted in duplicate in glass centrifuge tubes. Ultrasound treatment was applied using a Fisher Model 550 ultrasound apparatus in a pulse mode (a total of 15 pulses; 30 seconds on and 30 seconds off for each pulse) to mix the solution with the soil. All samples were maintained for two weeks on a shaker at laboratory temperature and then analyzed for residual PCBs.

RESULTS AND DISCUSSION

The batch tests results showed that TCE removal correlated with the concentration of $KMnO_4$; i.e., the higher $KMnO_4$ concentration resulted in higher TCE removal. Up to 53 percent of the TCE in the soil microcosm test was removed using a 4 percent solution of $KMnO_4$. The soil column test also showed that the infiltration of $KMnO_4$ solution resulted in effective destruction of TCE, suggesting that in situ treatment would be a feasible option for treatment of subsurface impacted soils. Based

on the results, it was estimated that the application rate of $KMnO_4$ for full-scale application would be on average 40 pounds per cubic yard of soil.

The results of the PCB testing indicated that $KMnO_4$ was effective in destroying the PCBs in the soil. The use of $KMnO_4$ resulted in 69 percent reduction in PCB concentrations after one week. The use of ultrasound in conjunction with potassium permanganate treatment increased the percentage removal of PCBs to approximately 79 percent. However, the residual concentrations after treatment remained above the cleanup criteria. Therefore, the PCB-impacted soils were excavated and disposed of off-Site at a hazardous waste landfill.

PILOT TEST

Based on the successful laboratory results, a small-scale field study was conducted at the Site to assess the effectiveness of $KMnO_4$ treatment for the TCE-impacted soils under actual field conditions.

The field study was conducted at the Site in two locations where previous soil sample analytical data reported elevated TCE concentrations. Two test areas at each location were subjected to chemical oxidation treatment using $KMnO_4$ solutions. Each test area was approximately 4 feet wide by 10 feet long. At those locations where the impacted soils were located below the surface, the un-impacted soils were excavated and stockpiled so that the $KMnO_4$ solution could be directly applied to the impacted soils. The $KMnO_4$ solution was mixed in a trailer-mounted, 330-gallon container and then applied to the impacted soils. The soil and $KMnO_4$ solution was mixed using a standard excavator with bucket. The impacted soil was generally treated in 1-foot lifts.

The first test involved applying approximately 120 gallons of a 2 percent $KMnO_4$ solution to the test area to determine if less-concentrated solutions could effectively treat the TCE-impacted soils. The soil/solution mixture did not initially solidify, so additional untreated soil material was incorporated into the mixture until the soils absorbed enough of the solution to form a thick slurry. In total, approximately 6 cubic yards of soil were required to solidify the 120 gallons of solution (i.e., 5 pounds of $KMnO_4$ per cubic yard of soil). Because this amount exceeded the soil absorption capacity, subsequent field tests utilized less water and greater concentrations of $KMnO_4$.

The second test involved applying 50 gallons of a 4 percent solution to the test area (equivalent to approximately 11 pounds of $KMnO_4$ per cubic yard of soil). Pre- and post-treatment soil samples collected during this test indicated a reduction in TCE concentrations of 83 percent.

The third test involved applying 50 gallons of a 4 percent solution to different soil types (fill versus native materials). The fill material quickly absorbed all of the solution, indicating that additional liquid/solution would be required in order to achieve complete mixing. Therefore, 80 gallons of 4 percent solution was applied to a second lift of native soils (equivalent to 20 pounds of $KMnO_4$ per cubic yard of soil). Again, the difference in pre- and post-treatment samples showed an average reduction in TCE concentrations of 90 percent. However, small clay nodules were identified in the post-treatment slurry, indicating that longer mixing times or better mixing techniques would be required in full-scale application.

The fourth test involved applying dry $KMnO_4$ material in addition to the prepared solution to assess if this combination would increase TCE destruction potential.

Approximately 37 pounds of dry $KMnO_4$ was applied directly onto the impacted soil, and then approximately 100 gallons of a 4 percent solution was added (equivalent to 46 pounds of $KMnO_4$ per cubic yard of soil). This combination was not sufficient to create a well-mixed slurry.

The results of Tests 2, 3, and 4 are summarized in Figure 1 below.

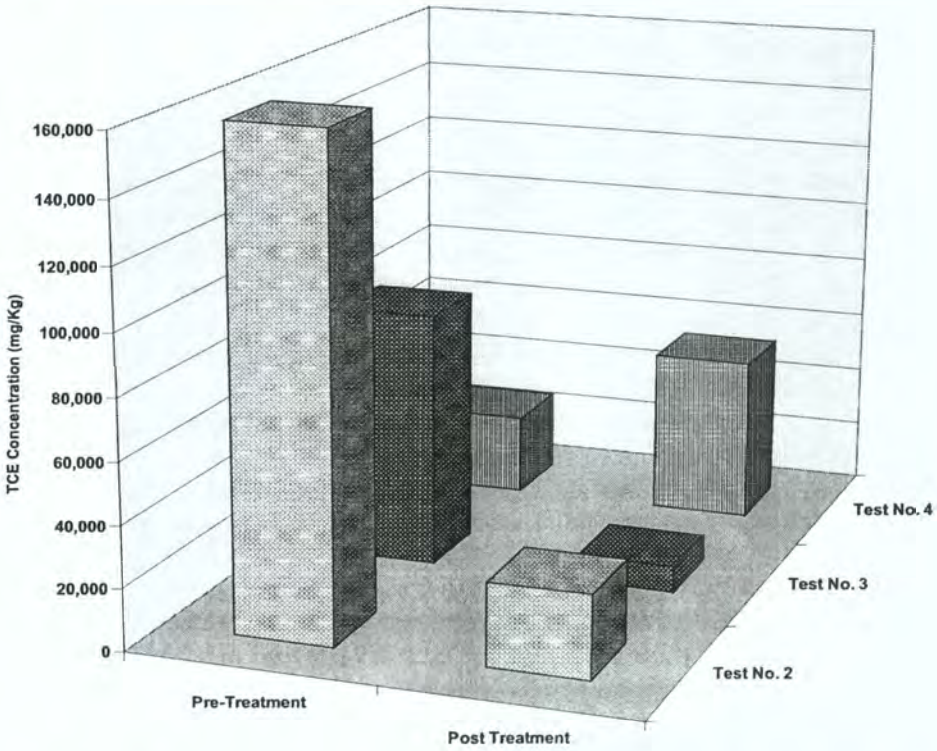

FIGURE 1. Reductions in TCE concentrations during pilot test.

CONCLUSIONS

Based on the successful pilot results, the following conclusions and recommendations from the field study were compiled:

- TCE reduction rates in the field (83 to 90 percent) were consistent with laboratory results (53 to 95 percent reduction). The reductions in field were observed 12 hours after application.
- $KMnO_4$ appeared to successfully reduce concentrations of TCE to acceptable levels (below the Site-specific industrial/commercial risk-based criteria of 56 mg/Kg).
- TCE reduction was most prominent in tests where $KMnO_4$ was applied in solution form and not as a solid.
- Field study results indicated that the application rate varied between 11 to 26 pounds of $KMnO_4$ per cubic yard of soil, depending on the soil characteristics and contamination levels.

The information obtained from the field study was incorporated into the design for full-scale application. Full-scale application for treatment of the soils was successfully completed early 2002.

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IN SITU THERMAL DESORPTION (ISTD) OF PCBs

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ABSTRACT

A field demonstration is described in which a new *in-situ* thermal desorption soil remediation process (ISTD–Thermal Wells) is shown to remove high-concentration PCB contamination from clay soils. The demonstration was conducted at the Missouri Electric Works (MEW) Superfund site in Cape Girardeau, Missouri, from April 21 through June 1, 1997. For this demonstration, twelve heater/vacuum wells were completed in a multiple triangular array with a 5-foot well spacing to a depth of 12 feet. During the remediation, electrical-resistance heating and vacuum were applied to the wells for a period of 42 days. Soil temperatures were monitored throughout the experiment, and soil samples were taken with a split-spoon sampler fitted with six-inch brass coring sleeves to verify the removal of contaminants. Temperatures above 1000°F were achieved in the interwell regions, and PCB concentrations in the treated area were reduced from a maximum concentration of approximately 20,000 ppm to non-detect (i.e., <33 ppb) by EPA Method 8080. The system destruction removal efficiency (DRE) for PCBs was 99.9999998%.

INTRODUCTION

The difficulty in remediating the large number of sites contaminated by toxic, carcinogenic, or radioactive chemicals has generated interest in developing improved processes for cleaning these sites. *In-situ* processes, which either destroy contaminants in place or remove them without disturbing the soil, offer distinct advantages over those requiring excavation in that they eliminate exposures and handling/preparation costs.

One of the most versatile and effective of these *in-situ* processes is *In-Situ* Thermal Desorption (ISTD), in which heat and vacuum are applied simultaneously to subsurface soils. For shallow soil contamination, an ISTD method using surface heater blankets[1-3] has been developed. Recently, ISTD–Thermal Blankets have been demonstrated[2-3] to be highly effective in removing polychlorinated biphenyls (PCBs) from soils, and commercial remediation services are now available.[4] For deep soil contamination, a similar thermal vacuum process using heater wells (ISTD–Thermal Wells) has been proposed.[5] As with the thermal blanket, this process is a clean, closed system that is simple and fast. It destroys pollutants in place without having to move the soil. It can be used under roads, foundations, and other fixed structures. If required, the thermal wells can be slanted or drilled horizontally. The operations are low profile and quiet and cause little disruption of adjoining neighborhoods. The process possesses a high removal efficiency because the narrow range of soil thermal conductivities provides excellent sweep efficiency and because its high operating temperature assures complete displacement efficiency of contaminants in the gas phase. Unlike fluid injection processes, ISTD is applicable to tight soils and clay layers or in soils with wide variations in permeability and water content.

The ISTD–Thermal Wells process utilizes an array of heater/vacuum wells emplaced vertically in the ground in triangular patterns. The wells are equipped with high-temperature electric heaters and connected to a vacuum blower. As heat is injected and soil temperatures rise, the vaporized formation fluids, including contaminants, are collected by the vacuum drawn at the wells. Produced vapors are treated in surface facilities to remove residual contaminants that have not been destroyed *in-situ*.

A twelve-well pilot of the ISTD–Thermal Wells Process was carried out by Shell Oil and General Electric Companies in the winter of 1996 at Shell's Gasmer Road Test Facility in Houston, Texas.[6] In that pilot, a sand pit was prepared with two surrogate high-boiling-point soil contaminants, hexadecane and methyl salicylate. The ISTD–Thermal Wells process completely removed the contaminants after electrical-resistance heating and vacuum were applied to the wells for a period of 70 days.

PROCESS DESCRIPTION

As shown in **Figures 1a** and **1b**, there are two forms of the ISTD technology: Thermal Blankets for removal of surficial contamination down to about 3 feet, and Thermal Wells which can be placed to virtually any depth. The fundamental processes, including heat flow, fluid flow, phase behavior and chemical reactions, are similar for each method. In each case, heat is applied to soil from a high-temperature surface in

contact with the soil, so that radiation and thermal conduction heat transfer are effective near the heater, and thermal conduction and convection occur in the bulk of the soil volume. Overall thermal conduction accounts for over 80% of the heat transfer. A significant feature of the ISTD process is the creation of a zone of very high temperature (>1000°F) near the heaters, which causes rapid destruction of the contaminants before they exit the soil.

CAPE GIRARDEAU FIELD DEMONSTRATION DESCRIPTION

Objectives

To test full-scale remediation of contaminants using the ISTD–Thermal Well technology, TerraTherm carried out a field demonstration at the Missouri Electric Works (MEW) Superfund site in Cape Girardeau, Missouri. The Thermal Well technology was demonstrated on deep soil contamination near a former storage pad area of the MEW site where the PCB contamination was as high as 20,000 ppm Aroclor 1260. The site clean-up level specified in the ROD was 2 ppm total PCBs. The objectives of the MEW field test included (1) clean-up clay soils in the interior portion of the well array to less than 2 ppm, (2) demonstrate that stack discharges were in compliance with state and federal standards for PCBs and polychlorinated dibenzodioxins/ polychlorinated dibenzofurans (PCDDs/PCDFs), and (3) obtain a system destruction removal efficiency (DRE) for PCBs greater than 99.9999%. The demonstration was conducted in support of TerraTherm's application for a modification of the TSCA permit for alternate PCB treatment. The Demonstration Test Plan for this project was accepted by EPA, Region VII and the Missouri Department of Natural Resources (MODNR) in January, 1997.

Description of Site

The MEW site was contaminated with PCBs in both shallow and deeper soils during past operations including selling, servicing, and re-manufacturing transformers, electric motors, and electrical equipment controls, and recycling dielectric fluids containing PCBs. The MEW site was issued a Record of Decision (ROD) by the EPA, Region VII in September, 1990 and was issued an Explanation of Significant Differences (ESD) in January, 1995. On-site thermal treatment, including thermal desorption technologies, is the selected remedy for the site.

The field demonstration was carried out in an area devoid of underground gas, water, or electric utilities. The natural stratigraphy is brown clay soil; the water table is about 40 feet deep.

Pre-Test Soils Characterization

The Thermal Well demonstration area was sampled to determine the pretest concentrations and the required depth of wells. Samples were obtained using Geoprobe tools and disposable plastic liners. The soils in the selected area of the site were brown clay with traces of silt, overlain by a thin layer of organically rich topsoil. Gravel had been spread over the area during previous investigation activities. Samples were collected from discrete 2 ft intervals from 0 to 12 ft at the locations of the twelve Thermal Wells. Sample intervals were homogenized and analyzed for total PCBs by Method 8080 by ATAS Labs of St. Louis, Missouri. **Table 1** and **Figure 2** show the results of the sample analysis. All Thermal Well areas deeper than 10 feet were determined to meet the site clean-up criteria.

Equipment

Heater/Vacuum Wells. The pattern of twelve wells used is shown in **Figure 3**. Well spacing was 5 ft. The wells were completed vertically in 6-in. OD boreholes to a depth of 12 ft. The well completion consisted of (1) a 10–20 mesh sand-filled annulus between the soil face and a liner; (2) a 4-in. OD stainless steel, slotted (0.032 in. x 2 in.) liner; (3) a 2.5-in. OD pipe sealed at the bottom to provide a "heater can" to isolate the heater element from the product stream; and (4) Nichrome wire heating elements threaded through ceramic insulators. Wells were equipped with 12 ft long, dual hairpin heaters in series. To compensate for heat losses to the atmosphere and to the lower soil, the upper 1 ft and the lower 2 ft were designed to deliver 57% more power than the middle 9 ft (Nichrome wire diameter 0.102 in. vs 0.128 in.). The sand-filled annulus improved inflow of fluids from the soil, and the gap between the slotted liner and the heater can allowed flow up the well and into the surface vacuum manifold connected to the wells. Thermal wells had the capability of injecting 350–700 watts/ft at heater temperatures in the range of 1600 to 1800°F. Surface heating pads were placed at the center of each triangle on the surface metal vapor seal to assist in heating the near-surface soils between the wells. The surface heating pads were 18-inch square and energized with 500 watts/ft^2.

Thermocouple Wells. A number of 1-in. OD steel thermocouple (TC) tubes were driven into the soil to a depth of 7 ft at locations A through O shown in Figure 3. These tubes, which were sealed at the bottom, allowed temperature logging during the experiment using fixed thermocouple arrays. The thermocouple tubes were located at the centroid of each of the thirteen triangular heating patterns and at additional locations within the center triangle.

Vapor Seal. A vacuum frame structure was constructed around the well area to insulate the surface and to provide a surface seal. The vapor seal was provided by rectangular steel shim stock (4 ft x 20 ft) on the soil surface. These sheets were fitted together along the 20 ft sides so as to cover the whole test area, and the sheets were welded to the heater and logging wells at their points of penetration. A 16-in. thick layer of vermiculite insulation was placed over the steel plates. This layer served to reduce heat losses and to insulate the surface piping manifold embedded within the vermiculite. The insulation was covered with an impermeable silicone tarpaulin to prevent rainwater inflow and to provide an additional seal against vapor emissions to the atmosphere. This cover extended 5 ft beyond the edges of the treated area.

Vacuum Monitoring. Subsurface vacuum monitoring in the array was conducted using two pressure monitoring wells, PW-1, -2, constructed from perforated pipe and completed with 1 foot of sand at a depth of 6 feet and sealed with bentonite grout to the surface. The pressure monitoring wells were located in the center triangle about 2 feet from the nearest heater/vacuum wells.

Water Influx. A 1 ft deep trench was added around the perimeter and equipped with a sump pump to control surface run-off water during the demonstration.

Description of MU-125 Mobile Process Unit

The Thermal Wells were connected to a single manifold which delivered the desorbed and partially treated *in-situ* vapors to the TerraTherm MU-125 mobile process unit. The MU-125 is a 125 scfm mobile demonstration trailer equipped with a particulate cyclone, flameless thermal oxidizer (Thermatrix ES-125), two carbon canisters in series, main and backup vacuum blowers, discharge stack with continuous emission monitoring (CEM) system, and control room for the system operator. The control room houses the programmable logic controller (PLC), heater controllers, and PC-based data acquisition system. The system is powered from shore power but has a backup 70 Kw diesel generator in case of power failure to the site. The stack emissions are continuously monitored for wet and dry oxygen, carbon monoxide, carbon dioxide, and total petroleum hydrocarbons. In addition, Drager tubes are used to monitor HCl emissions from the stack.

OPERATION OF THE DEMONSTRATION

After equipment shakedown, the Thermatrix oxidizer was started, vacuum was applied to the wells, and emissions were monitored at a baseline flow rate for 24 hours to assure acceptable levels of stack emission before well heating was initiated. The vacuum was applied to the twelve wells by opening knife valves at each well and adjusting them to roughly equal vacuum in the range of 25 inches of water. The vacuum levels in the pressure monitoring wells (PW-1, -2) two feet away were 1 inch of water, indicative of the low permeability of the clay soil.

Well heaters were energized on April 21, 1997. Power to the twelve injectors was increased over a 3-hour period to an average initial rate of 500 watts/ft. Power was increased in all injectors until the control thermocouples next to the heating elements reached the maximum operating temperature (1600°F). Within 48 hours the vacuum decreased at the heater wells from 25 to 5 inches of water and the pressure monitoring wells increased in vacuum from 1 to 4.5 inches of vacuum. This indicated a substantial increase in soil permeability from the heating process. Once the soil permeability had increased, the surface heating pads were energized at 500 watts/ft^2. Injected power was slowly decreased once the maximum heating element operating temperatures was reached.

The flow rate from the well manifold was maintained between 50–70 scfm with a well vacuum of 3–5 inches of water for the majority of the 42-day demonstration.

TEMPERATURE PROFILES

The temperatures in the process were recorded using fixed thermocouples (TC) at 1 ft intervals with thermocouple arrays. Temperatures were measured every 12 hours during the test.

Because of the additional contribution from the surface heating pads, heating progressed from the surface downwards. After the upper foot of soil reached 900°F, the power to the surface heating pads was reduced to avoid excessive corrosion of the metal shim-stock vapor seal.

The temperature history at the centers of the triangles near the middle of the heated interval (depth 6 ft) is shown in **Figure 4**. There were three distinct phases in the heating process. During the first phase, the soil temperature rose nearly to the boiling point of water in about 250 hours from the start of heating. During the second phase, water boiling occurred and the temperature remained near the boiling point of water. The duration of this phase was dependent on the pore water content and the water inflow. This phase ended at between 560 and 630 hours, with the center and adjoining triangles drying first and the outer triangles later. During the third (superheating) phase, soil temperatures rose rapidly until the heaters were turned off on day 42. Maximum temperatures over 900°F were reached at the center of the triangles, and about 50% of the

volume was over 1100°F. **Figure 5** shows the maximum temperatures reached along profile I7-G.

SAMPLING METHOD AND RESULTS

Soil samples were taken after 42 days of heating, at the locations shown in Figure 3. The coring was performed on the hot soils by Philips Environmental using a truck-mounted drill rig, hollow-stem augers, and split spoon sampler with brass sleeves. After retrieval of the coring tube, the contents of each sleeve were immediately emptied into a glass bottle and sealed. The total coring depth was 10 ft except at the center location where the coring proceeded until moist soil was contacted at 16 ft. Most of the samples were observed to be reddish-brown, very dry, high porosity and fine grained. On rehydrating, the clay plasticity appeared to be lost and the soil behaved as a siltstone.

Post-heat soil samples showed a large increase in both porosity and permeability. The porosity increased from approximately 30% of pore volume initially to a post-heat value of 40%. The horizontal air permeability, measured with *in-situ* moisture retained, increased from 3×10^{-3} md to 50 md. The vertical air permeability increased from 1×10^{-3} md to 30 md. Mechanisms for increasing porosity and permeability included fracturing, clay desiccation, and removal of organic material (as evidenced by scanning electron microscopy, SEM). Additional air permeability was created through the evaporation of *in-situ* moisture.

The heating process also affected soil texture. In areas exposed to at least 1100°F, the soil became solidified (to a siltstone) and ochre in color from an iron oxide grain coating observed in SEM dispersive images. The solidification of the silica grains may occur by sintering silicate minerals, particularly the clay minerals which are dispersed through the soil and bridge between particles. The iron oxide coating may also be contributing to cementing the grains together. Analysis by X-ray diffraction showed that thermal effects alter the structure of the clays from a crystalline to an amorphous state, reducing the measured values from about 12% illite/smectite volume to 8% amorphous clay material.

Soil samples were analyzed for total PCBs by EPA Method 8080 at ATAS Labs. Results of this sampling are given in **Table 2**. All samples were treated to below the site clean-up criteria of 2 ppm. Nearly all of the samples in the center treated area (0 to 10 ft) were treated to below the limits of method detection (<33 ppb). These results indicated no evidence of vertical or lateral migration of contaminants at the end of the test.

Additionally, soil samples were composited vertically and areally in the treated zone and analyzed for PCDD and PCDF by EPA Method 8280 at Triangle Labs in Durham, North Carolina. The vertical composite sample 0–10 ft at the center of the treated pattern was non-detect for PCDD/PCDF by EPA Method 8280. The 0–2 ft areal composite showed 0.00284 ppb toxic equivalent (TEQ), the 2–4 ft areal composite showed 0.00684 ppb TEQ, and the 4–6 ft areal composite showed 0.0033 ppb TEQ. These levels are well below the RCRA universal treatment standard of 1 ppb TEQ, and even below the background level of 8 ppt for uncontaminated soil in North America.

STACK SAMPLING

HCl emissions in the stack were used to select the period of peak emissions for the 30-hour stack sampling test. Effluent stack sampling by EPA Method 23/modified 680 and CEM demonstrated that the discharge of PCBs and combustion byproducts (PCDDs/PCDFs) was in compliance with the ambient air requirements prescribed by MODNR and USEPA 40CFR Part 266 Appendix V.

Continuous emission monitoring (CEM) showed the average stack composition contained about 20,000 ppm CO_2, 2 ppm CO, and 1 ppm THC. The peak HCl concentration in the stack was 60 ppm from the decomposition of the PCBs. The HCl concentration in the stack was found to be a good indicator of when the remediation process was complete.

AMBIENT AIR MONITORING RESULTS

Vacuum was maintained in the soil and in the vapor treatment equipment throughout the whole test. Organic vapor analysis of the ambient air around the demonstration area was performed periodically using NIOSH Method 5503 to check for leakage of contaminants. No PCB contaminants (<10 $\mu g/m^3$) were detected, and no odors were noticed at any time during the test.

SUMMARY

The principal results of the Cape Girardeau field demonstration are as follows:

1. About 500 watts/foot were initially injected into the clay soil at heater temperatures of 1600°F. Later in the process, as the soil dried, about 350 watts/ft could be injected.
2. After 42 days of heating with well spacing of 5 ft between triangular patterned wells, soil temperatures reached over 900°F at the center of all triangles and exceeded 1100°F in about half of that volume.

3. Sampling after 42 days showed complete clean-up of all contaminants to levels below 1 ppm to a depth of 10 feet below ground surface. Eighty-one samples in the treatment zone were non-detect (<33 ppb) by EPA Method 8080.
4. No evidence of vertical or lateral migration of contaminants was observed.
5. Stack testing of emissions from the process indicated 99.9999998% destruction removal efficiency (DRE) of the PCBs by combined *in-situ* and surface treatment. The sampling and analysis results of the Method 680 analysis performed on the stack samples indicates that a total of 0.10 mg of PCB were emitted from the MU-125 stack from a conservative estimate of 40 kilograms of PCB in the treated area.
6. Post-treatment soil samples composited vertically and areally from the treated zone were analyzed for PCDD and PCDF and exhibited TEQ levels from non-detect to 0.00684 ppb, with an average of 0.003 ppb. This is below the background level of 8 ppt for uncontaminated soil in North America.

In summary, the ISTD–Thermal Well technology was effective in achieving the site remediation goals of <2.0 ppm at all locations sampled within the well treatment zone. The Thermal Well technology volatilized, extracted, and effectively treated high concentrations of the highest-boiling-point PCBs from dense clay overburden soils without excavation. The discharge of PCBs and combustion by-products detected during stack testing activities conducted on the MU-125 treatment system during the demonstration confirmed that ambient air quality was not adversely impacted by the ISTD process.

ACKNOWLEDGMENTS

We gratefully acknowledge the help of James Menotti and Bruce Hunsucker of Shell for assistance with the thermal oxidizer, Bob Burnett and Bill Savage of TerraTherm for construction of the MU-125, Phillip Holt and Sonny Trevino of TerraTherm for field data acquisition. Bill Edelstein and Richard Sheldon of General Electric Co. provided many useful suggestions during the demonstration.

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2. Iben, I.E.T., et al.: "Thermal Blanket for In-Situ Remediation of Surficial Contamination: A Pilot Test," *Environmental Science and Technology* (Nov. 1996) **30**, No. 11.
3. Sheldon, R.B., et al.: "Field Demonstration of a Full-Scale In-Situ Thermal Desorption System for the Remediation of Soil Containing PCBs and Other Hydrocarbons," HAZWaste World–Superfund XVII, Washington, D.C., Oct. 15–17, 1996.
4. "Low-Cost Solutions to Difficult Cleaning Problems," TerraTherm Environmental Services, Inc., an affiliate of Shell Technology Ventures, Inc., Houston, TX.
5. Vinegar, H.J., Stegemeier, G.L., de Rouffignac, E.P., and Chou, C.C.: "Vacuum Method for Removing Soil Contaminants Utilizing Thermal Conduction Heating," U.S. Patent Nos. 5,190,405, issued March 2, 1993, and 5,318,116, issued June 7, 1994.
6. Vinegar, H.J. et al: "Remediation of Deep Soil Contaminants Using Thermal Vacuum Wells," paper SPE 39291, 1997 SPE Annual Technical Conference, San Antonio, Texas, October 5–8.

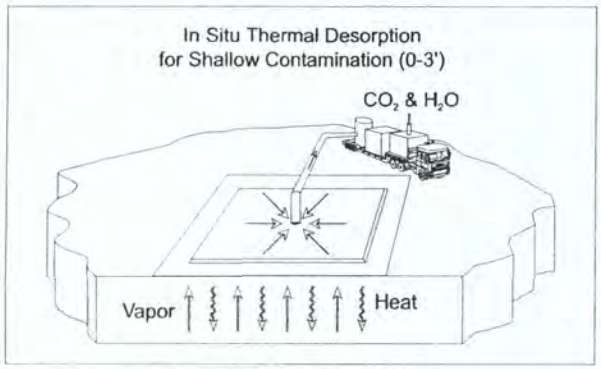


Figure 1a - ISTD-Thermal Blankets.

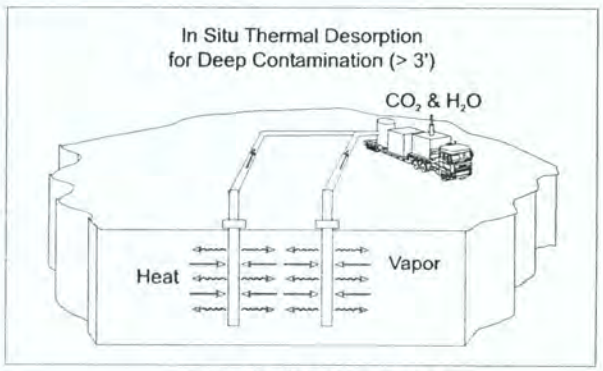


Figure 1b - ISTD-Thermal Wells.

CLIENT REFERENCES:

Warren Mueller - Union Electric, St. Louis, MO. - (314) 554-3063

REGULATORY AGENCY REFERENCES:

Donald Van Dyke, MODNR - Jefferson City, MO (573) 751-3176

Paulette France-Isetts, EPA Region VII - Kansas City, KS (913) 551-7701

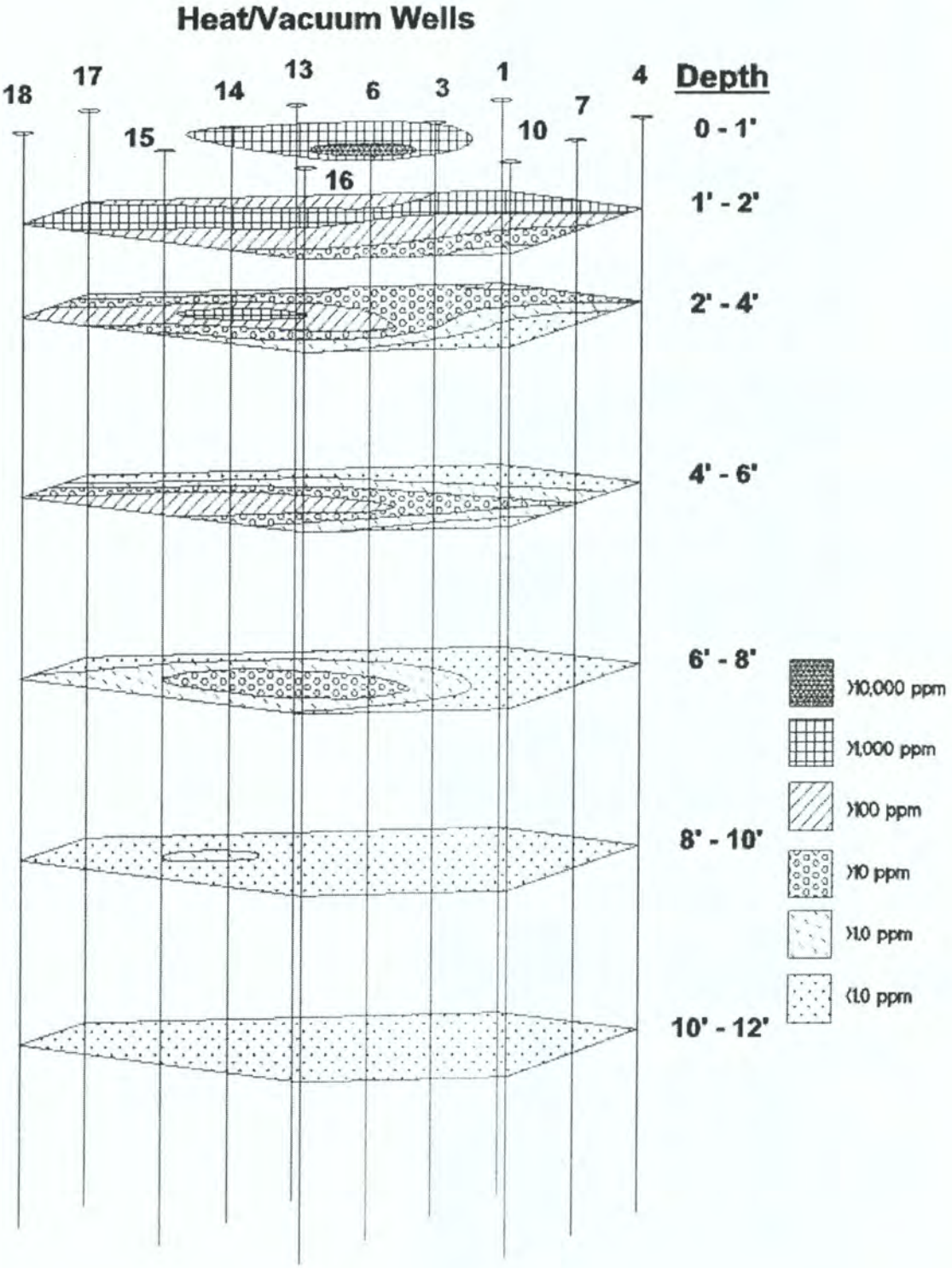
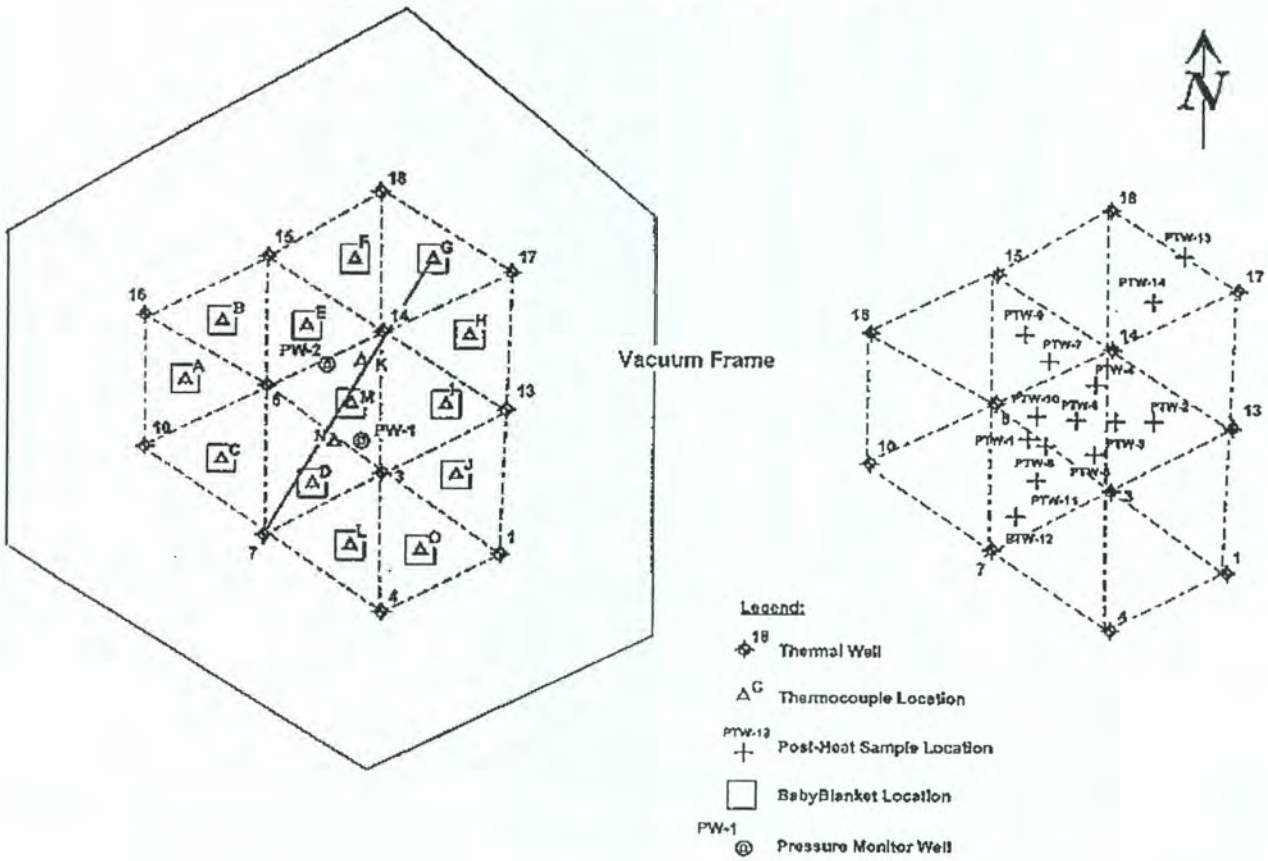


Figure 2.Contour values of initial PCB concentration

MEW - Cape Girardeau Demonstration

Thermal Well Pattern Layout

Figure 3



Soil Temperature History at 6 Feet Depth

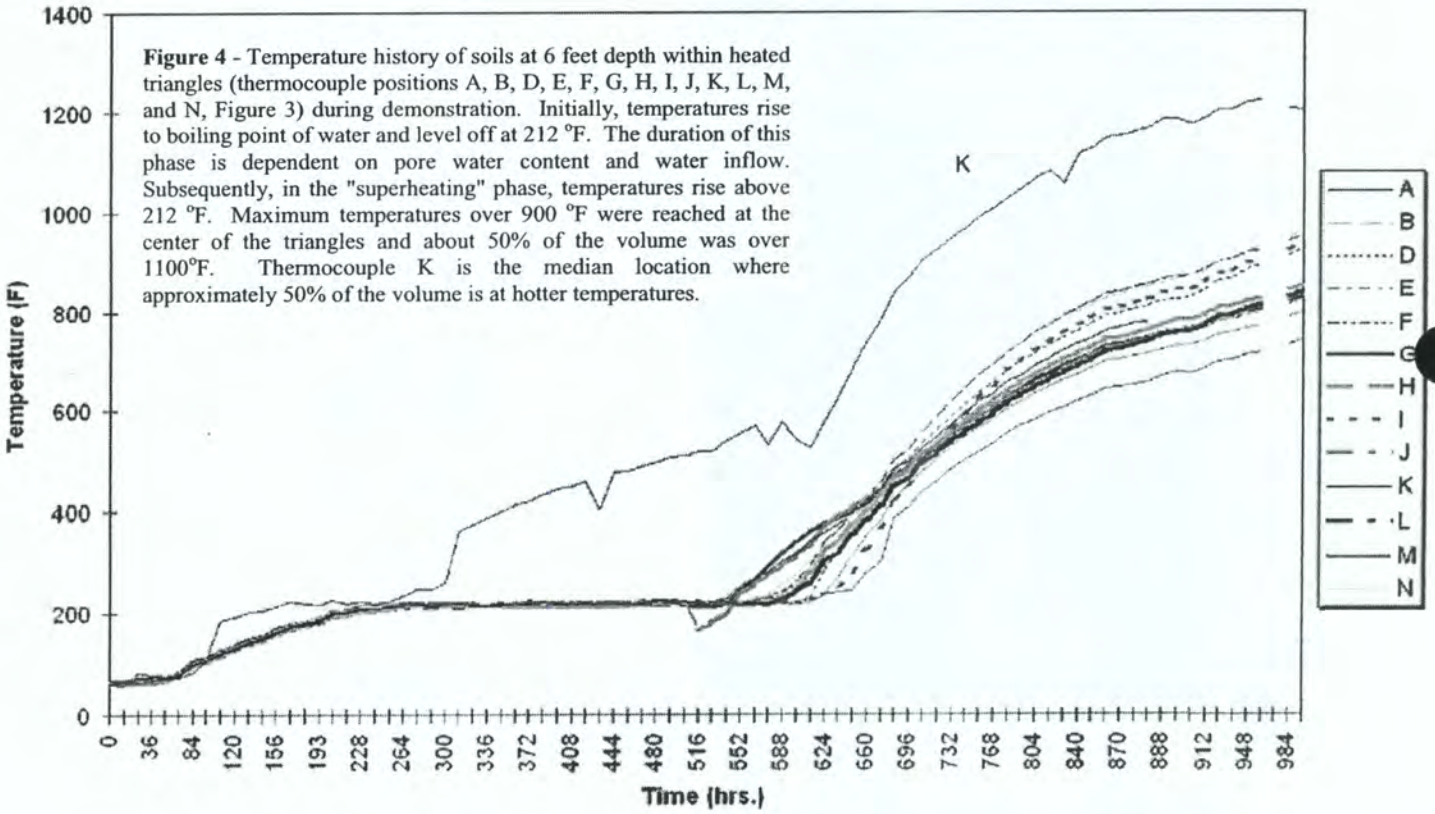
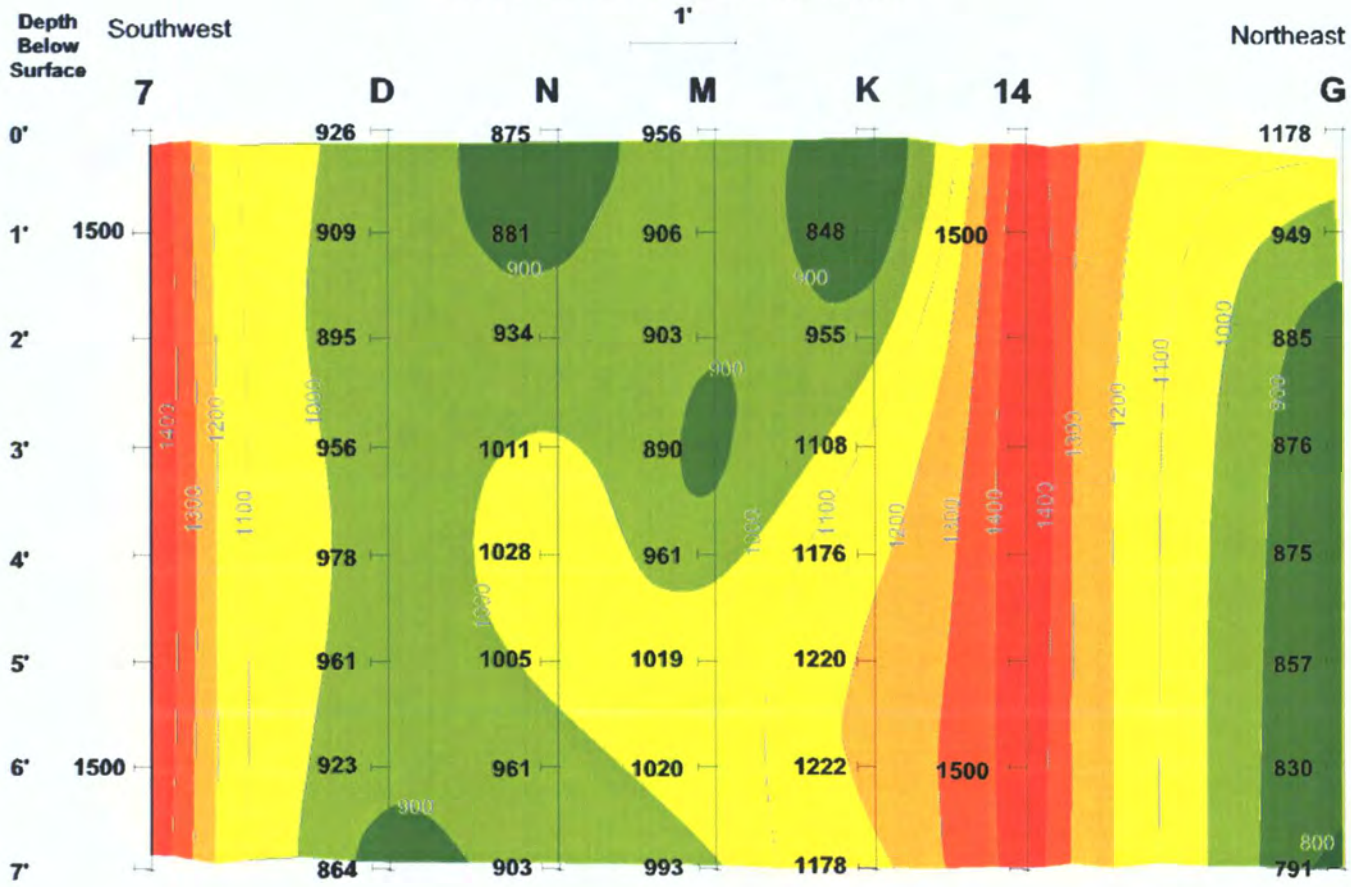


Figure 4 - Temperature history of soils at 6 feet depth within heated triangles (thermocouple positions A, B, D, E, F, G, H, I, J, K, L, M, and N, Figure 3) during demonstration. Initially, temperatures rise to boiling point of water and level off at 212 °F. The duration of this phase is dependent on pore water content and water inflow. Subsequently, in the "superheating" phase, temperatures rise above 212 °F. Maximum temperatures over 900 °F were reached at the center of the triangles and about 50% of the volume was over 1100°F. Thermocouple K is the median location where approximately 50% of the volume is at hotter temperatures.

Figure 5.

Maximum Temperatures, Deg. F

Profile Through Well Pattern



CAPE GIRARDEAU, MO.
SOIL SAMPLE RESULTS SUMMARY

Table 1. Thermal Wells Pre-Demo Soil Sampling Results

Boring ID	Sample #	Depth (ft)	ATAS Lab Result PCB Concentration (ppm)	Boring ID	Sample #	Depth (ft)	ATAS Lab Result PCB Concentration (ppm)
TW-1	S1-A	0.0-2.0	1590	TW-13	S1	0.2-2.2	253
	S1-B	2.0-3.4	357		S2	2.2-4.2	2.23
	S2-A	3.4-5.4	<0.5		S3	4.2-6.2	0.099
	S2-B	5.4-8.1	<0.5		S4	6.2-8.2	NA
	S5	8.2-10.0	NA		S5	8.2-10.2	<0.50
	S6	10.0-12.0	13.5*		S6	10.2-12.2	<0.50
TW-3	S1-A	0.2-2.2	2190	TW-14	S1	0.2-2.2	4100
	S1-B	2.2-4.2	59.5		S2	2.2-4.2	1060
	S2-A	4.2-6.2	ND		S3	4.2-6.2	276
	S2-B	6.2-8.2	ND		S4	6.2-8.2	67.5
	S5	8.2-10.0	6.37*		S5	8.2-10.2	3.98
	S6	10.0-12.0	4.34*		S6	10.2-12.2	<0.50
TW-3T	S1	0.0-0.5	614	TW-14T	S1	0.0-0.5	9210
	S2	0.5-1.0	2970		S2	0.5-1.0	1450
	S3	1.0-2.0	16.5		S3	1.0-2.0	984
	S4	2.0-4.0	0.694		S4	2.0-4.0	1470
	S5	4.0-6.0	4.42		S5	4.0-6.0	134
	S6	6.0-8.0	2.32		S6	6.0-8.0	11.8
	S7	8.0-10.0	0.084		S7	8.0-10.0	<0.033
	S8	10.0-12.0	<0.033		S8	10.0-12.0	<0.033
	S9	12.0-14.0	<0.033		S9	12.0-14.0	<0.033
	S10	14.0-16.0	<0.033		S10	14.0-16.0	<0.033
TW-4	S1-A	0.2-2.2	3030/8030				
	S1-B	2.2-4.2	NA	TW-15	S1	0.2-2.2	93.8
	S2-A	4.2-6.2	0.913		S2	2.2-4.2	5.3
	S2-B	6.2-8.2	<0.50		S3	4.2-6.2	NA
	S5	8.2-10.0	0.418		S4	6.2-8.2	2.03
	S6	10.0-12.0	3.63*		S5	8.2-10.2	NA
TW-5	S1-A	0.2-2.2	299		S6	10.2-12.2	8.35*
	S1-B	2.2-4.2	393				
	S2-A	4.2-6.2	342	TW-16	S1	0.2-2.2	61.8
	S2-B	6.2-8.2	114		S2	2.2-4.2	NA
	S3-A	8.2-10.2	<0.50		S3	4.2-6.2	1.14
	S3-B	10.2-12.2	0.973		S4	6.2-8.2	NA
TW-5T	S1	0.0-0.5	19900		S5	8.2-10.2	3.11
	S2	0.5-1.0	2190		S6	10.0-12.0	1.22 (10.2)*
	S3	1.0-2.0	885				
	S4	2.0-4.0	234	TW-17	S1	0.0-0.5	93.7
	S5	4.0-6.0	46.2		S2	0.5-1.0	2530
	S6	6.0-8.0	5.33		S3	1.0-2.0	<0.50
	S7	8.0-10.0	0.061		S4	2.0-4.0	1.66
	S8	10.0-12.0	0.158		S5	4.0-6.0	<0.50
	S9	12.0-14.0	0.22		S6	6.0-8.0	<0.033
	S10	14.0-16.0	0.043		S7	8.0-10.0	0.146
					S8	10.0-12.0	<0.033
TW-7	S1-A	0.2-2.2	25.7		S9	12.0-14.0	1.27
	S1-B	2.2-4.2	<0.50		S10	14.0-16.0	0.395
	S2-A	4.2-6.2	11.4				
	S2-B	6.2-8.2	<0.50	TW-18	S1	0.0-0.5	9090
	S3-A	8.2-10.2	<0.50		S2	0.5-1.0	1690
	S3-B	10.2-12.2	<0.50		S3	1.0-2.0	762
					S4	2.0-4.0	450
TW-10	S1-A	0.2-2.2	2.39		S5	4.0-6.0	293
	S1-B	2.2-4.2	<0.50		S6	6.0-8.0	1.53
	S2-A	4.2-6.2	<0.50		S7	8.0-10.0	0.421
	S2-B	6.2-8.2	<0.50		S8	10.0-12.0	0.136
	S5	8.2-10.0	0.475		S9	12.0-14.0	0.051
	S6	10.0-12.0	<0.50		S10	14.0-16.0	<0.033

Table 2. Thermal Wells Post-Demo Soil Sampling Results

Boring ID	Sample #	Depth (ft)	ATAS Lab Result PCB Concentration (ppm)	Boring ID	Sample #	Depth (ft)	ATAS Lab Result PCB Concentration (ppm)
PTW-1	S1	0.0-0.5	<0.033	PTW-8	S1	0.0-0.5	<0.033
	S2	0.5-1.0	<0.033		S2	0.5-1.0	<0.033
	S3	1.0-1.5	<0.033		S3	1.0-2.0	<0.033
	S4	1.5-2.0	<0.033		S4	2.0-4.0	<0.033
	S5	2.0-2.5	<0.033		S5	4.0-6.0	0.036
PTW-2	S1	0.0-0.5	<0.033	PTW-9	S1	0.0-0.5	<0.033
	S2	0.5-1.0	<0.033		S2	0.5-1.0	<0.033
	S3	1.0-2.0	<0.033		S3	1.0-2.0	<0.033
	S4	2.0-4.0	<0.033		S4	2.0-4.0	<0.033
	S5	4.0-6.0	<0.033		S5	4.0-6.0	<0.033
	S6	6.0-8.0	<0.033		S6	6.0-8.0	<0.033
	S7	8.0-9.9	<0.033		S7	8.0-9.9	<0.033
PTW-3	S1	0.0-0.5	<0.033	PTW-10	S1	0.0-0.5	<0.033
	S2	0.5-1.0	<0.033		S2	0.5-1.0	<0.033
	S3	1.0-2.0	<0.033		S3	1.0-2.0	<0.033
	S4	2.0-4.0	<0.033		S4	1.0-2.0	<0.033
	S5	4.0-6.0	<0.033		S5	2.0-4.0	<0.033
	S6	6.0-8.0	<0.033		S6	4.0-6.0	<0.033
	S7	8.0-9.9	<0.033		S7	6.0-8.0	<0.033
					S8	8.0-9.9	0.302
PTW-4	S1	0.0-0.5	<0.033				
	S2	0.5-1.0	<0.033	PTW-11	S1	0.0-0.5	<0.033
	S3	1.0-2.0	<0.033		S2	0.5-1.0	<0.033
	S4	2.0-4.0	NS		S3	1.0-2.0	<0.033
					S4	1.0-2.0	<0.033
PTW-6	S1	0.0-0.5	<0.033		S5	2.0-4.0	<0.033
	S2	0.5-1.0	<0.033		S6	4.0-6.0	<0.033
	S3	1.0-2.0	<0.033		S7	6.0-8.0	<0.033
	S3 DUP	1.0-2.0	<0.033		S8	8.0-9.0	<0.033
	S4	2.0-4.0	<0.033		S9	9.0-9.9	<0.033
	S5	4.0-6.0	<0.033				
	S6	6.0-8.0	<0.033	TW-12	S1	0.0-0.5	<0.033
	S7	8.0-10.0	<0.033		S2	0.5-1.0	<0.033
	S8	10.0-12.0	<0.033		S3	1.0-2.0	<0.033
	S9	12.0-13.5	<0.033		S4	1.0-2.0	<0.033
	S10	13.5-14.0	0.072		S5	2.0-4.0	<0.033
	S11	14.0-15.5	<0.033		S6	4.0-6.0	<0.033
					S7	6.0-8.0	<0.033
PTW-7	S1	0.0-0.5	<0.033		S8	8.0-9.9	<0.033
	S2	0.5-1.0	<0.033				
	S3	1.0-2.0	<0.033	TW-13	S1	0.0-0.5	0.045
	S4	2.0-4.0	<0.033		S2	0.5-1.0	0.045
	S5	4.0-6.0	<0.033		S3	1.0-2.0	0.042
	S6	6.0-8.0	<0.033		S4	2.0-4.0	<0.033
	S7	8.0-9.9	0.168		S5	4.0-6.0	<0.033
					S6	6.0-8.0	<0.033
					S7	8.0-9.9	<0.033
				PTW-14	S1	0.0-0.5	<0.033
					S2	0.5-1.0	<0.033
					S3	1.0-2.0	<0.033
					S4	1.0-2.0	<0.033
					S5	2.0-4.0	<0.033
					S6	4.0-6.0	<0.033
					S7	6.0-8.0	<0.033
					S8	8.0-9.9	<0.033

NOTES:
1. NA denotes that sample analysis results are not available at this time.
2. NS indicates no sample was collected.
3. Samples taken at locations of thermal wells, e.g., TW-1 as shown on Figure 3.
4. "T" denotes twinned geoprobe location.
5. * Split spoon sample, possible contamination from shallow cavings
6. PTW-8 samples were collected adjacent to the PTW-1 location.

Paper 2C-24, in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds—2002*. Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2002). ISBN 1-57477-132-9, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

CHLOROBENZENE NAPL OXIDATION USING POTASSIUM PERMANGANATE: BENCH- AND FIELD-SCALE DEMONSTRATION

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ABSTRACT: Potassium permanganate ($KMnO_4$) was selected for use in a short-term field demonstration of chemical oxidation at an active industrial site in the eastern United States. The demonstration was designed to evaluate the feasibility of using permanganate (MnO_4^-) to destroy separate-phase, adsorbed-phase, and dissolved-phase monochlorobenzene (MCB) and 1,2-dichlorobenzene (DCB) present in the saturated soils and groundwater beneath the Site. A bench-scale treatability study confirmed the suitability of the technology for application at the Site. During the field demonstration, approximately 1,540 pounds of $KMnO_4$ were delivered to the subsurface in the form of a three-percent solution (by weight) through a series of ten injection events completed over a period of 12 weeks. The results of groundwater monitoring conducted during the field demonstration indicate that 1) the selected delivery method is effective and 2) the $KMnO_4$ was able to overcome the natural reductive poise throughout the pilot test area. However, it appears that the ability of the permanganate to sustain reaction with the target compounds was limited by an insufficient concentration of permanganate in the subsurface. An attempt to overcome this limitation through the use of an alternate source of permanganate with a higher solubility, such as sodium permanganate ($NaMnO_4$), has been proposed.

INTRODUCTION:

The subject Site is an active industrial facility located in the eastern United States. Overburden at the Site is comprised of unconsolidated deposits of silty sands and gravels ranging in thickness from approximately 30 to 65 feet. Specifically, surficial soils are comprised of an approximately 5 foot thick layer of fill material. Beneath the fill material, a layer of ablation till (poorly sorted sand, silt, and gravel) extends to between 25 and 45 feet below land surface (bls) to a layer of dense basal till ranging from 5 to 20 feet in thickness. The basal till lies directly over the regional bedrock. Groundwater at the site occurs in both the unconsolidated deposits and the fractured bedrock, and is encountered at an average depth of approximately 4.5 feet bls.

Elevated concentrations of MCB and DCB in groundwater indicate the presence of non-aqueous phase liquid (NAPL) in localized areas throughout the Site. The elimination of NAPL in such areas would remove the continuing source of groundwater impacts, thus reducing the total duration and cost to achieve Site-wide remediation goals. In support of this objective, in-situ chemical oxidation was selected for application in the form of a pilot-scale demonstration. Following an evaluation of available oxidation techniques, permanganate (MnO_4^-) in the form of potassium permanganate ($KMnO_4$) was selected for use in the pilot demonstration. This oxidant was selected for several reasons, as follows: 1) commercial availability; 2) high comparative oxidation potential; 2) ability to oxidize compounds with carbon-carbon double bonds, such as those found in MCB and

DCB (LaChance, 1998; Meyers, 1998; Oberle, 2000); 3) ability to react under a wide range of pH conditions and at normal groundwater temperatures (Meyers, 1998; Oberle, 2000); 4) ability to diffuse into lower permeability zones in heterogeneous geologic environments, such as those encountered at the Site (LaChance, 1998); and, 5) the low-energy of the resulting chemical reactions as compared to other oxidation technologies, such as Fenton's reagent. The final pilot demonstration work plan provided for the following:

- A bench-scale treatability study to confirm the suitability of the selected oxidation technology for application at the Site.
- A well network including two injection wells, six monitoring wells, and two sets of three piezometers.
- Delivery of permanganate to the subsurface through a series of ten injections involving a dilute $KMnO_4$ solution.
- Groundwater monitoring, including a baseline-sampling event prior to the injections, five sampling events during the injections, and one sampling event one to two months following completion of the injections.

Evaluation of the treatability study results, the success of the selected delivery method, and the data from the groundwater monitoring activities would be evaluated to determine whether the pilot demonstration was successful and the technology should be retained for use at the Site.

TREATABILITY STUDY

Prior to initiating the field demonstration, a bench-scale treatability study was completed in a laboratory. The objective of the study was to estimate oxidant demand in the Site subsurface. In order to complete the test, a bulk saturated soil sample and a bulk groundwater sample were collected in the area selected for the pilot demonstration and submitted to the ARCADIS laboratory in Durham, North Carolina. Upon receipt of the soil, the bench-scale treatability study was initiated. The key elements of the study were as follows:

- At the laboratory, the Site soil was homogenized and analyzed for total organic carbon (TOC) content. A total of five samples were analyzed for TOC: four were analyzed using the Walkley-Black method, which does not detect elemental carbon (charcoal/coal); and one was analyzed using the Lloyd Kahn method, which does detect elemental carbon.
- The homogenized soil was spiked with 1,000 microliters of MCB and 500 microliters of DCB (this equates to approximately 1,210 milligrams of MCB and 655 milligrams of DCB). The spiked homogenate was left undisturbed for ten days to allow time for the MCB and DCB to achieve partitioning equilibrium. The homogenate was then used to fill three equal-volume glass test columns.

- Each test column was saturated with clean water. In a closed-loop, the water in each test column was circulated several times to assure that equilibrium conditions had been achieved. Pre-treatment desorption samples of the water were then collected and submitted for VOC analysis.
- 500 milliliters (ml) of a 3% $KMnO_4$ solution was then introduced into each test column. In each column, the initial dilution resulted in a 1.89% solution that was recirculated until the concentration of $KMnO_4$ stabilized.
- The $KMnO_4$ solution was then drained, and each column was flushed once with clean water. Post-treatment desorption samples were collected from this water and were submitted for VOC analysis.

Based on numerous published studies and the results of similar testing previously completed in the ARCADIS laboratories, it was assumed that the permanganate molecule could effectively oxidize dissolved-phase constituents with carbon-carbon double bonds (such as MCB and 1,2-DCB). In an effort to make the treatability study more cost-effective, concentrations of the constituents of concern (COCs) in the permanganate effluent were not measured. The treatability study focused on the total oxidant demand assuming that reductions in COC concentrations were the result of successful oxidation.

The overall oxidant demand is generally comprised of two elements: contaminant demand and matrix demand. The matrix demand is principally comprised of naturally occurring organic material in the soil that will consume the oxidant. Matrix demand is generally larger than contaminant demand, such that it controls the magnitude of the overall oxidant demand at a Site. Consequently, soils with high organic content can result in a matrix demand that is hundreds to thousands of times greater than the contaminant demand, making oxidation technology impractical due to cost. Conversely, soils with minimal organic content can result in a very low overall oxidant demand. Based on the results of the TOC analyses, the natural organic carbon content in the Site soil is minimal, less than 500 milligrams per kilogram (mg/Kg), confirming the Site as an ideal candidate for oxidation technology.

The VOC analytical results of the pre- and post-treatment samples collected during the study are summarized below:

Measurement	MCB		1,2-DCB	
	Dissolved (ug/L)	In Soil (mg/Kg)	Dissolved (ug/L)	In Soil (mg/Kg)
Pre-treatment concentration	61,667	34,333	32,667	30,333
Post treatment concentration	346	<38	650	140
Apparent reduction:	99.4%	99.9%	98.0%	99.5%

Notes:
ug/L Micrograms per liter
mg/Kg Milligrams per kilogram

Using the average concentrations of MCB and DCB detected in the desorption samples, a conservative estimate of the sorbed-phase concentration of MCB and DCB was developed using published organic carbon/water partitioning coefficients (USEPA 1996b; Montgomery and Welkom, 1990) and equilibrium relationship equations (USEPA, 1996a). Knowing the average mass of the soil matrix in each test column, the total sorbed-phase mass of MCB and DCB oxidized in each column could be then determined. By comparing these results to the average total $KMnO_4$ consumed by each column, Site-specific oxidant utilization ratios were determined for MCB and DCB, as follows:

- 35 pounds of KMnO4 required to oxidize 1 pound of MCB (35:1)
- 54 pounds of KMnO4 required to oxidize 1 pound of DCB (54:1)

The above utilization ratios take into consideration the matrix demand created by the naturally occurring organic material in the Site soil. Due to the lack of matrix demand, the utilization ratios determined through the treatability study are less than ten times the stoichiometric utilization ratio of approximately 6:1 for both MCB and DCB. As previously mentioned, matrix demand can range from hundreds to thousands of times greater than the contaminant demand. Consequently, the results of the treatability study confirm the suitability of the technology for application at the Site.

PILOT DEMONSTRATION WELL NETWORK

The well network associated with the pilot demonstration was installed in an area of the Site where sufficient impacts were known to be present. The well network was configured such that both the performance of the oxidation process and the extent of the resulting in situ reactive zone could be evaluated. The injection wells were configured to target two discrete lithologic zones in the Site subsurface, one shallow and one deep (just above bedrock). The monitoring wells were arranged radially around the injection points, and were configured to monitor the entire saturated interval across which the chemical oxidant would be injected. The layout and profile of the pilot demonstration well network are depicted on Figures 1 and 2, respectively.

FIELD ACTIVITIES

A total of 10 injection events were completed over a period of 12 weeks. Over the course of the injection events, a total of 1,540 pounds of $KMnO_4$ was delivered to the subsurface in approximately 6,000 gallons of solution (approximately 3 percent by weight). In conjunction with the injection events, a total of seven groundwater sampling events were completed (one baseline, five during the treatment period, and one post-treatment). Based on the data collected, the following observations can be made:

- Injection pressures were negligible through all ten events, indicating that precipitation of manganese dioxide (MnO_2, a by product of $KMnO_4$ oxidation reactions) had a minimal effect on the soil permeability in the pilot area. This validates the effectiveness of the delivery method selected for the pilot demonstration.

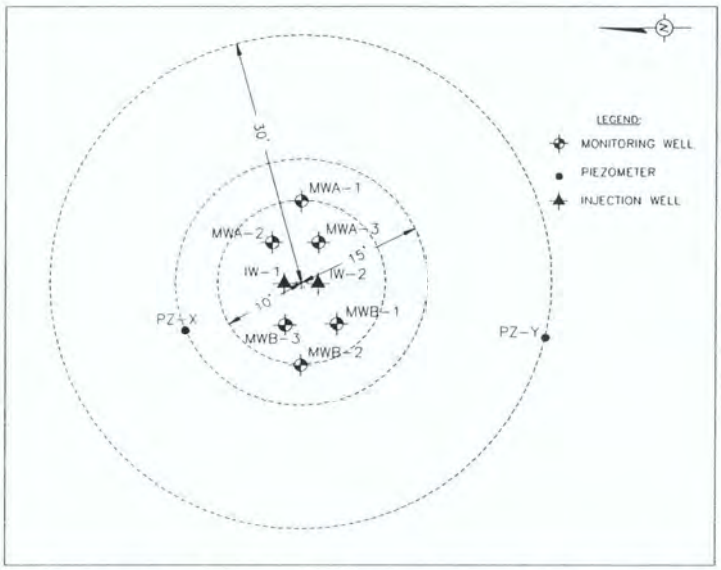


FIGURE 1: Pilot Demonstration Well Network, Layout

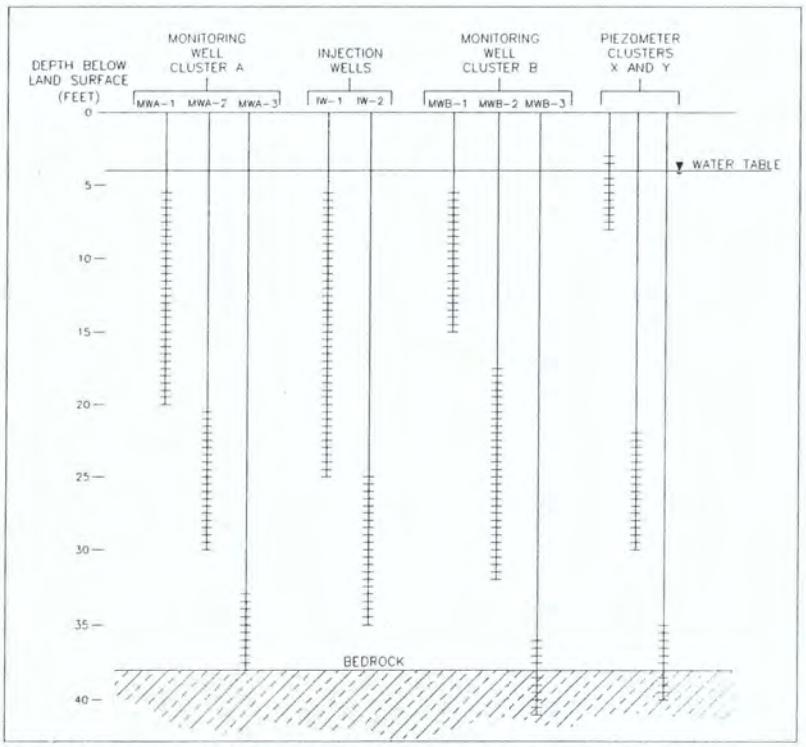
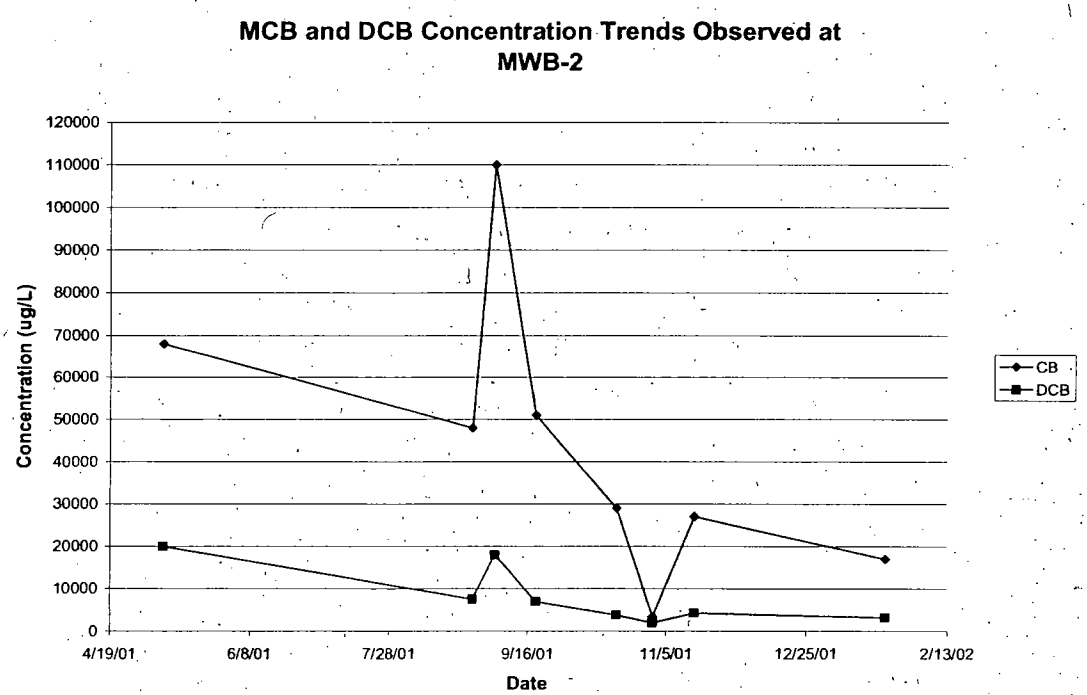


FIGURE 2: Pilot Demonstration Well Network, Profile

- The injected $KMnO_4$ was successfully delivered to the formation and distributed throughout the entire treatment area of the pilot demonstration. This is apparent based on the increase in dissolved potassium and manganese concentrations in groundwater samples collected from the monitoring wells, an increase in the specific conductivity of the groundwater at the monitoring locations, and the presence of unreacted $KMnO_4$ at the monitoring locations.
- The $KMnO_4$ was successful in overcoming the natural reductive poise (naturally occurring organic carbon and other sources of oxidant demand in the aquifer). This is evident by the significant increase in oxidation-reduction potential (ORP) throughout the treatment area.
- Evidence of the reaction between permanganate and the target compounds was observed in at least two of the monitoring well locations, as follows: 1) a 92% decrease in MCB concentration at MWB-1; and 2) a 75% decrease in MCB and 84% decrease in 1,2-DCB concentration at MWB-2 (see chart below). However, target compound concentrations in most of the pilot test monitoring wells exhibited stable to fluctuating trends, indicating that the ability of the permanganate to sufficiently react with the target compounds was limited.



CONCLUSIONS

Because the oxidation reaction associated with permanganate is dependant upon both the concentration of the target contaminant and the permanganate concentration (second order reaction), an insufficient concentration of permanganate in the subsurface would diminish its ability to react with the target compounds (Yan, 1998; Urynowicz,

2000). The low solubility of $KMnO_4$ only permitted the injection of a three percent by weight solution. Once injected, the three percent solution was further diluted in the treatment area after mixing with groundwater. This, in turn, appears to have limited the ability to sustain the desired reaction rates throughout the entire treatment area. We believe that the limited reaction between the oxidant and the target compounds can be overcome through the use of an alternate source of permanganate with a much higher solubility. Specifically, sodium permanganate ($NaMnO_4$) has a solubility ranging up to 50 percent by weight. By increasing the strength of the injected permanganate solution, the resulting in-situ permanganate concentrations should reach a point adequate to sustain sufficient reaction with the target compounds throughout the entire treatment area.

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PILOT-SCALE DEMONSTRATION OF IN-PILE THERMAL DESTRUCTION OF CHLOROBENZENE-CONTAMINATED SOIL

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Hugh McLaughlin (Groton, Massachusetts, USA)

ABSTRACT: At the Eastland Woolen Mill Superfund site in Corinna, Maine, decades of textile manufacturing led to contamination of approximately 75,000 cubic yards (57,300 cubic meters) of soil by mono-, di-, and trichlorobenzenes, which were components of the dyes used to add color to wool. In April 2000, Roy F. Weston, Inc. (Weston) completed demolition of the mill buildings, under the direction of the U.S. Army Corps of Engineers (USACE) pursuant to an Interagency Agreement with USEPA. Weston is now charged with implementing a Non-Time Critical Removal Action (NTCRA). Under the NTCRA, TerraTherm, Inc. performed a pilot test and evaluated the applicability of its In-Pile Thermal Destruction (IPTD) technology for treatment of contaminated soils in an aboveground soil pile. The soils requiring treatment are moist and derived from silty glacial till. TerraTherm's IPTD technology is an ex situ version of In Situ Thermal Destruction (ISTD), by which TerraTherm utilizes simultaneous application of thermal conduction heating and vacuum to treat contaminated soil without excavation. In IPTD, as with ISTD, the applied heat volatilizes both water and organic contaminants within the soil, enabling them to be carried in the air stream toward vacuum extraction wells for destruction within the soil and transfer of the remaining vapor to an air quality control (AQC) unit. It is anticipated that >95% of the contaminant mass will be destroyed in the heated soil.

INTRODUCTION

Eastland Woolen Mill owned and operated a textile mill in Corinna, Maine adjacent to the East Branch of the Sebasticook River between 1936 and 1996. Mill operations resulted in the release of chlorinated benzenes. In 1997, the Town of Corinna took title to the property for back taxes, and in 1999 the site was placed on the USEPA's National Priority List (NPL), designating it a Superfund Site. Under the direction of the U.S. Army Corps of Engineers (USACE), Roy F. Weston Inc., (Weston), pursuant to an Interagency Agreement with USEPA Region 1, completed demolition of the mill buildings in 2000. The major contaminants present in soils at the site are mono-, di-, and tri-chlorobenzenes. Table 1 provides a summary of the contaminants of concern, the observed range of concentrations, and their boiling points. The soils requiring treatment are moist and derived from silty glacial till excavated from locations next to the river.

Weston is currently implementing a Non-Time Critical Removal Action (NTCRA) for the Eastland Woolen Mill. Under the NTCRA, TerraTherm, Inc. performed a pilot test and evaluated the applicability of its In-Pile Thermal Destruction (IPTD) technology for treatment of the contaminated soils and sediments. TerraTherm's IPTD technology is an ex situ version of In Situ Thermal Destruction (ISTD), by which TerraTherm utilizes simultaneous application of thermal conduction

heating and vacuum to treat contaminated soil without excavation. In IPTD, as with ISTD, the applied heat volatilizes both water and organic contaminants within the soil, enabling them to be carried in the air stream toward thermal vacuum extraction wells for destruction within the soil and transfer of the remaining vapor to an air quality control (AQC) unit. It is anticipated that >95% of the contaminant mass will be destroyed in the heated soil.

TABLE 1. General Characteristics of Soil and Remedial Goals of Contaminants of Concern (COCs) at Eastland Woolen Mill, Corinna, Maine

Compound	Boiling Point (°C)	Stockpiled Soil Requiring Treatment			Pilot Test Soil Avg (ug/kg)	Cleanup Objective (ug/kg)
		Avg (ug/kg)	Maximum (ug/kg)	Minimum (ug/kg)		
Benzene	80.1	50	88	17 U	<53	30
Chlorobenzene	132.0	2,500	32,000	34 U	716	1,000
1,2-Dichlorobenzene	180.5	12,560	140,000	34 U	3,942	6,000
1,3-Dichlorobenzene	173.0	740	6,600	35 U	176	6,000
1,4-Dichlorobenzene	174.0	8,920	65,000	34 U	3,345	2,000
1,2,3-Trichlorobenzene	221.0	20,040	190,000	68 U	7,714	----
1,2,4-Trichlorobenzene	213.5	66,630	620,000	190	20,000	5,000

Source of BPs: Weast et al., 1985.
U indicates non-detect result. Result reported is the laboratory quantitation limit.

IPTD CONCEPT FOR EASTLAND WOOLEN MILL

TerraTherm's concept for using IPTD to treat the soils at the Eastland Woolen Mill (patents pending) would be to construct a series of rectangular soil piles, approximately 30 feet wide, 120 feet long and 12 feet high (10 m x 40 m x 4 m) on a liner placed on the concrete floor that remains of the former mill building. The fixed IPTD facility would be capable of treating many batches of soil. Figure 1 presents a conceptual cross-section through one of the soil piles. The end walls of the soil pile would consist of buttressed concrete slabs. A leachate collection system, consisting of a layer of gravel, collection pipes, and a liner would be installed beneath each soil pile prior to construction of the soil pile. This would allow removal and treatment of any drainage prior to treatment. The soil would be placed between the end walls and the surface sloped to maintain stability and covered with a temporary insulating cap and infiltration barrier. The soil pile would be constructed in lifts with the heating wells, heater/vacuum wells, and air intake wells installed as the lifts are placed.

Heat and vacuum would be applied simultaneously to the soil using an array of horizontal heater and heater/vacuum wells running the length of the soil pile (see Figure 1). A 30-foot wide by 12-foot high (10 m x 4 m) soil pile configuration would include 12 heater wells and 4 heater/vacuum wells arrayed in a triangular grid (see Figure 1). Each soil pile would also include an air-inlet well located in the center of the pile to provide a source of oxygen and to promote the migration of vapors through the pile to the heater/vacuum wells located at the outer corners of the pile (see Figure 1). Depending on the desired total IPTD treatment time (heat-up plus treatment), the spacing between the wells would typically be between 3 and 4 feet (0.9 and 1.2 m). The conceptual design for the Eastland Woolen Mill included a 4-foot (1.2 m) spacing between heater and heater/vacuum wells. With this spacing, the time to reach the desired treatment

temperatures (>150°C or >302°F) was estimated to be approximately 30 days (see below). Thermocouples and pressure transducers placed in the soil would track the progress of heating and the off-gas would be treated in an AQC unit consisting of a heat exchanger, condensate knockout, extraction blower, dry scrubber media and dual granular activated carbon (GAC) beds. Emissions from the AQC would be monitored during treatment. This conceptual full-scale treatment design was designed and evaluated by TerraTherm but not submitted to Weston and USACE for evaluation/consideration for use at the Eastland Woolen Mill Superfund site.

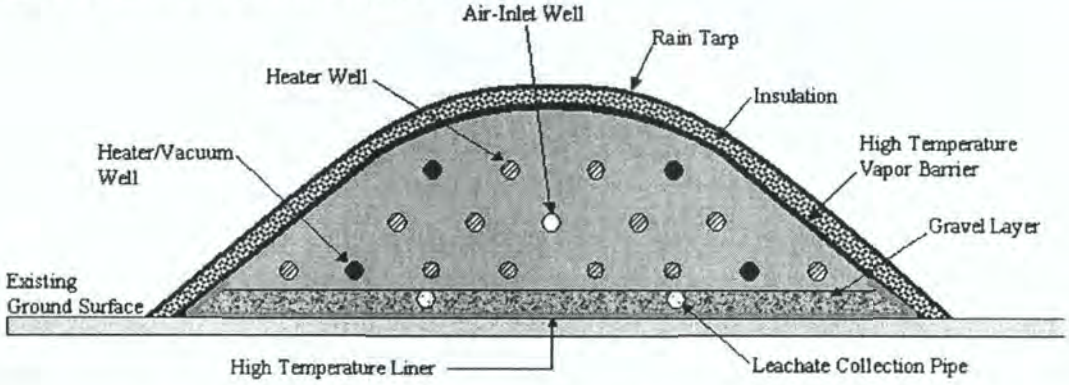


FIGURE 1. Conceptual Cross-Section Through IPTD System.

TARGET TREATMENT TEMPERATURES

The target treatment temperature was selected by considering: (1) the boiling points of the COCs (see Table 1), (2) ISTD processes, (3) the remedial goals, and (4) the desired treatment time. Based on boiling points alone, a temperature of 213.5°C (the highest boiling point of the COCs) would be required to boil off all of the primary COCs. Morever, in-situ distillation and steam stripping processes can result in significant removal of volatile and semivolatile organic compounds at temperatures around 100°C. For example, the boiling points of pure water and chlorobenzene are 100°C and 132°C, respectively. However, a mixture of water and chlorobenzene (present as non-aqueous phase liquid [NAPL] would boil at 90.2°C (i.e., the eutectic temperature of the azeotropic mixture) and the vapor would contain 71.6 percent by weight of chlorobenzene.

Theoretically, based on consideration of distillation and stream stripping processes alone, attaining 100°C in the coldest portions of the soil pile should result in sufficient treatment. However, potential non-uniform vapor flow through the soil pile and resulting mass transfer limitations could prevent attaining the cleanup goals uniformly throughout the soil pile. Thus, in order to ensure uniform treatment, a minimum target treatment temperature of 150°C was selected (i.e., the minimum temperature the coolest regions of the soil pile would attain). Experience from past ISTD projects indicates that after the water is boiled off, the superheated soil becomes desiccated, increasing its gas permeability by several orders of magnitude. In addition, at superheated temperatures below the boiling points of the COCs, their vapor pressures will rise sufficiently (e.g., to > 100 mm Hg) to ensure their rapid desorption from the soil matrix. Past research and field experience with other high-boiling compounds such as PCBs and PAHs (Stegemeier and Vinegar, 2001) suggests that the COCs at the Corinna

site will be completely removed after several days of the coolest portions of the soil volume having achieved 150°C.

Based on analytical modeling TerraTherm has conducted, adopting conservative input parameters for soil properties, it was expected that a target temperature of 150°C would be achieved throughout the soil pile within 30 days of heating with a 4-foot (1.2 m) spacing between thermal wells. The majority of the soil volume would have achieved considerably higher temperatures by that time, with maximum soil temperatures near the heaters approaching 700°C. Past research indicates that typically 95-99% of the contaminant mass is destroyed as the vapors are drawn through superheated soil in proximity to the heater-vacuum wells (Stegemeier and Vinegar 2001; Baker and Bierschenk, 2001).

PILOT TEST SETUP AND OBJECTIVES

In order to evaluate the applicability of TerraTherm's IPTD system to treat soils at the Eastland Woolen Mill, a pilot-scale test was conducted in two 55-gallon (208 L) drums located at the mill (see Figure 2). Band heaters were installed around the outside of the drums to simulate the heating from a thermal well. Drum 1 was filled with contaminated soil from the stockpiled soil requiring treatment and Drum 2 contained clean "cutback soil" excavated to access the contaminated soil.

FIGURE 2. Pilot Test Layout

During the treatment phase of the pilot test the drums were connected in series with clean air entering Drum 1 and the vapors flowing from Drum 1, through Drum 2, and then on to the AQC unit (see Figure 2). The second drum was pre-heated to the target treatment temperature prior to initiating heating of the first drum.

The objectives of the pilot test were as follows: (1) Evaluate whether the soil in the pre-heated drum, representing a treated soil pile, could serve as an effective vapor pre-treatment medium while ending up with COC concentrations that achieve soil

cleanup objectives, i.e., showing that contaminants are not merely transferred from the contaminated soil to the clean soil; (2) Determine if the exhaust from the pre-heated soil drum has low levels of emissions; and, (3) Determine that emissions from the GAC drum are consistent with attainment of Maine Ambient Air Guidelines (MAAGs) at the fenceline.

Thermocouples were installed within the soil contained in each drum, one adjacent to the circumference of the drums in proximity to the band heaters, and one in the center of the drums which, being farthest from the band heaters, were the last locations to heat up. Data from the thermocouples therefore bracketed the range of soil temperatures experienced in the drums. Pre-treatment sampling of the soil designated for each drum was conducted and a composite sample from each drum was submitted to a USACE-certified lab for the following analyses: (1) Polychlorinated Dibenzo-Dioxins and Furans (PCDD/Fs) by EPA Method 8290, (2) DRO analysis by Method ME 4.1.25, and (3) Total Organic Carbon (TOC). In addition, 5 discrete soil samples from each drum were collected and submitted to an on-site lab, for volatile organic compounds (VOC) analyses of the soil by Modified EPA Method 8021B and soil moisture content analyses by EPA Method 160.3.

PILOT TEST OPERATION

Drum 2 was heated until its central thermocouple achieved a temperature of 150°C. This temperature represented soil in the cooler, interwell regions of a fully-heated soil pile. By this time, superheated soil in the proximity of the band heaters was considerably hotter. A source of fresh air was supplied to Drum 2 during pre-heating of the clean soil. The exhaust from Drum 2 was piped to an AQC system, which consisted of a small air-to-air heat exchanger and a 55-gal (208 L) drum of GAC. It took approximately 30 hours to pre-heat Drum 2 to the target temperature. Drum 1 was then connected between the air supply and the inlet port of Drum 2, and heating of Drum 1 began. As before, the exhaust from Drum 2 was piped to the AQC system. Vapor samples were collected from the inlet and outlet of Drum 2 and from the GAC discharge two times per day, over a 2-day heating period, for a total of 12 vapor samples. These samples were analyzed for VOCs by Modified EPA Method TO-15. After the target temperature of 150°C was maintained for approximately 24 hours in Drum 1, the heaters were shut off, the piping disconnected, and representative composite soil samples were collected from each drum. These samples were analyzed at a USACE-certified analytical laboratory for PCDD/Fs by EPA Method 8290. TerraTherm also submitted 5 discrete soil samples from each drum to an on-site lab, which conducted VOC analyses of the soil by Modified EPA Method 8021B and soil moisture content analyses by EPA Method 160.3.

PILOT TEST RESULTS

Figure 3 shows the temperature data collected from Drum 1 and 2 during the pilot test. There are several notable interactions evidenced in Figure 3, which will be individually discussed. First, Drum 1 (which was the drum containing the contaminated soil) was not heated until Drum 2 was preheated sufficiently. As such, Drum 1 heating began shortly after noon (10/30 12:00 PM on the temperature figures) on the second day of the pilot test. Following the preheating of Drum 2, the internal temperatures of

Drum 1 gradually increased over the first 18 hours, followed by the "steam drive" at 100°C (212°F), where the soil-bound water was driven off. The initial high temperatures exiting Drum 1 (D1 out) was attributed to a cartridge heater present in the exit of the Drum 1 line, which was intended to simulate the effect of the heater element in the vacuum well. The cartridge heater failed during the second day of operation, as indicated by the lower temperatures in the "D1 out" vapor stream later in the pilot test.

The temperature history of Drum 2 shows the relatively rapid heating of the drum initially, followed by the prolonged period of steam drive (see Figure 3). It is likely that the edge of the drum was desiccating ahead of the center, since the heat was provided by band heaters on the circumference of the drum at three heights.

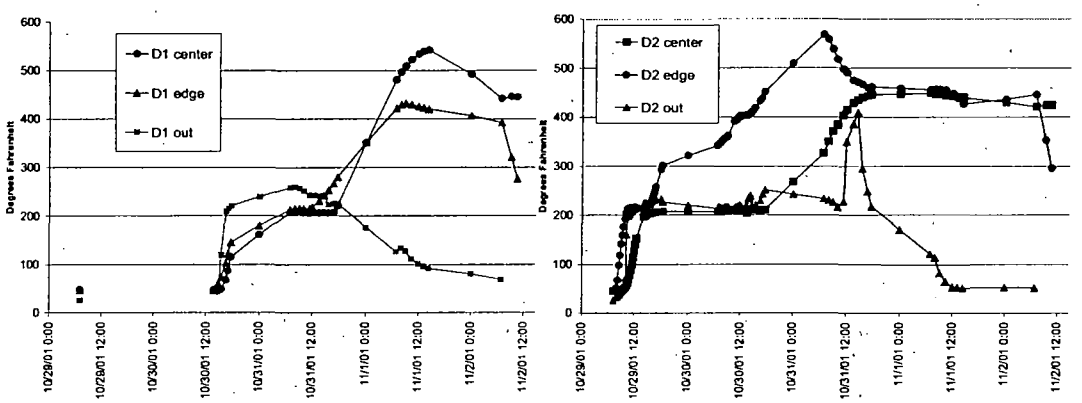
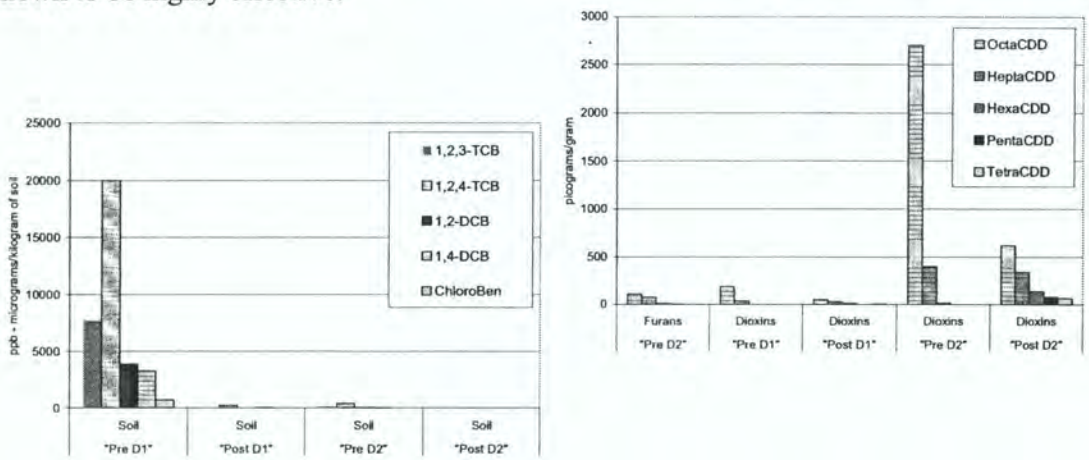


FIGURE 3. Temperature Histories for Drums 1 and 2

Figure 3 also shows an interesting temperature spike in the "D2 out" occurring the afternoon of 10/31, followed by a relatively rapid temperature decrease. This phenomenon is attributed to the effect of the stream drive from Drum 1 passing through Drum 2 and becoming superheated by the high temperatures in Drum 2. When the steam drive from Drum 1 ceased, the total vapor flow through Drum 2 decreased rapidly and the heat losses from the piping to the surroundings resulted in the cooler temperatures observed later in the Drum Test.

Figure 4 compares the level of chlorinated benzenes in the soils used in the test drums before and after the Drum Test. As expected, Drum 1 contained elevated levels of chlorinated benzenes, with a total of over 35,000 ppb of chlorinated benzenes. Prior to the Drum Test, even Drum 2 (filled with "cutback soil") measured roughly 2% of the level in Drum 1. After the Drum test, Drum 1 contained less than 1% of the starting level of aromatics and Drum 2 was non-detect for all analytical tests. It is apparent that the conditions utilized during the Drum Test are effective at removing the chlorinated benzenes from the soil matrix in the test drums. Figure 4 also shows the levels of dioxins in the soils before and after the pilot test, in addition to the "Pre Drum 2" level of furans for comparison to the dioxin levels. These data indicate that dioxins were not generated during the heating of the soil in Drum 1 or Drum 2. Moreover, the levels of dioxins/furans in the pre-treatment soil samples were below the soil standard of 1 ppb TEQ. As discussed above, the starting material in Drum 1 contained elevated levels of chlorinated benzenes. Figure 5 shows the measured levels of tri- and dichlorobenzenes

after Drum 1 and after Drum 2 in the vapor phase during the pilot test (note that the start of Drum 1 heating is the starting point of the x axis of Figure 5). The vapor phase levels exiting the GAC canister are not shown, since all but one data point was "below reportable limits" of the analytical method and the concentration of the one "hit" represented a 99.8% removal efficiency. Data presented in Figure 5 present a consistent pattern in that Drum 2 did not effectively remove the chlorinated benzenes, once volatized from Drum 1. In contrast, the GAC treatment of the cooled vapor stream was shown to be highly effective.



F IGURE 4. Pre- and Post-Treatment Concentrations of Chlorinated Benzenes and PCDD/Fs

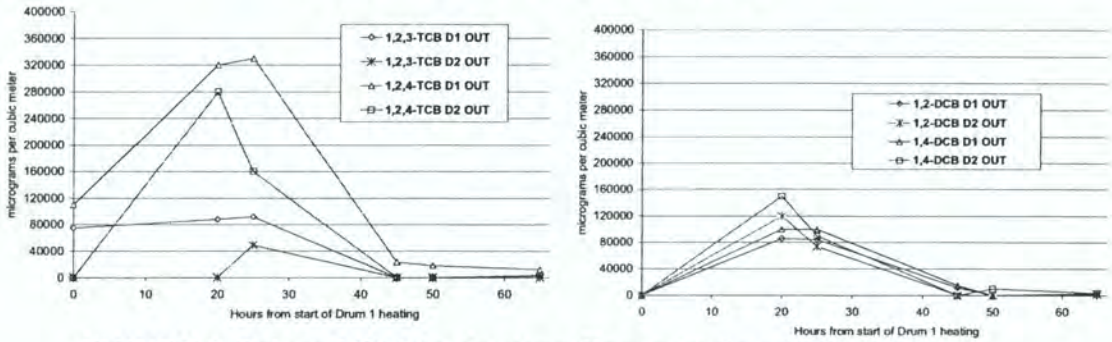


FIGURE 5. Tri- and Dichlorobenzene Concentrations in Vapor Phase

DISCUSSION

A mass balance performed on the data from the pilot test indicates that 60 to 75 percent of the original chlorobenzenes were destroyed by IPTD. The majority of the destruction likely occurred in Drum 1 after the steam drive. The chlorinated benzenes that were steam stripped from Drum 1 during the steam drive were largely transported through Drum 2 and removed effectively by the GAC canister. The 95-99% of the contaminant mass that is typically destroyed within the soil during ISTD and IPTD is attributable to the slow passage of contaminant vapors through superheated soil in the proximity of operating heater-vacuum wells, prior to the collection of the gas from the soil for aboveground treatment (Stegemeier and Vinegar 2001). Soil temperatures in the

proximity of heater-vacuum wells are generally in the 400-500°C range. By contrast, the use of the band heaters around the circumference of Drum 2 and the lack of a heater-vacuum well within Drum 2 limited the maximum soil temperature to ~230°C, thereby also limiting the amount of in-soil destruction that could occur there. Baker and Bierschenk (2001), summarizing the work of Kuhlman (2001), report that for polycyclic aromatic hydrocarbons heated to 230°C, pyrolysis is too slow to result in significant amounts of destruction. Oxidation rates, while higher, are still orders of magnitude slower within soil at 230°C than would occur at 400-500°C. Although we lack similar data for chlorobenzenes, the same trends can be expected.

SUMMARY

The pilot test indicated that TerraTherm's IPTD technology is potentially capable of removing chlorinated benzenes from the soils at the Eastland Woolen Mill site and ultimately meeting the remedial target soil concentrations. In addition, vapor emissions from the GAC drum were below the method detection limits for all but one sample, indicating that TerraTherm's IPTD would be capable of attaining the Maine Ambient Air Guidelines (MAAGs) at the fenceline. Although the overall performance of the pilot test was promising, design and operational limitations prevented a true evaluation of the feasibility and effectiveness of using a heated/treated soil pile for pre-treatment of the vapors. The pilot test did demonstrate that in situ distillation and steam stripping processes can effectively remove chlorinated benzenes at temperatures below their boiling points. It is believed that if the vapors produced during the distillation and steam stripping phase were to have passed through a typical superheated region around a heater/vacuum well (soil temperatures of 400-500°C), very high in-situ destruction efficiencies (e.g., 95-99%) would have occurred. In addition, comparison of the pre- and post-treatment 2,3,7,8-tetrachloro-dibenzodioxin toxicity equivalent (TEQ) data indicated that IPTD did not create dioxins during the course of the pilot test.

ACKNOWLEDGMENTS

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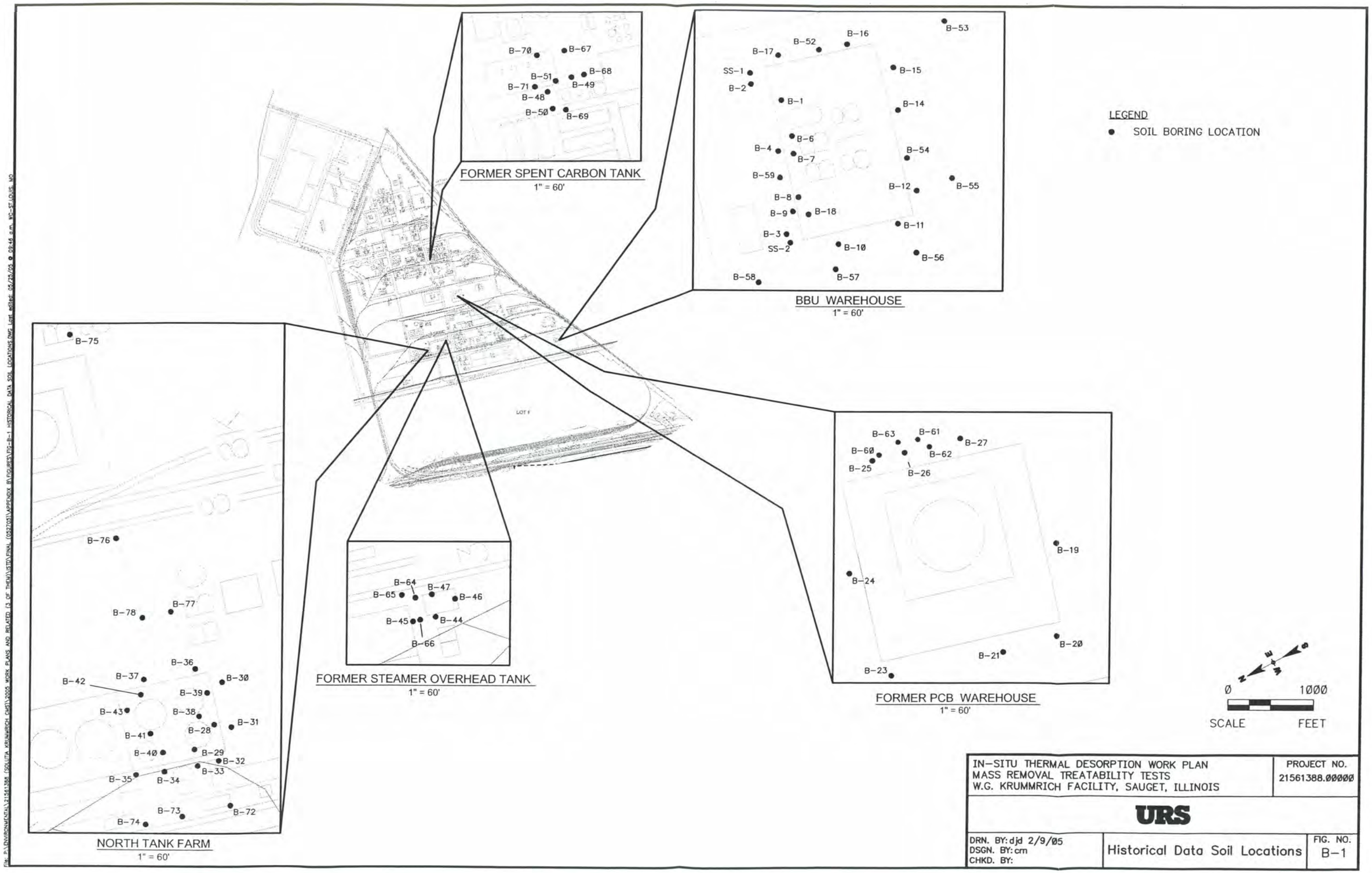
EVS PCB DATA SET



IN-SITU THERMAL DESORPTION WORK PLAN MASS REMOVAL TREATABILITY TESTS W.G. KRUMMRICH FACILITY, SAUGET, ILLINOIS	PROJECT NO. 21561388.00000
URS	
DRN. BY: djd 2/9/05 DSGN. BY: cm CHKD. BY:	Historical Data Soil Locations — FIG. NO. B-1

File: P:\ENVIRONMENTAL\21561388 (SOLUTIA KRUMMRICH GIST)\2005 WORK PLANS AND REPORTS (3 OF THE UNISTS)\FINAL (09272005)\APPENDIX B\FIGURES\FIG-B-1 HISTORICAL DATA SOIL LOCATIONS.DWG Last edited: 03/29/05 @ 09:46 a.m. WC-ST.LOUIS, MO

IN-SITU THERMAL DESORPTION WORK PLAN MASS REMOVAL TREATABILITY TESTS W.G. KRUMMRICH FACILITY, SAUGET, ILLINOIS	PROJECT NO. 21561388.00000
URS	
DRN. BY: 4/9/05 DSGN. BY: cm CHKD. BY:	Phase I and Phase II Data Soil Locations
	FIG. NO. B-2

APPENDIX B
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 2.1 THROUGH 2.3

Point ID	Easting	Northing	Depth (ft bgs)	PCB Concentration (ppm)
Historical Boring Data Soil Locations (see Figure B-1)				
BBUB3	2294318	701865	5	1.49
KR/BCB39	2294972	703154	5	34.3
KR/BCB40	2294949	703201	7	6.4
NTFB72	2294892.2	703176.8	5	<1
NTFB73	2294902.1	703210.2	3	<1
NTFB73	2294902.1	703210.2	7	<1
NTFB74	2294908.4	703234.8	3	<1
NTFB74	2294908.4	703234.8	7	<1
NTFB75	2295244.3	703115.9	1	<1
NTFB76	2295099.4	703159	1	0.155
NTFB77	2295035.5	703149.4	1	1.08
NTFB78	2295041.3	703168	2.5	<1
PCBB19	2295339	702516	5	<1
PCBB20	2295281	702546	5	<1
PCBB21	2295289	702585	5	0.322
PCBB23	2295311	702662	5	0.404
PCBB24	2295388	702655	7	14.2
PCBB25	2295451	702603	5	<1
PCBB26	2295446	702581	3	9200
PCBB27	2295436	702542	5	0.6
PCBB60	2295453	702597	1	47.5
PCBB60	2295453	702597	5	0.218
PCBB61	2295450	702568	1	7.4
PCBB61	2295450	702568	5	<1
PCBB62	2295441	702563	3	0.054
PCBB62	2295441	702563	7	<1
PCBB63	2295455	702581	4.5	494
SCTB51	2295947	702618	7	0.416
SOTB45	2295018	702925	5	0.276
Phase I and Phase II Data Soil Locations (see Figure B-2)				
CT2a1	2294840	702068.2	14	0.39
CT2b1	2294838.95	702067.56	14	0.21
S0406	2295014.9	703608.4	11	<1
S0408	2295522.8	703501.4	7	<1
S0411	2294657.3	703101.7	15	<1
S0412	2294653.9	702803	14	<1
S0415	2295353.6	702848.8	13	<1
S0502	2295271.7	703195.7	7	2.506
S0505	2294902.3	702579.5	11	<1
S0511	2294963.3	702241.7	9	13.93
S0602	2294702.7	702125.2	7	1.2
S0603	2294805.5	702205.4	7	32.3

Notes:
1) <1 ppm indicates sample results was below the lowest concentration depicted on the figure.
2) ft bgs = feet below ground surface

APPENDIX B
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 2.1 THROUGH 2.3

Point ID	Easting	Northing	Depth (ft bgs)	PCB Concentration (ppm)
Phase I and Phase II Data Soil Locations (see Figure B-2)				
S0607	2294381.7	701988	2	66.2
S0608	2294713.9	702092.3	2	38.9
S0609	2294357.7	701681.5	2	1090
S0609	2294357.7	701681.5	15	0.11
S0610	2294646.6	701721.8	2	7.8
S0701	2294926.9	702183	7	<1
S0704	2295160.1	702043.7	15	2.74
S0705	2295267.2	702364.1	3	10.64
S0709	2295873.5	702341.6	3	14.6
S0710	2295808.3	702178.7	14	29.1
S0711	2295867.2	702215.2	13	2.58
S0712	2296178.5	702321.3	4	<1
S0714	2295124.6	702249.3	2	1.852
S0715	2295017.8	701874.6	2	1.21
S0715	2295017.8	701874.6	7	33
S0716	2295465.9	702363.8	2	0.95
S0718	2295714.1	702086.5	11	12.9
S0718	2295714.1	702086.5	15	5.64
S0719	2296080.7	702524.7	11	5.8
S0801	2296569.5	703060.9	5	<1
S0801	2296569.5	703060.9	15	<1
S0802	2296633.5	703196.7	3	2570
S0803	2296786.5	703032.1	2	8.3
S0804	2296651.6	703202.2	1.5	1140
S0806	2296626.3	703184	3.5	154
S0808	2296611.9	703202.6	3.5	728
S0810	2296619.8	703237.6	1.5	3290
S0813	2296624.7	703237.6	1.5	2200
S0819	2296638.5	703144	5.5	1.46
S0819	2296638.5	703144	9.5	430
S0822	2296612.1	703149.2	9.5	2207
S0823	2296612.1	703149.2	5.5	930
S0825	2296705.1	703119.2	1.5	3820
S0825	2296705.1	703119.2	5.5	57.2
S0825	2296705.1	703119.2	9.5	22100
S0826	2296655	703138.3	9.5	3130
S0827	2296532.1	703199	1.5	98
S0827	2296532.1	703199	5.5	1.84
S0830	2296708.1	703201.9	5.5	1470
S0831	2296689.9	703143	13.5	2030
S0834	2296631.3	703220.6	13.5	85
S0835	2296604.4	703214.6	13.5	9300

Notes:
1) <1 ppm indicates sample results was below the lowest concentration depicted on the figure.
2) ft bgs = feet below ground surface

APPENDIX B
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 2.1 THROUGH 2.3

Point ID	Easting	Northing	Depth (ft bgs)	PCB Concentration (ppm)
Phase I and Phase II Data Soil Locations (see Figure B-2)				
S0836	2296604.4	703254.5	9.5	10.6
S0904	2296801.8	702627.5	7	12.8
S0905	2296990.9	702530.6	2	4.62
S1207	2295996.3	702693.9	2	<1
S1207	2295996.3	702693.9	9	<1
S1207	2295996.3	702693.9	15	<1
S1211	2296080.3	702867.9	15	<1
S129	2295746	702855.7	2	<1

Notes:
1) <1 ppm indicates sample results was below the lowest concentration depicted on the figure.
2) ft bgs = feet below ground surface

FIELD SAMPLING PLAN

FIELD SAMPLING PLAN/QUALITY ASSURANCE PROJECT PLAN

IN-SITU THERMAL DESORPTION

MASS REMOVAL TREATABILITY TEST

Solutia, Inc.

W,G. Krummrich Facility

Sauget, Illinois

May 27, 2005

Prepared for
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575 Maryville Centre Drive
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May 2005

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Project #21561388

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SOP-2 Field Analysis of Sample Headspace for Volatile Organics
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SOP-7 Sample Containers, Preservation, and Holding Times
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Appendix B Laboratory Standard Operating Procedures (SOP)
Volatile Organic Compounds - Method 8260B
(Including Monochlorobenzene and Dichlorobenzene [MCB, DCB])
Semi Volatile Organic Compounds - Method 8270C
Polychlorinated Biphenyl - Method 680
Extractable Organic Halides - Method 9023
Moisture Content – ASTM D 2216
Particle Size ASTM D 422
Permeability ASTM D 2434 (granular soil), ASTM D 5084 (fine grain)

Appendix C Chain of Custody

SECTIONONE Project Description

1.1 INTRODUCTION

On August 27, 2004, Solutia Inc. submitted to USEPA, a Corrective Measures Study (CMS) Report for the W.G Krummrich facility in Sauget, Illinois. On November 18, 2004, USEPA issued 51 pages of comments on Volumes I, II and III of the W.G. Krummrich RCRA CMS, including 21 general comments and 71 specific comments. A "RCRA Corrective Measure Study (CMS) Response to Comments (CMS RTC)" was submitted by Solutia on February 9, 2005. On May 4, 2005 USEPA responded to the CMS RTC.

In partial response to USEPA's November 18, 2004, and May 4, 2005 comments, Solutia will undertake bench-scale treatability tests, to assess whether or not mass removal at the Former PCB Manufacturing area and the Former Chlorobenzene Process Area. These bench-scale treatability tests are designed to provide a yes/no answer as to whether or not it is technically feasible to remove contaminant mass in the Former PCB Process Area, and the Former Chlorobenzene Process Area. This Field Sampling Plan describes the sample collection and sample analysis procedures that will be used to collect and analyze the mass removal treatability test soil samples.

SECTION TWO Project Objectives and Rationale

2.1 OBJECTIVES AND RATIONALE

In-Situ Thermal Desorption (ISTD) was identified as the best technology for performing bench-scale PCB and Chlorobenzene (MCB) and Dichlorobenzene (DCB) mass removal treatability tests on unsaturated soil samples from the Shallow Hydrogeologic Unit at the Former PCB Manufacturing Area and the Former Chlorobenzene Process Area. See **Figure 1**. , soil samples for a bench-scale ISTD treatability test will be collected from the unsaturated zone (0 to 15 feet bgs) of the Former PCB Manufacturing Area and the Former Chlorobenzene Process Area. As directed by USEPA, a soil sample will be collected from the saturated SHU unit (15 feet to 35 feet bgs) from the Former Chlorobenzene Process Area. In addition, samples for characterization will be collected from these locations. The proposed sampling locations are shown on **Figure 2**.

This Field Sampling Plan (FSP) describes the sampling procedures for the collection of soil samples for the baseline and bench-scale treatability tests. In addition, the FSP provides objectives, organization, functional activities, and specific Quality Assurance (QA) and Quality Control (QC) activities for sampling, sample handling and storage, chain of custody, and laboratory and field analysis efforts associated with sampling of environmental media as in accordance to EPA Region 5 Model Quality Assurance Project Plan (QAPP). Field Sampling Procedures are located in **Appendix A.**

URS Corporation (URS) will perform the field activities, in accordance to the FSP, Standard Operation Procedures (SOPs), and an approved Health Safety Plan (HASP). URS will coordinate with Solutia personnel to obtain the appropriate permits and clearance to perform the subsurface activities.

Severn-Trent Laboratories (STL) Savannah, Georgia will provide analytical services for this FSP. Geotechnical testing analysis may be provided by STL out of Burlington, New Hampshire, or URS geotechnical out of Totowa, NJ. Chemical and geotechnical testing will be conducted in accordance with the Laboratory SOPs located in **Appendix B.**

After the collection of baseline samples, bench-scale treatability test samples will be collected from the same and adjacent locations from where the baseline samples were collected. The treatability samples will be properly packaged and shipped to Kemron Environmental Services Inc. (Kemron) for preparation of treatability tests.

Upon completion laboratory analyses and data validation, a study report that describes testing protocols, treatability test results, and includes all data collected during the study including laboratory notes and reports, will be prepared and submitted to USEPA.

SECTIONTHREE Field Procedures

3.1 SOIL DRILLING AND SAMPLING

A soil sample will be collected for baseline characterization from the unsaturated zone, from the Former PCB Manufacturing Area and from the Former Chlorbenzene Process Area. In addition, a baseline soil sample from the saturated SHU will be collected from the Former Chlorbenzene Process Area. The samples will be collected from approved sample locations from the estimated depths as shown in **Table 1**. The baseline sample locations are shown on **Figure 2**. The proposed sample locations were selected because these locations contained the highest concentrations detected for PCBs, MCB, and DCB. The baseline samples will be collected, properly packaged and shipped to STL laboratories for analysis in accordance with the SOP guidelines included in **Appendix A**.

After collection of the baseline samples, additional samples will be collected for the ISTD tests. These samples are expected to be collected from same depth intervals immediately adjacent to the baseline sampling locations. Refer to **Table 1** for estimated sample depths.

For the unsaturated SHU locations, six- one gallon containers (approximately 66 lbs) will be collected from the Former PCB Manufacturing Area, and from the former Chlorobenzene Process Area. For the saturated SHU location, four – one gallon containers (approximately 44 lbs) will be collected.

The above samples will be properly packaged and shipped in accordance to SOP guidelines to Kemron (Kemron) in Atlanta Georgia for homogenization and bench-scale treatability testing.

Borings will be advanced using one or more of various methodologies in order to obtain the adequate soil volume necessary for analysis. Some of the methodologies include:

Direct Push Technology (Geoprobe®): The Geoprobe® hydraulically drives a stainless steel, acetate-lined MacroCore® sampler (2-inch diameter by 4-foot length) to the desired subsurface sample depths. Continuous samples will be collected from the surface to the proposed sampling depths as shown on **Table 1**. Estimated depths for the unsaturated zone and saturated SHU are approximately 0 to 15 feet, and 15 to 35 feet bgs, respectively. The MacroCore® sampler can retrieve up to 150 in^3 (assuming 100% recovery on a 4 feet soil core). This volume is sufficient to fill up 2 quarts, or approximately one ½ gallon sample container, (or approximately 6.5 lbs per ½ gallon). Multiple probes at each sample location will be necessary to collect the required sample volume. Should larger (large gravel to cobble) size materials be encountered, additional

core samples will be obtained and placed into additional containers. Direct push technology may be a viable option for the collection of shallow samples, and for locations where access is restricted.

Conventional Drilling Technology: 4 ¼ -inch Hollow Stem Augers (HSA) with a 3-in by 5 feet continuous tube sampler will be used to collect the soil samples from the proposed sample locations as shown on **Table 1**. Estimated depths for the unsaturated zone and saturated SHU are approximately 0 to 15 feet, and 15 to 35 feet bgs, respectively. The continuous tube sampler can retrieve up to 339 in^3, (assuming 100% recovery on a 4 feet soil core), or approximately 5 quarts, or approximately 1.25 gallons. Convention drilling technology may be a viable option for collection of deeper samples, assuming there is no access restriction. However, multiple borings at each sample location will be necessary to collect the required sample volume.

Rotosonic Drilling Technology. Rotosonic technologies utilize a 6-inch by 10 feet outer casing with a 4-inch by 10 feet continuous sampler for collection of soil samples. The proposed sample depths are shown on **Table 1**. Estimated depths for the unsaturated zone and saturated SHU are approximately 0 to 15 feet, and 15 to 35 feet bgs, respectively. The continuous tube sampler can retrieve up to 603 in^3, (assuming 100% recovery on a 4 feet soil core), or approximately 10.4 quarts. Rotosonic drilling technology may be the best viable option for collection of deeper samples, assuming that there is no access restriction. In addition, a limited number of borings will be necessary to collect the required sample volume.

Soil borings will be advanced using one, or a combination of the above technologies. The boring will be advanced to the estimated depth as shown in **Table 1**.

Multiple borings adjacent to the boring with the highest constituent concentration will be needed in order to collect the required soil for each ISTD treatability tests. The soil sample cores will be collected in four-foot lengths to help ensure that the samples are collected within the horizon of the highest known concentration. Visual observations and PID measurements of the soil core will be made to help ensure representativeness. Additional borings will be located within less than 5 feet from each other to help ensure that a representative soil sample is obtained.

At the completion of each soil boring, the boreholes will be backfilled with bentonite chips instead of bentonite grout to reduce the potential of the grout to come in contact with adjacent soil from the additional borings.

Upon completion, the soil boring locations will be surveyed to obtain X-Y coordinates.

3.2 LOGGING UNCONSOLIDATED SAMPLES

The subsurface stratigraphy will be logged during drilling operations by a qualified URS field scientist in accordance with the USCS protocols. The field scientist will note soil attributes such as color, particle size, consistency, moisture content, structure, plasticity, odor (if obvious) and organic content (if visible). Soil samples from each boring will be visually evaluated for evidence of impact and screened in the field using a Photoionization Detector (PID). Information pertaining to the subsurface soil and drilling conditions will be recorded in the field on a standard field boring log form in accordance to SOP guidelines. Scaled, color digital photographs will be taken of each soil sample to provide a record of materials present at this site.

3.3 SOIL SAMPLE ANALYSIS

The baseline soil samples will be analyzed by STL for the following parameters and methods as shown below and in **Table 2.**

Parameter	Analytical Method
Volatile Organic Compounds (VOCs)	USEPA Method 8260B
Semivolatile Organic Compounds (SVOCs)	USEPA Method 8270C
Polychlorinated Biphenyls	USEPA Method 680
Extractable Organic Halides (EOX)	USEPA Method 9023
Moisture Content	ASTM D 2216
Particle Size	ASTM D 422
Permeability	ASTM D 2434 (Granular Soil) ASTM D 5084 (Fine-Grained Soil)

The bench-scale samples, which are scheduled to be submitted to Kemron will also be analyzed for the following parameters.

Bench-Scale Treatability Tests

Parameter	Analytical Method
VOCs	USEPA Method 8260B
SVOCs	USEPA Method 8270C
PCBs	USEPA Method 680
EOX	USEPA Method 9023
Moisture Content	ASTM D 2216

Bench-Scale Treatability Tests

Parameter	Analytical Method
Particle Size	ASTM D 422
Permeability	ASTM D 2434 (Granular Soil) ASTM D 5084 (Fine-Grained Soil)

Kemron will homogenize the bulk samples in accordance to the Work Plan, and following SOPs guidelines.

SECTION FOUR Field Documentation and QA/QC

Field activities for the W.G. Krummrich site, such as documentation, QA/QC activities, equipment decontamination, and handling of investigation derived waste, and sampling procedures are presented below.

4.1 FIELD DOCUMENTATION

URS personnel will keep a bound field notebook while performing sampling and oversight activities on-site. Forms that will be used include: chain-of-custody, test boring log, and field log, and soil sampling data sheets. The field logbooks will contain tabulated results of field measurements and documentation of field instrument calibration activities. The field logbooks will also record the following:

- Personnel conducting the site activities, their arrival and departure times and their destination at the site
- Incidents and unusual activities that occur on the site such as, but not limited to, accidents, breaches of security, injuries, equipment failures, or weather related problems
- Changes to the FSP and the HASP
- Daily information such as:
  - Work accomplished and the current site status
  - Equipment calibrations, repairs and results
  - Site work zones.
- Date, time, weather conditions, equipment, and personnel on site
- Location where the work was performed
- Specific work activities conducted
  - Work zone and headspace readings.

In the field sampler's individual bound field logbook, samplers will note, with permanent ink, meteorological data, equipment employed for sample collection, calculations, information regarding collection of QA/QC samples, and any observations. All entries will be signed and dated, and any entry, which is to be deleted will have a single cross out which is signed and dated. The following sampling-related information will be recorded in the field logbook by the field sampling team:

- Sample number
- Project identification
- Sampling location
- Required analysis
- Date and time of sample collection
- Type and matrix of sample
- Sampling technique
- Preservative used, if applicable
- Sampling conditions
- Observations
- Initials of the sampler.
- Samples collected
- Depth of borings

Field data documentation procedures will be minimal in scope. Only direct reading instrumentation will be employed in the field. If errors are made, results will be legibly crossed out, initialed, and dated by the field member. Errors will be corrected in a space adjacent to the original entry.

Photographic records will be developed through the use of digital photographs, showing pre-sampling and post-sampling conditions at each site.

4.2 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

To verify field and laboratory procedures, quality assurance/quality control (QA/QC) samples consisting of duplicate samples, matrix spike/matrix spike duplicate (MS/MSD) samples, field blanks and trip blanks may be collected and submitted to the laboratory. It should be noted that no QA/QC sampling is anticipated for the baseline samples. However, QA/QC sampling and procedures at a frequency of 10% for duplicates and blanks and 5 % for MS/MSD will follow during the segregation of aliquots samples for treatability testing.

Samples (including QA/QC samples) will be tracked using appropriate Chain-of-Custody documentation. The Chain-of-Custody procedures are described in Section 4.7.3 of this FSP. A sample chain-of-custody form is also presented in **Appendix C.**

4.3 DECONTAMINATION

In order to reduce the potential for exposure to hazardous materials and limit the possibility of cross contamination of samples, all personnel and equipment will be subject to the decontamination program for this project. All equipment used on-site, from a small handheld PID to a large conventional drilling rig, will be decontaminated prior to beginning work, between sampling locations and/or uses, and prior to demobilizing from the site. Refer to SOP-9 in **Appendix A** of this FSP for decontamination procedures.

4.4 INVESTIGATION DERIVED WASTE

All Investigation Derived Waste (IDW) (i.e. soil cuttings and PPE) will be placed in 55-gallon drums and stored at a centralized area pending appropriate disposal.

4.5 QA/QC PROCEDURES

QA/QC procedures for the field work will consist of equipment test checks.

4.6 SAMPLE DOCUMENTATION

4.6.1. Sample Identification System

The sample identification system will involve the following nomenclature "AA-BBB-CCC-DDD-EE" where:

"AA" will denote

- BS- Baseline Sample
- TT- Thermal Treatability Test Sample

"BBB" will denote

- USH- Unsaturated Shallow Hydrogeologic Unit
- SSH- Saturated Shallow Hydrologic Unit
- MDU - Saturated Middle/Deep Hydrogeologic Unit

"CCC" will denote

- CPA- Former Chlorobenzene Process Area
- PMA – Former PCB Manufacturing Area

"DDD" will denote

- 001- Sample Depth

"EE" will denote QA/QC sample

- EB- equipment blank
- AD- analytical duplicate
- MS or MD – Matrix Spike or Matrix Duplicate
- TB- Trip Blank.

4.6.2 Sample Labels

For proper identification in the field and proper tracking by the analytical laboratory, samples will be labeled in a clear and consistent fashion. Sample labels will be waterproof, or sample containers will be sealed in plastic bags. Field personnel will maintain a sampling log sheet containing information sufficient to allow reconstruction of the sample collection and handling procedures at a later time.

A completed sample label will be attached to each investigative or QC sample. The following will be recorded with permanent ink on sample labels by the field sampling team:

- Project name and number

- Sample number identification
- Initials of sampler
- Sampling location (if not already encoded in the sample number)
- Required analysis
- Date and time of sample collection
- Space for laboratory sample number
- Preservative used, if applicable.

4.6.3 Chain-of-Custody Records

Chain-of-custody procedures will be instituted and followed throughout the sampling activities Samples are physical evidence and will be handled according to strict chain-of-custody protocols. The field sampler is personally responsible for the care and custody of the sample until transferred. For proper identification in the field and proper tracking by the analytical laboratory, samples will be labeled in a clear and consistent fashion.

Field personnel will record the following information with permanent ink on the chain-of-custody:

- Project identification and number
- Sample description/location
- Required analysis
- Date and time of sample collection
- Type and matrix of sample
- Number of sample containers
- Analysis requested/comments
- Sampler signature/date/time
- Air bill number.

The laboratory will assign a number for each sample upon receipt. That sample number will be placed on the sample label. The label will be attached to the sample container. A chain-of-

custody document providing all information, signatures, dates, and other information, as required on the example chain-of-custody form in **Appendix C** will be completed by the field sampler and provided for each sample cooler. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the chain-of-custody. The field sampler will sign the chain-of-custody form when relinquishing custody, make a copy to keep with the field logbook, and include the original form in an air-tight plastic bag in the sample cooler with the associated samples.

4.7 DATA MANAGEMENT RETENTION

The field data and documentation, as described in this section, will become a part of the final evidence file. The final evidence file will be the central repository for all documents, which constitute evidence relevant to sampling and analysis activities as described in this FSP and the QAPP. URS is the custodian of the evidence file and maintains the contents of evidence files for the site, including all relevant records, logs, field logbooks, pictures, subcontractor reports, data reviews, and the database management system.

Upon completion of the analyses, URS will begin assimilating the field and laboratory notes. In this way, the file for the samples will be generated. The final file for the samples will be stored at URS and will consist of the following:

- Laboratory data packages, including summary and raw data from the analysis of environmental and QC samples, chromatograms, mass spectra, calibration data, work sheets, and sample preparation notebooks
- Chain-of-custody records
- Data validation reports.

4.8 DATA VALIDATION

Data validation procedures shall be performed for both field and laboratory operations.

4.8.1 Procedures Used to Evaluate Field Data

Procedures to evaluate field data for this project primarily include checking for transcription errors on the part of field crew members and review of field notebooks. This task will be the responsibility of the URS Field Leader, who will otherwise not participate in making any of the field measurements or in adding notes, data, or other information to the notebook.

4.8.2 Procedures to Validate Laboratory Data

Data validation will be performed by the URS QA Manager in accordance with QA/QC criteria established in EPA Region 5 Model QAPP. Excursions from QA/QC criteria will be qualified based on guidance provided in the following documents or the most recent USEPA data validation guidelines:

- *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*. USEPA 540/R-94/012 (USEPA, October 1999)
- *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*. USEPA 540/R-94/013 (USEPA, 1994d)

The analytical data from each method and matrix will be reviewed for the QC parameters as presented in the following section. Data validators will recalculate 10% of the laboratory sample calculations using raw data when verifying sample results. In addition, data validators will review 10% of the raw data to verify that compound identification was performed correctly and transcription errors are not present.

Data quality will be evaluated using method or laboratory control limits. Any control limits outside of the acceptable range shall be identified and reported. Sample data will be qualified based on excursions from method or laboratory control limits. Data not within control limits require corrective action by the laboratory. Data validators will check corrective actions and results of reanalysis and document these events in the validation report.

Minor deficiencies in the data generation process noted in the data validation will result in approximation of sample data. Approximation of a data point indicates uncertainty in the reported concentration of the chemical but not its assigned identity. Major deficiencies noted in the data, validation will result in the rejection of sample results. Rejected data would be considered unusable for quantitative or qualitative purposes. Data qualifiers may include the following:

U Indicates that the compound was analyzed for, but was not detected. The sample quantitation limit is presented and adjusted for dilution and percent moisture. This qualifier is also used to signify that the detection limit of an analyte was raised as a result of analytes detected in laboratory and/or field blank samples.

J Indicates that the detected sample result should be considered approximate based on excursions from QA/QC criteria.

UJ Indicates that the detection limit for the analyte in this sample should be considered approximate based on excursions from QA/QC criteria.

R Indicates that the previously reported detection limit or sample result has been rejected due to a major excursion from QA/QC criteria, for example percent recoveries of less than ten percent. The data should not be used for qualitative or quantitative purposes.

The following method specific QA/QC parameters will be evaluated (at a minimum) during the data validation, where applicable.

Analyses for VOCs and SVOCs (where applicable)

- Holding times, sample preservation, and percent solids
- Dilutions
- GC/MS tuning criteria
- Initial and continuing calibration
- Blank analysis
- Surrogate recovery
- MS/MSD analysis
- Field duplicate analysis
- Laboratory Control Sample (LCS) analysis
- Internal standards performance
- Compound identification and quantitation
- Reported detection limits
- System performance
- Documentation completeness
- Overall assessment.

Analyses for PCBs, (where applicable):

- Holding times, sample preservation, and percent solids
- Dilutions

- GC performance
- Analytical sequence
- Initial and continuing calibration
- Blank analysis
- Surrogate recovery
- MS/MSD analysis
- Field duplicate analysis
- LCS and MS blank analysis
- Retention time windows
- Analyte identification, quantitation, and reported detection limits
- Cleanup efficiency verification
- Confirmation analysis
- System performance
- Documentation completeness
- Overall assessment.

Analysis for Extractable Organic Halides (EOX), (where applicable):

- Holding times, sample preservation, and percent solids
- Contract required detection limit (CRDL) standard analysis criteria
- Initial and continuing calibration
- Blank analysis
- ICP interference check sample analysis
- Spike duplicate analysis
- Field duplicate analysis LCS analysis
- Laboratory duplicate analysis

- ICP serial dilution analysis
- Furnace atomic absorption analysis
- Verification of instrument parameters
- Instrument detection limits
- Linear ranges
- Analyte quantitation, and reported detection limits
- Documentation completeness
- Overall assessment.

The laboratory will be conducting analyses on samples in accordance with methods listed in Table 2 and the laboratory's SOPs. Data generated by this FSP will be computerized in a format organized to facilitate data review and evaluation. The computerized data set will include the data flags provided by Savannah Labs as well as the data validation results.

The following documentation will supplement the chain-of-custody records:

- Field logbooks and data
- Field collection report
- Photographs and drawings
- Contractor and subcontractor reports
- Correspondence.

The evidence file must be maintained in a secured, limited access area until all submittals for the project have been reviewed and approved, and for a minimum of six years past the submittal date of the final report.

SECTIONFIVE Sample Packaging and Shipping

A completed sample label will be attached to each investigative or QC sample and the sample placed in a shipping container. Information to be recorded on sample labels are described in Section 4.7.2 Information to be recorded on chain-of-custody forms is described in Section 4.7.3. The sample identification system used in the field is described in Section 4.7.1.

Sampling containers will be packed in such a way as to help prevent breakage and cross-contamination. Samples will be shipped in coolers, each containing a chain-of-custody form and ice and ice packs to maintain inside temperature at approximately 4°C. Sample coolers will then be sealed between the lid and sides of the cooler with a custody seal prior to shipment. The custody seal will be an adhesive-backed tape that easily rips if it is disturbed. Samples will be shipped to STL and/or Kemron by common overnight carrier.

Sample transportation will comply with U.S. Department of Transportation and IICAO/IATA (1999) regulations. Special sampling packing provisions will be made for samples requiring additional protection.

Samples will remain in the custody of the sampler until transfer of custody is completed. Transfer consists of:

- Delivery of samples to the laboratory sample custodian
- Signature of the laboratory sample custodian on the chain-of-custody document as receiving the samples, and signature of sampler, as relinquishing the samples.

If a carrier is used to take samples between the sampler and the laboratory; a copy of the air bill must be attached to the chain-of-custody to maintain proof of custody.

SECTIONSIX References

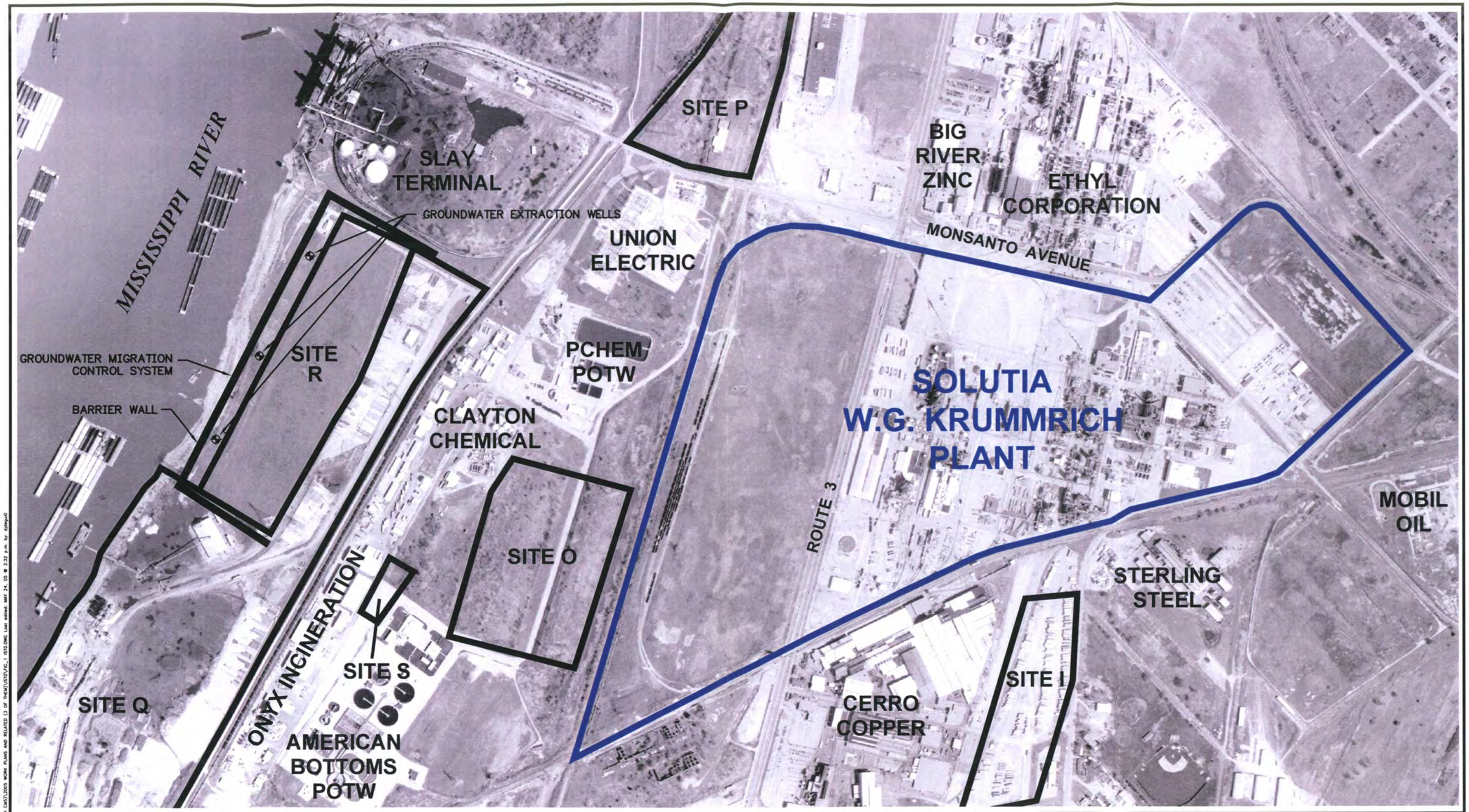
URS Corporation, 2001. *Health and Safety Plan, Sauget Area II Support Sampling Project, Sauget and Cahokia, Illinois. Volume 2C.*

URS Corporation, 2001. *Quality Assurance Project Plan, Sauget Area II Support Sampling Project, Sauget and Cahokia, Illinois, Volume 2B.*

Solutia Inc. 1999. *EFICA and RJ/FS Support Sampling Plan.*

U.S. Environmental Protection Agency (USEPA). 1988. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,* EPA/600/4-89/017, June 1988, Research Triangle Park, NC

Figures

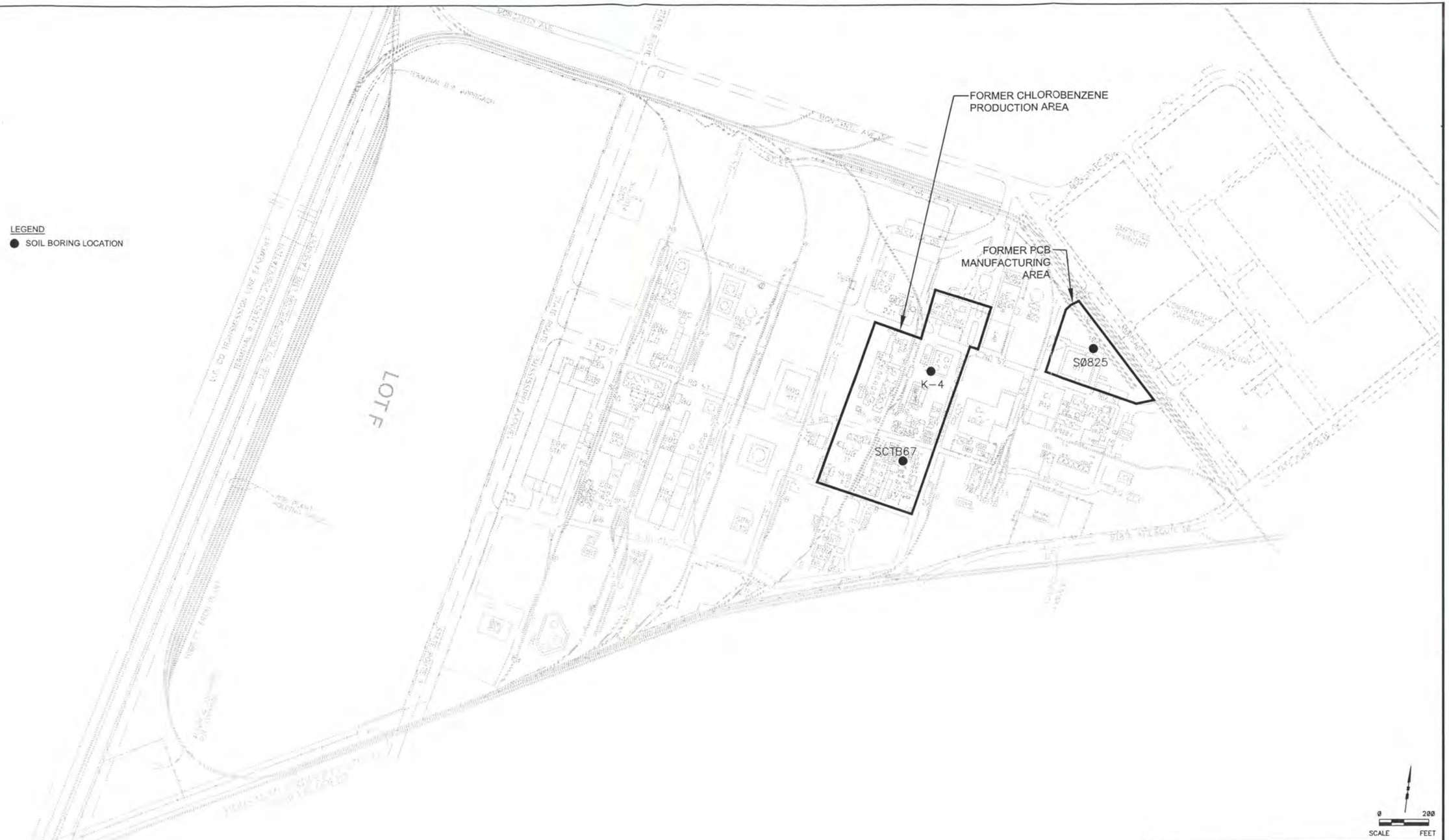


NOTES:
1) SITE I IS A SAUGET AREA 1 SITE (CERCLA).
2) SITES O, P, Q, R AND S ARE SAUGET AREA 2 SITES (CERCLA).

SOURCE: SURDEX AERIAL PHOTOGRAPHY DATED APRIL 2000.

0 600
SCALE FEET

IN-SITU THERMAL DESORPTION SOLUTIA W.G. KRUMMRICH PLANT SAUGET, ILLINOIS	PROJECT NO. 21561388.00000
URS	
DRN. BY: djd 5/24/05 DSGN. BY: jg CHKD. BY:	Site Location Map
	FIG. NO. 1



IN-SITU THERMAL DESORPTION
SOLUTIA W.G. KRUMMRICH PLANT
SAUGET, ILLINOIS

SAMPLING LOCATIONS

Date: 5/24/05	Project Number: 215613888.00000	Drawing Number: 2
Drawn by: djd	Design by: tja/bbb	Checked by:

URS

file: P:\ENVIRONMENTAL\215613888 (SOLUTIA KRUMMRICH CMS)\2005 WORK PLANS AND RELATED (3 OF THEM)\STDVERG-2 (STD.DWG Last edited: MAY 24, 05 @ 4:57 p.m. by: dldavid)

Tables

Table 1
Proposed Sample Collections for In-Situ Thermal Desorption
W.G.Krummrich Solutia Facility
Sauget, Illinois

TEST	Area of Sample Collection	Geologic Unit	Estimated Thickness	Estimated Sample Depth	Number of Samples
Baseline	Former PCB Manufacturing Area	Unsaturated SHU	0-15 ft	7.5 to 11.5 ft	1 - for Chemical Analysis
Baseline	Former Chlorobenzene Process Area	Unsaturated SHU	0-15 ft	8 to 12 ft	1 - for Chemical Analysis
Baseline	Former Chlorobenzene Process Area	Saturated SHU	15-35 ft	15 to 19 ft	1 - for Chemical Analysis
Bench-Scale	Former PCB Manufacturing Area	Unsaturated SHU	0-15 ft	7.5 to 11.5 ft	1 - for Treatability Test
Bench-Scale	Former Chlorobenzene Process Area	Unsaturated SHU	0-15 ft	8 to 12 ft	1 - for Treatability Test
Bench-Scale	Former Chlorobenzene Process Area	Saturated SHU	15-35 ft	15 to 19 ft	1 - for Treatability Test

Table 2
Sample Container, Preservation Requirements
In-Situ Thermal Desorption
W.G.Krummrich Solutia Facility
Sauget, Illinois

Parameter Group	EPA Reference Method	Sample Container and Preservative	Sample Storage
Volatile Organic Compounds (VOCs) including Chlorbenzene and Dichlorobenzene	8206B	3-5 g glass vials, headspace free 125 mL glass jar (note-1)	4+/ 2° C
Semi Volatile Organic Compounds (SVOCs)	8270C	250 or 500 mL glass jar	4+/ 2° C
Polychlorinated Biphenyls (PCBs)	680	250 or 500 ml glass jar	4+/ 2° C
Extractable Organic Halides (EOX)	9023	250 mL HDPE jar	4+/ 2° C
Moisture Content	ASTM D 2216	250 mL HDPE jar	4+/ 2° C
Particle Size	ASTM D 422	250 mL HDPE jar	4+/ 2° C
Permeability	ASTM D 2434 ASTM D 5084	250 mL HDPE jar 250 mL HDPE jar	4+/ 2° C 4+/ 2° C

Note 1:Soil samples to be preserved with 5 mL 5% sodium bisulfate, methanol, or frozen in water

APPENDIX A Standard Operating Procedures (SOPs)

1.0 SCOPE

This procedure describes the methods to be used for the calibration and use of the Photoionization Detector (PID) for field headspace analysis and health and safety monitoring.

2.0 PURPOSE

The purpose of this procedure is to develop and maintain good quality control in field operations and to create uniformity between field personnel involved with PID use.

3.0 EQUIPMENT NEEDED

PID (Model P1 101, probes with 11.7 eV lamp or equivalent), log book, user's manual, calibration gas.

4.0 PROCEDURE

Calibration:

1. Prior to calibration, check the function switch on the control panel to make sure it is in the "OFF" position. The probe nozzle is stored inside the instrument cover. Remove cover plate by pulling up on the pins that fasten the cover plate.
2. Remove the nozzle from the cover. Assemble probe by screwing nozzle into casing.
3. Attach probe cable to instrument box inserting 12 pin interface connector of the probe cable into the connector on the instrument panel. Match the alignment keys and insert connector. Turn connector in clockwise direction until a distinct snap and lock is felt.
4. Turn the function switch to the Battery Check position. When the battery is charged, the needle should read within or above the green battery arc on the scale plate. If the needle is below the green arc or the red LED light comes on, the instrument should be recharged prior to making any measurements.
5. Turn the function switch to the "ON" position. In this position, the UV light source should be on. To verify, glance at the end of the probe for a purple glow. <u>Do Not Look Directly at the Lamp Itself</u>. If the lamp does not come on refer to the Instruction Manual.
6. To zero the instrument, turn the function switch to the standby position and rotate the zero potentiometer until the meter reads zero. Clockwise rotation of the zero potentiometer produces an upscale deflection while counter clockwise rotation yields a downscale deflection. (Note: No zero gas is needed since this is an electronic zero adjustment.) If the span adjustment is changed during instrument calibration, the zero should be rechecked and adjusted. If necessary, wait 15 to 20 seconds to ensure that the zero reading is stable. Readjust as necessary.

Instrument Daily Calibration:

1. Insert one end of T-tube into probe. Insert second end of probe into calibration gas in the 20-200 ppm range. The third end of probe should have the rotometer (bubble meter) attached.

2. Set the function switch in the 0-200 ppm range. Crack the valve on the pressured calibration gas container until a slight flow is indicated on the rotameter. The instrument will draw in the volume required for detection with the rotameter indicating excess flow.
3. Adjust the span potentiometer so that the instrument is reading the exact value of the calibration gas. (Calibration gas value is labeled on the cylinder.)
4. Turn instrument switch to the standby position and check the electronic zero. Reset zero potentiometer as necessary following step 6 above.
5. Record all original and readjusted settings in log book.
6. Set the function switch to 0-20 ppm. Remove the mid-range (20-200 ppm) calibration gas cylinder and attach the low-range (0-20 ppm) calibration gas cylinder as described above.
7. Do not adjust the span potentiometer. The observed reading should be ±3 ppm of the concentration specified for the low-range calibration gas. If this is not the case, recalibrate the mid-range scale repeating Steps 1 through 6 above. If the low-range reading consistently falls outside the recommended tolerance range, the probe light source window likely needs cleaning. Clean window according to instruction manual. When the observed reading is within the required tolerances, the instrument is fully calibrated.

Instrument Calibration Check:

1. Exit the exclusion zone and turn meter to "ON" position. Check that the meter is reading a value of zero.
2. Insert one end of T-tube into probe and other end into calibration gas. The third end of the T-tube should be attached to a flow meter.
3. Crack the valve on the calibration gas and read the value shown by the instrument. Record the value and calibration gas concentration on a field-data sheet.
4. If the value shown by the instrument is greater than ±20% of the calibration gas concentration, take meter outside of exclusion zone and recalibrate as outlined above.

Sample Measurement:

1. Place function switch in 0-20 ppm range for field monitoring. This will allow for most sensitive, quick response in detecting airborne contaminants.
2. Before entering a contaminated area, determine background concentration. This concentration should be used as a reference to readings made in the contaminated area. <u>Under no circumstance should one attempt to adjust the zero or span adjustments while the instrument is being operated in the field.</u>
3. Take measurements in contaminated area, recording readings and locations. Should readings exceed the 0-20 scale, switch the function switch to the 0-200 or 0-2,000 range as appropriate to receive a direct reading. Return the instrument switch to the 0-20 range when readings are reduced to that level. Record measurements on field-data sheet.

Note: The instrument will not function properly in high humidity or when the window to the light housing is dirty. If the instrument response is erratic or lower than expected, recalibrate or obtain a different meter and calibrate as outlined above.

4. When finished, reverse Steps 1 through 6 in Instrument Setup section to shut down the instrument.

1.0 SCOPE

This procedure describes the methods to be used in measuring organic vapors emitted from soils collected with a mechanical device or hand augering device. Results will be used as a field screening for volatile organic vapors.

2.0 PURPOSE

The purpose of this procedure is to maintain uniformity between field personnel performing the measurements and to provide representativeness of readings obtained.

3.0 EQUIPMENT NEEDED

Personal protective equipment, PID, wide-mouth sample jars and aluminum foil or polyethylene bags (Ziploc type), rubber bands, field data forms.

4.0 PROCEDURES

1. Samples are collected and placed in wide-mouth sample jars or polyethylene bags (zip-loc type) so that the jars or bags are approximately half full. The jars or bags are labeled to document sample location and depth, time, date, and field personnel collecting the sample.
2. The glass jar is capped with aluminum foil, a rubber band, and the lid, if it will fit or the bag is zipped shut.
3. The air-tight sample container is then allowed to warm for at least one hour to allow the liberation of soil gases into the headspace.
4. Calibrate and prepare PID for use as per SOP-1.
5. Puncture the aluminum foil or polyethylene bag with the calibrated monitor probe and allow headspace gases to be drawn through the PID unit.
6. Record the highest response obtained on an appropriate sampling log.
7. Remove the punctured foil and seal jar with the proper lid.
8. Allow instrument to return to zero and repeat procedure for next sample.

1.0 OBJECTIVE

To obtain representative subsurface soil samples for geologic logging and physical and chemical laboratory testing.

2.0 EQUIPMENT

The following equipment is typically required:

- Hydraulic percussion hammer Geoprobe
- 1 inch diameter by 3 foot length steel probe rods
- Barrel sampler - 2 1/4 in diameter by 4 ft length
- Acetate liners
- Disposable sample retainers
- Photoionization detector (OVM, PID)
- Surveyor's stakes
- Stainless steel pans, knives and plastic Zip-loc bags
- Sample containers
- Decontamination equipment.

3.0 PROCEDURE

The general procedure for using the Geoprobe equipment for sampling is as follows:

1. Locate boring using facility drawings to check utilities
2. Log boring location on site base map
3. Hydraulically push or drive 1 in. diameter probe rods with barrel sampler attached to the first sample depth
4. Remove barrel sampler and retrieve acetate liner. Visually log and classify the soil, select specimen for physical and/or chemical testing. Record information on field data sheets
5. Decontaminate barrel sampler and install new acetate liner
6. Measure VOC concentrations with PID at top of probe hole prior to sampling the next depth interval (if VOCs are a concern)
7. Insert barrel sampler in exiting probe hole and push or drive sampler to the next sample depth, repeat sampling procedure
8. Repeat Geoprobe sampling until the target depth is reached
9. Record total depth
10. Retrieve probe rods
11. Backfill probe hole with bentonite

12. Place survey stake at boring location
13. Record data collected on boring log and log book
14. Decontaminate equipment.

4.0 DECONTAMINATION

Refer to the HSP for personnel decontamination procedures; refer to Operating Procedure No. 9 (SOP-9) for equipment decontamination procedures.

1.0 SCOPE

The operating procedure describes the ways and means of obtaining a soil sample from a boring via a split-spoon sampler, continuous tube sampler, and/or rotosonic continuous sampler for the purpose of visual description, organic vapor screening, and laboratory analysis.

2.0 PURPOSE

The purpose of this procedure is to assure good quality control in field operations and create uniformity of technique among field personnel.

3.0 EQUIPMENT NEEDED

Split-spoon sampler, continuous tube sampler, rotosonic continuous sampler, tape measure, hand lens, sample/core log, log book, sample containers with labels, chain-of-custody record, knife or trowel, disposable gloves, and plastic sheeting.

4.0 PROCEDURES

1. Place sheeting in a designated area where the split-spoon sampler will be opened.
2. Position sampler over point to be sampled.
3. Drive the sampler by pushing or percussion driven, or rotosonic vibrated down.
4. Remove the sampler, open and extract the sample, and place the sample in the appropriate sample jar or bag for headspace screening as described in SOP-2. Fill out sample label.
6. Proceed to fill sample containers designated for laboratory analysis in the following order per analytical method (as appropriate): VOCs (see SOP-5 regarding the En Core® sampling system for soil VOCs), SVOCs, PCBs, EOX, particle size, Moisture content, and permeability.
7. Examine and record sample description on sample/core log sheet. Make special note of any obviously affected zones.
8. Clean sampler by dry brushing, followed by a detergent wash using Alconox® or equivalent detergent solution, followed by potable water rinse.

1.0 OBJECTIVE

Collection of soil samples for low level VOC analysis that will minimize the loss of contaminants due to volatilization and biodegradation

2.0 EQUIPMENT

The following equipment is required for each sample point.

- Stainless steel T-Handle
- Two or three 5 g EnCore™ samplers (or equivalent)
- One 125 ml jar or one 25 g EnCore™ sampler for screening and/or high level analysis, and dry weight conversions (or as specified by laboratory)
- Paper towels
- Indelible pen
- Clear Tape and Labels.

3.0 PROCEDURE

1. The following general procedures are followed for collection of soil samples with the EnCore™ sampler
2. Remove sampler and cap from package and attach T-handle to sampler body
3. Inspect sampler piston to ensure it can be pushed up to accommodate soil core
4. Push the T-handle and sampler straight down into a freshly exposed surface of soil until the sampler is full
5. Slowly remove sampler and T-handle and inspect bottom of sampler. If sampler is not full, repeat step 3
6. Remove excess soil from the sampler rim lip
7. Place cap on sampler and push down evenly until the end cap clicks on the sampler body
8. Turn the sampler piston until it locks to prevent the sample core from being extruded
9. Repeat procedures 1 through 7 for the other EnCore™ samplers
10. Place EnCore™ samplers in EnCore™ packages and attach sample label
11. Secure label with clear tape and place in cooler, keep sample at 4 degrees Celsius
12. Collect additional soil and place in glass jar or 25 mg sampler to be used for dry weight conversion.

1.0 PURPOSE AND SCOPE

This document defines the standard protocols for sample handling, documentation, and tracking. This SOP serves as a supplement to the Work Plan Addendum and Sampling and Analysis Plan.

2.0 PROCEDURES FOR SAMPLE IDENTIFICATION, HANDLING, AND DOCUMENTATION

Sample Identification

Samples collected during site activities shall have discrete sample identification numbers. These numbers are necessary to identify and track each of the many samples collected for analysis during the life of this project. In addition, the sample identification numbers will be used in the data base to identify and retrieve the analytical results received from the laboratory.

Each sample is identified by a unique code which indicates the site identification number, sample location number, sample matrix identifier, and sample depth. The sample locations will be numbered sequentially starting at location number 0001.
Sample matrix identifiers include the following:

SB - Subsurface Soil Sample
SW - Surface Water Sample
SD - Sediment Sample
TB - Trip Blank
RN - Rinsate (Deionized Water)

An example of the sample identification number codes for a soil sample collected for analysis will be: SB-0A2B-004-05.

Where AUS indicates Additional Uncharacterized Sites, 0A2B indicates the site location, 004 indicates the sample location, SL indicates the sample media, and 05 indicates the sampling interval.

Sample Labeling

Sample labels will be filled out as completely as possible by a designated member of the sampling team prior to beginning field sampling activities each day. The date, time, sampler's signature, and the last field of the sample identification number should not be completed until the time of sample collection. All sample labels shall be filled out using waterproof ink. At a minimum, each label shall contain the following information:

- Sampler's company affiliation
- Site location
- Sample identification code
- Date and time of sample collection
- Analyses required
- Method of preservation (if any) used
- Sample matrix (i.e., soil, groundwater, surface water)
- Sampler's signature

Sample Handling

This section discusses proper sample containers, preservatives, and handling and shipping procedures.

Sample Handling and Shipping

After sample collection, each container will be labeled as described above, and then stored on ice at 4°C in an insulated cooler until packed for shipment to the laboratory. The ice will be double bagged in Ziploc-type storage bags.

The sample containers will be placed in reclosable Ziploc plastic storage bags and wrapped in protective packing material (bubble wrap). Samples will then be placed right side up in a cooler with ice (double bagged using plastic bags), and taped with a custody seal for delivery to the laboratory. Samples will be hand delivered or shipped by overnight express carrier for delivery to the analytical laboratory. All samples must be shipped for laboratory receipt and analyses within specific holding times. This may require daily shipment of samples with short holding times. A chain-of-custody (COC) form will accompany each cooler. The temperature of all coolers will be measured upon receipt at the laboratory. A temperature blank will be included in each cooler for temperature measurement purposes.

Sample Documentation and Tracking

This section describes documentation required in the field notes and on the sample Chain-of-Custody forms.

Field Notes

Documentation of observations and data acquired in the field will provide information on the acquisition of samples and also provide a permanent record of field activities. The observations and data will be recorded using pens with permanent waterproof ink in a permanently bound weatherproof field log book containing consecutively numbered pages.

The information in the field book will include the following as a minimum. Additional information is included in the specific SOPs regarding the field books.

- Project name
- Location of sample
- Sampler's printed name and signature
- Date and time of sample collection
- Sample identification code including QC and QA identification
- Description of samples (matrix sampled)
- Sample depth (if applicable)
- Number and volume of samples
- Sampling methods or reference to the appropriate SOP
- Sample handling, including filtration and preservation, as appropriate for separate sample aliquots
- Analytes of interest
- Field observations
- Results of any field measurements, such as depth to water, pH, temperature, and conductivity
- Personnel present
- Level of PPE used during sampling

Changes or deletions in the field book should be lined out with a single strike mark, initialed, and remain legible. Sufficient information should be recorded to allow the sampling event to be reconstructed without relying on the sampler's memory.

Each page in the field books will be signed by the person making the entry at the end of the day, as well as on the bottom of each page. Anyone making entries in another person's field book will sign and date those entries.

Sample Chain-of-Custody

During field sampling activities, traceability of the sample must be maintained from the time the samples are collected until laboratory data are issued. Initial information concerning collection of the samples will be recorded in the field log book as described above. Information on the custody, transfer, handling, and shipping of samples will be recorded on a COC form.

The sampler will be responsible for initiating and filling out the COC form. The COC will be signed by the sampler when the sampler relinquishes the samples to anyone else. One COC form will be completed for each cooler of samples collected daily. The COC will contain the following information:

- Sampler's signature and affiliation
- Project number
- Date and time of collection
- Sample identification number
- Sample type
- Analyses requested
- Number of containers
- Signature of persons relinquishing custody, dates, and times
- Signature of persons accepting custody, dates, and times
- Method of shipment
- Shipping air bill number (if appropriate).

The person responsible for delivery of the samples to the laboratory will sign the COC form, retain the last copy of the three-part COC form, document the method of shipment, and send the original and the second copy of the COC form with the samples. Upon receipt at the laboratory, the person receiving the samples will sign the COC form and return the second copy to the Project Manager. Copies of the COC forms documenting custody changes and all custody documentation will be received and kept in the central files. The original COC forms will remain with the samples until final disposition of the samples by the laboratory. The analytical laboratory will dispose of the samples in an appropriate manner 60 to 90 days after data reporting. After sample disposal, a copy of the original COC will be sent to the Project Manager by the analytical laboratory to be incorporated into the central files.

DAILY QUALITY CONTROL REPORT

Date _____

Day	S	M	T	W	TH	F	S

COE Project Manager _____
Project _____
Project No. _____
Contract No. _____

Weather	Bright Sun	Clear	Overcast	Rain	Snow
Temp	To 32	32-50	50-70	70-85	85 up
Wind	Still	Moderate	High	Report No.	
Humidity	Dry	Moderate	Humid		

Subcontractors on Site:
Equipment on Site:
Visitors on Site:
W-C Personnel on Site:
Work Performed (including sampling):

Quality Control Activities (including field calibrations):
Health and Safety Levels and Activities:
Problems Encountered/Corrective Actions Taken:
Downtime/Standby:
Special Notes:

By _____ Title _____

1.0 OBJECTIVE

This document defines the standard protocols for sample handling, documentation, and tracking. This SOP serves as a supplement to the Work Plan Addendum and Sampling and Analysis Plan.

2.0 EQUIPMENT

The following equipment will be required for this SOP:

- Waterproof coolers (hard plastic or metal)
- Custody Seals
- Field forms such as COC or sample collection sheet
- Field Notebook
- Ice
- Bubble Wrap
- Clear Tape
- Duct Tape
- Zip Loc Bags
- Sample Containers
- Waterproof Pen
- Permanent Marker.

3.0 SAMPLE CONTAINERS

Certified commercially clean sample containers will be obtained from the contract analytical laboratory. The lab will indicate the type of sample to be collected in each bottle type. The work plan will list the appropriate sample containers for the specific analyses require for each project.

4.0 SAMPLE PRESERVATION

Samples will be preserved at the time of the sample collection. Chemical preservatives, if necessary, will be added to the sample containers either by the laboratory prior to shipment to the field, or in the field by sampling personnel.

After sample collection, each container will be labeled and stored on ice at 4°C in an insulated cooler until packed for shipment until packed for shipment to the laboratory. The ice will be double bagged in Zip Loc storage bags. Freezing samples will not be permitted. Any breakable sample bottles need to be wrapped in protective packing material (bubble wrap) to prevent breakage during shipping.

5.0 SAMPLE HOLD TIMES

Samples will be hand delivered or shipped by overnight express carrier for delivery to the analytical laboratory. All samples must be shipped for laboratory receipt and analyses within specific holding times. This may require daily shipment of samples with short holding times. The hold time varies for each type of analysis. It will be necessary to check with the lab to verify the hold times to determine how frequently samples need to be sent to the lab.

Documentation of observations and data acquired in the field will provide information on the acquisition of samples and also provide a permanent record of field activities. The observations and data will be recorded using pens with permanent waterproof ink in a permanently bound weatherproof field log book containing consecutively numbered pages.

1.0 OBJECTIVE

This document defines the standard procedure for the control and custody of environmental samples.

2.0 EQUIPMENT

The following equipment will be needed for sample control and custody procedures:

- Waterproof coolers (hard plastic or metal)
- Custody Seals
- Field forms such as a Chain of Custody (COC) or sample collection sheet
- Field Notebook
- Ice
- Sample Log-in Book
- Clear Tape
- Duct Tape
- Zip-Loc Bags
- Waterproof pens
- Permanent Markers.

3.0 SAMPLE CONTROL AND CUSTODY PROCEDURES

Once the samples are collected, they must remain in the custody of the sampler or another worker from the site. The samples can also remain unattended in a locked vehicle so tampering with the samples will not be possible. Right before shipment, a custody seal should be placed over the opening of the cooler and then the cooler should be taped all the way around with clear packing tape to prevent tampering with the samples. Samples will be hand delivered or shipped by overnight express carrier for delivery to the analytical laboratory. All samples must be shipped for laboratory receipt and analyses within specific holding times. This may require daily shipment of samples with short holding times. Each cooler will contain a chain of custody (COC) form.

During field sampling activities, traceability of the samples must be maintained from the time the samples are collected until the laboratory data is issued. Initial information concerning the collection of the samples will be recorded in the field log book as outlined in SOP 6 – Sample Handling, Documentation, and Tracking. Information on the custody, transfer, handling, and shipping of samples will be recorded on a COC form.

The sampler will be responsible for initiating and filling out the COC form. The COC will be signed by the sampler or the field person responsible for sample handling when the sampler relinquishes the samples to anyone else. One COC form will be completed for each cooler of samples collected daily and if samples are not hand delivered, the COC will be placed in a Zip-Loc bag and shipped inside the cooler. COC forms will be used to document the transport and

receipt of samples from the field to the lab. Information required on a COC includes the following:

- Samplers signature and affiliation
- Project Number
- Date and time of collection
- Sample identification number
- Sample Type
- Analyses requested
- The total number of containers being sent to the lab for each sample
- The appropriate preservative used
- If any samples are to be placed on hold at the laboratory, this should be clearly indicated on the COC in the comments section
- Signature of person(s) relinquishing custody, dates, and times
- Signature of person(s) accepting custody, dates, and times
- Method of shipment
- Shipping air bill number (if appropriate).

The person responsible for delivery of the samples to the laboratory will sign the COC form, retain the last copy of the three-part COC form, document the method of shipment, and send the original and the second copy of the COC form with the samples. Upon receipt at the laboratory, the person receiving the samples will sign the COC form. The original COC will remain with the samples until final disposition of the samples by the laboratory.

1.0 OBJECTIVE

This document defines the standard procedure for decontamination of equipment used in environmental sites.

2.0 EQUIPMENT

The following equipment will be needed for decontamination procedures:

- Brushes
- Wash Tubs
- Buckets
- Scrapers, flat bladed
- Hot water – high pressure washer
- Paper towels
- Alconox detergent (or equivalent)
- Potable tap water
- Laboratory-grade deionized or distilled water
- Garden-type water sprayers

3.0 DECONTAMINATION PROCEDURES

31. Sampling Equipment

Sampling equipment will be decontaminated at the sampling location under the following procedures:

- Personnel will wear the proper PPE to reduce the potential for exposure as required by the HASP.
- Partially fill two buckets with potable tap water, and add Alconox detergent to one of the buckets
- Use brushes to wash the sampling equipment (i.e. stainless steel bowls, stainless steel spoons, sampling utility knife, etc)
- Rinse sampling equipment in bucket containing potable tap water
- Rinse clean equipment with water sprayers containing distilled water (or equivalent)
- Place decontaminated equipment in clean area and allow to air dry.

3.2 Drilling and Heavy Equipment

Drilling rigs will be decontaminated at a decontamination station located near a staging area. The decontamination station may be a temporary structure, or mobile trailer, capable of collecting all decontamination fluids. The following steps will be used to decontaminate drilling and heavy equipment.

- Personnel will suit up in proper PPE to reduce the potential for exposure as required by the HASP.
- Equipment showing gross impacted soil materials will be scrapped with a flat-bladed scrapper, and material containerized.
- Equipment that cannot be damaged by water, such as a drill rig, augers, drill bits, sampling equipment, shovels, etc, will be washed with a hot water, high-pressure sprayer, the rinsed with potable water.
- Following decontamination, drilling equipment will be placed on the clean drill rig and moved to the next sampling location. If equipment is not immediately used, it should be stored in a clean designated area.

Equipment rinsante samples of the decontaminated sampling equipment may be collected to verify the effectiveness of the decontamination procedures.

APPENDIX B Laboratory Standard Operating Procedures

PREPARATION, SCREENING, AND STORAGE OF VOLATILES SAMPLES

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Approved by:

R. Wayne Robbins — 30 Aug 2002
R. Wayne Robbins — Date

Title: Technical Manager

STL X Savannah __ Tallahassee __ Mobile __ Tampa

1.0 SCOPE AND APPLICATION

This SOP describes the procedures that are used to prepare and screen samples for volatile organic compounds (VOC) in water and soils by GC and GC/MS.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Aqueous samples are checked for sample integrity and pH and are screened by GC/FID. The pH of the sample is documented at log-in. If the sample integrity or hold time has been compromised, the project manager must be notified.

2.2 Soils are routinely collected in Encore devices. Three Encore devices and a bulk container are routinely received for each sample. The bulk sample is used to determine the type of preservation required, the percent solids, and to perform the screening analysis. Samples collected in Encore devices are transferred to vials and preserved within 48 hours of collection. Two of the vials are routinely used for low-level analysis and the third preserved in methanol for high level analysis, if required. If the sample integrity or hold time has been compromised, the project manager must be notified.

2.3 Definitions

VOC – volatile organic compound(s)
VOA – volatile organic analytes (analysis)

2.4 This method is based on the guidance in SW-846 Methods 5021, 5030, 5035.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or that will put yourself or others in a potentially hazardous situation.

3.2 Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, eye protection, or other equipment should be used. Standards and highly contaminated samples should be handled in a hood.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst. These sheets specify the type of hazard that each chemical poses and the procedures that are used to safely handle these materials.

4.0 INTERFERENCES

4.1 VOCs commonly used in the laboratory are potential sources of contamination. Methylene chloride, acetone, Freon-113, MEK, hexane, toluene, and isopropanol are used in the laboratory and tend to present the most problems.

4.2 The volatiles lab must be kept as free from contamination as possible. Highly contaminated samples must be segregated from routine samples. Contact with sections of the laboratory where solvents are used should be minimized. Refrigerator blanks should be prepared, stored, and analyzed to evaluate the sample storage areas for possible contamination. Guidance is provided in SOP AN70: *Compositing and Homogenization of Field Samples and Segregation of Low and High Concentration Volatile and Semivolatile Samples.*

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

5.1 Liquids: Aqueous samples are routinely collected with no headspace in 40mL vials equipped with Teflon-lined caps. The samples are acidified at the time of collection with about 0.30mL of concentrated HCl per 40mL of sample. The acid prevents the biological degradation of the aromatic compounds and prevents the dehydrohalogenation of some of the chlorinated alkanes. The sample must be iced at the time of collection and refrigerated at 4C (less than 6C with no frozen samples) in the lab until analysis.

The holding time for samples preserved with HCl is 14 days for all target compounds. The holding time for unpreserved samples is 7 days.

5.2 Soils: Soils are routinely collected in triplicate in Encore samplers. A "bulk" sample is also routinely collected in a 125-mL jar fitted with a Teflon-lined cap. The bulk sample is used for determining the percent solids and can be used for the methanol extraction if the concentration of the sample collected in the Encore exceeds the working range of the analytical system.

Soils collected in Encore samplers must be analyzed within 48 hours of collection or must be preserved using sodium bisulfate solution within 48 hours of collection. If the sample contains high levels of carbonates, the sample is preserved with water and frozen until the time of analysis. The procedure for preparing soil samples is given in Section 9.2.

The hold time for the preserved sample is 14 days from the date of collection. The hold time for frozen samples is 14 days from the date of collection.

5.3 Field Preserved Soils
Soil samples may be collected in pre-weighed vials containing either sodium bisulfate or methanol preservative. The vials with preservative are routinely weighed in the lab, the tare weight is recorded, and the containers sent to the field. The samples are collected and returned to the lab where the container is weighed and the weight of the sample determined by the difference. The hold time for field preserved samples is 14 days from the date of collection.

5.4 High level soil and waste samples are collected in glass containers (usually 125-mL clear glass) equipped with Teflon-lined caps. Soil samples may also be submitted as core samples contained in Encore samplers, in metal or plastic "tubes", or in 40-mL VOA vials. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples). The holding time for soil and waste samples subjected to methanol extraction is 14 days from date of collection. Extraction and analysis must be completed within 14 days of collection.

5.5 TCLP leachate samples are collected with no headspace in Tedlar bags or syringes. The leachate samples are acidified after the leaching procedure with about 0.10mL of concentrated HCl per 40mL of sample and stored at 4C (less than 6C with no frozen samples) from the time leaching is completed until the analysis. The acidified leachate sample must be analyzed within 14 days of the leaching procedure. If the sample is not acidified, the leachate must be analyzed within 7 days of the leaching procedure.

NOTE: Samples that are suspected of having very high concentrations of VOC should be segregated from the "routine" samples and stored in a manner that will minimize sample and laboratory contamination. See SOP AN70: *Compositing and Homogenization of Field Samples and Segregation of Low and High Concentration Volatile and Semivolatile Samples* for guidance. If possible, keep the field QC in the same storage refrigerator as the samples.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph with flame ionization detector (FID)

6.2 Headspace device: Tekmar 7000 or equivalent

6.3 Data System compatible with the analytical system

6.4 Microsyringes: 100uL

6.5 Gastight syringe: 5mL, 25mL

6.6 Volumetric flasks: various sizes

6.7 Recommended Column: J&W DB-624, 30m x 0.53mmID x 3.0um or equivalent

6.8 Headspace vials with crimp-top septum caps

6.9 40-mL VOA vial with methanol preservative: weigh and record vial before sending to the field

6.10 40-mL VOA vial with sodium sulfate preservative: weigh and record vial before sending to the field

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability*.

7.1 Reagent water - free of volatile contaminants (obtained by purging with inert gas or carbon filtration)

7.2 Methanol - Purge and Trap grade

7.3 Sodium bisulfate - reagent grade. This salt is hydroscopic and should be stored in a dessicator.

7.4 Sodium bisulfate soil preservation solution - Slowly add, while stirring, 200g of sodium bisulfate to a 1.0-L volumetric flask containing about 700mL of reagent water. After the salt has dissolved, dilute to volume with reagent water, transfer to a storage container, and store the solution in an area free from VOC - especially water-soluble solvents such as acetone. The reagent should be tested prior to use by the analysis of a blank containing 5mL of the solution. The reagent is acceptable if it meets the same criteria as a method blank.

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions purchased from vendors or from stock standards prepared from neat materials. Certificates of analysis or purity must be received with all stock solutions or neat compounds. All preparation steps must be in accordance with SOP AN41: *Standard Material Traceability*.

Prepare calibration standards containing the following compounds at 50, 100, 200, 400, 800, and 1600ug/L in reagent water: methlyene chloride, 1,1-dichloroethene, cis-1,2-dichoroethene, chloroform, benzene, trichloroethene, toluene, tetrachloroethene, ethylbenzene, m/p-xylene, o-xylene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2-dichlorobenzene.

Transfer 4mL of the calibration standard to a labeled headspace vial and add 1mL of reagent water. Analyze according to Section 10.

9.0 SAMPLE PREPARATION

Composite samples can be prepared using the guidance in SOP AN70: *Compositing and Homogenization of Field Samples and Segregation of Low and High Concentration Volatile and Semivolatile Samples.*

9.1 Preparation of Aqueous Samples

Aqueous samples are analyzed directly by purge and trap GC and GC/MS. No sample preparation is necessary except to homogenize the sample prior to subsampling. The pH of liquid samples is checked and recorded prior to analysis and recorded on the appropriate log.

9.1.1 Samples are logged into the Volatiles' Liquid Logbook. Three vials are routinely received and the vials are designated A, B, and C. If more than three vials are received, then letter accordingly. Use the last vial for the screening and pH determination.

9.1.2 Check each sample vial at the time of receipt for the presence of "bubbles". If the bubbles are less than 3mm in diameter, the vial is acceptable. If all vials contain bubbles greater than 3mm, notify the department supervisor or project manager that there are no acceptable vials for analysis.

9.1.3 Use the "C" vial (or last vial) for screening and pH check. (If a vial contains air bubbles, then sacrifice this vial for screening and pH determination, since the sample is already compromised. Save acceptable vials for analyis.)

Determine the pH of the sample using narrow range pH paper and record in the Volatiles' Liquid Logbook.

If the sample pH is greater than 2, fill out a 7-Day Hold Sheet and notify the department supervisor. All samples with pH greater than 2 must be analyzed within 7 days of collection. All samples with pH less than 2 must be analyzed within 14 days of collection.

Transfer 4mL from the C vial to a labeled headspace vial and add 1mL of reagent water. Analyze this screening vial according to Section 10. Evaluate the results according to Section 11.

9.1.4 Transfer the A and B vials to the storage racks. Store the screening C vial separately from the A and B vials.

9.2 Preparation of Soil Samples (5035)

The preparation of soil samples must be performed within 48 hours of collection. Three Encore devices and one bulk container are routinely received for each sample. Two of the Encores are prepared for low level analysis, and one is extracted in methanol. The bulk container is used for determining the type of preservation for the low level samples and, if required, for screening. The Encores are labeled as the A, B, and C samples.

NOTE: If soil samples are received in 25-g Encore devices, contact the supervisor immediately to confirm the preparation steps. The procedures given below are to be used as the default.

9.2.1 Low Level Preparation (A and B Vials)

9.2.1.1 Carbonate Test

Transfer a small aliquot (~0.5g) of sample from the bulk container to a 20-mL scintillation vial.

Add approximately 5mL of the sodium bisulfate preservation solution.

If the sample fizzes (effervesces), preserve with volatile-free water and place in a freezer at –10C. If no fizzing is noted, preserve with 5mL of the soil preservation solution (sodium bisulfate) and store at 4C in the soil storage refrigerator.

9.2.1.2 Add a stir bar to a 40-mL vial. Attach the bar code label and ID label to the 40-mL vial. Write the sample ID and vial designation (A or B) on the ID label. Place the vial on the balance and tare the vial and stir bar weight by pressing the autotare button.

9.2.1.3 Transfer the sample from the Encore device to the labeled, tared vial and record the weight of the sample to the nearest 0.01g in the Volatile Soil Sample logbook.

NOTE: If the sample is received in a 25-g Encore device, transfer two 5-g (5.0-5.5g) aliquots from the device to the tared vials (A and B). Transfer a third 5-g aliquot to the C-vial for methanol preservation (Section 9.2.2). A plastic syringe may be used to remove an aliquot of the sample from the 25-g sampler. On average, a 3mL plug of soil will be approximately 5g.

If the sample fizzed during the carbonate test (9.2.1.1), add 5mL of reagent water and freeze at –10C. If the sample did not fizz, add 5mL of the soil preservation solution and store the sample at 4C until the time of analysis. The preserved samples must be analyzed within 14 days of collection.

Place samples from the same log number with the same preservation in a plastic bag and seal. Write the log number and type of preservation on the outside of the bag. For example, put all of the sodium bisulfate preserved samples together, all of the water preserved samples together, and all of the methanol preserved samples together. Do not put samples from different log numbers in the same bag.

9.2.2 Methanol Preservation (C Vial)
A methanol extraction is prepared from the third Encore device or from the bulk container when an Encore is unavailable. Carry out the preparation quickly to minimize the loss of volatiles.

9.2.2.1 Attach the bar code label and ID label to a 40-mL vial. Write the sample ID and vial designation (C) on the ID label. Place the vial on the balance and tare the vial and stir bar weight by pressing the autotare button.

9.2.2.2 Transfer the sample from the Encore to a 40-mL VOA vial.

NOTE: If the sample is received in a 25-g Encore device, transfer 5-g aliquot to the C-vial for methanol preservation after taking the two 5-g aliquots for low level analysis (Section 9.2.1.2).

Add 5mL of methanol and shake vigorously for approximately 10 seconds.

Put in bag and seal. Samples preserved in methanol from the same log number may be put in same bag. Do not put samples from different log numbers in the same bag.

Store in refrigerator at 4C.

9.2.2.3 Transfer 100uL (0.1mL) of the methanol extract (Vial C) to 5mL of reagent water contained in a labeled headspace vial. Analyze this screening vial according to Section 10. Evaluate the results according to Section 11.

9.3 Pre-Weighed Vials with Methanol or Sodium Bisulfate Preservative

9.3.1 Pre-sampling

9.3.1.1 Select number of vials for sampling. Attach label if not already attached but do not obscure the vial identification number. Inspect each vial to ensure that there is preservative at the correct volume, that the cap is secure, and that there is no extraneous material or moisture adhering to the outside of the vial.

9.3.1.2 Weigh the vial and record the weight and vial identification in the appropriate logbook. Record the weight to the nearest 0.01g.

9.3.1.3 Pack the vials and transfer to the shipping and receiving department. Include at least one trip blank with each set of vials.

9.3.2 Post-sampling

9.3.2.1 Remove vials from storage and allow them to come to room temperature.

9.3.2.2 Wipe off any extraneous moisture or material adhering to the outside of the vial.

9.3.2.3 Weigh and record the weight of the vial, sample, and preservative to the nearest 0.01g. Calculate the weight of the sample as:

$$W_{sample}(g) = W_2 - W_1$$

where:
W_2 = weight of sample, vial, and preservative (g)
W_1 = weight of vial and preservative (g)

9.3.2.4 Shake the vial for approximately two minutes.

9.3.2.5 Screening
Remove 100uL (o.10mL) of the extract through the septum and transfer to 5.0mL of water. Screen sample as in Section 10.

9.3.2.6 Store the remaining extract at 4C until the time of analysis.

10.0 PROCEDURE

10.1 Screening Instrument Conditions

The instrument parameters are provided as examples. The actual operating parameters and conditions must be documented in the appropriate log.

Gas Chromatograph Program for DB-624 column:

Initial temperature:	50 C for 2.0 minutes
Temperature Ramp:	16 C per minute
Final Temperature:	200 C for 1.0 minute

Set column flow to provide adequate separation of analytes. Set makeup and detector gases according to manufacturer's instructions.

Tekmar 7000 Headspace Analyzer Parameters:

Temperature to heat vials:	85C
Equilibration time:	10 minutes
Mixing time:	1 minute
Volume of headspace analyzed:	1mL
Heated line temperatures:	100C

10.2 Screening Calibration

Analyze the six calibration standards outlined in Section 8.0. Prepare a calibration curve in accordance with SOP AN67: *Evaluation of Calibration Curves*. An external calibration curve is prepared with nanograms (ng) of compound plotted on the x-axis.

ICAL Criterion: Use professional judgement
CCV Criterion: +/-50% of true value

10.3 Screening Analysis

An ICAL should be analyzed initially and when the percent difference of the CCV exceeds 50%. The CCV and a method blank should be analyzed daily prior to sample screening.

10.3.1 Liquid Samples

Transfer the screening vial from Section 9.1.3 to the autosampler and analyze. Evaluate data according to Section 11.

10.3.2 Soil Samples

Transfer the screening vial from Section 9.2.2.3 to the autosampler and analyze. Evaluate data according to Section 11.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Identify the compounds based on the retention time and compare the nanograms (ng) of compound to the upper level of the liquid or soil calibration curve.

11.2 Liquids: Calculate the dilution (as dilution factor, DF) to run on the instrument as follows:

$$DF = \frac{ng(screen)}{ng(cal)}$$

where:
ng(screen) = nanograms of compound from screening run
ng(cal) = nanograms of upper level of calibration curve

If the ratio is<=1, run at DF=1. If the ratio is >1, run at next highest whole number DF. For example, if ratio is 1.5, run at DF=2.

11.3 Soils: Calculate the dilution (as dilution factor, DF) to run on the instrument as follows:

$$DF = \frac{ng(screen)}{ng(cal)} \otimes 50$$

where:
ng(screen) = nanograms of compound from screening run
ng(cal) = nanograms of upper level of calibration curve

If the ratio is<=5, run at DF=1. If the ratio is >5, run methanol extraction.

NOTE: the factor of 50 is the ratio of the low level soil weight (5g) divided by the weight of sample (0.1g) analyzed in the screening analysis.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

There are no formal QC or QA requirements for this SOP since the results are used to estimate the dilution used for the definitive analysis of the samples. The analyst must use good professional judgement in evaluating the data. A method blank should be analyzed each day screening takes place.

13.0 TROUBLE-SHOOTING AND PREVENTIVE MAINTENANCE

See instrument manufacturer's manual and SOP AN53: *Maintenance Procedures for Laboratory Instruments* for preventive maintenance and troubleshooting guidance.

14.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Excess samples, extracts, reagents, and standards must be disposed in accordance with SOP CA70: *Waste Management.*

15.0 REFERENCES

Test Methods for Evaluating Solid Wastes, Third Edition, SW-846 including Update III U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

VOLATILE COMPOUNDS BY GC/MS (EPA 8260B)

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Approved by: _____ 3 April 2001
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STL X Savannah ___ Tallahassee ___ Mobile ___ Tampa West

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedures that can be used to determine the concentration of volatile organic compounds (VOC) in water, wastewater, soils/sediments, wastes, oils, sludges, and solids. The attached quantitation report lists the target compounds, an example of the retention time order of each target compound, the quantitation and confirmation ions of the target compounds, and internal standard assignments.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria for each target compound are listed in Section 5 of the current revisions of the STL Laboratories' *Comprehensive Quality Assurance Plan* and *Corporate Quality Assurance Plan.*

2.0 SUMMARY OF METHOD

2.1 Volatile organic compounds (VOC) are purged from the sample matrix with helium. The VOC are transferred from the sample matrix to the vapor phase. The vapor is swept through a sorbent tube where the VOC are trapped. After the purging is completed, the trap is heated and backflushed with helium to desorb the VOCs onto a GC column. The GC is temperature-programmed to separate the VOC, which are then detected by a mass spectrometer. Qualitative identification of the target compounds in the sample is based on the relative retention time and the mass spectra of the characteristic masses (ions) determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

2.2 Aqueous samples may be purged at ambient conditions (recommended) or at 40C (optional). Five to twenty-five milliliter aliquots of the sample may be purged. The calibration standards and the associated QC must be analyzed under the same conditions and volume.

2.3 Low-level (nominally <1mg/kg) soil samples are purged at 40C in a purge and trap instrument designed to add water and internal standards to the vial containing the sample without breaking the seal. The sample is stirred during purging to thoroughly mix the soil and water. The calibration standards are purged under the same conditions.

2.4 High level soils (nominally >1mg/kg) and waste samples are extracted with methanol-1mL of methanol per gram of sample. An aliquot of the methanol extract is injected into reagent water. The methanol extract/reagent water is purged at ambient temperature using the same instrument conditions and calibration used for aqueous samples.

2.5 This method is based on the guidance in SW-846 Methods 8260B and 5035.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or that will put yourself or others in a potentially hazardous situation.

3.2 Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, eye protection, or other equipment should be used. Standards and highly contaminated samples should be handled in a hood.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst at each lab division. These sheets specify the type of hazard that each chemical poses and the procedures that are used to safely handle these materials.

3.4 The exit vent of the split injector must have a carbon trap in-line to collect the volatile compounds that are vented during the injection of the sample. The traps should be changed a minimum of every three months and disposed of in accordance with STL-SL SOP CA70: *Waste Management.*

4.0 INTERFERENCES

4.1 VOCs commonly used in the laboratory are potential sources of contamination. Methylene chloride, acetone, Freon-113, MEK, hexane, toluene, and isopropanol are used in the laboratory and tend to present the most problems.

4.2 The volatiles lab must be kept as free from contamination as possible. Highly contaminated samples must be segregated from routine samples. Contact with sections of the laboratory where solvents are used should be minimized. Refrigerator blanks should be prepared, stored, and analyzed to evaluate the sample storage areas for possible contamination. Guidance is provided in STL-SL SOP AN70: *Segregation of Low and High Concentration Volatile and Semivolatile Samples.*

4.3 Matrix interferences may be overcome by the use of the secondary ions for quantitation. An example of this is the use of mass 82 for quantitation with chlorobenzene-d5 internal standard when a potential co-eluter, 1,1,1,2-terachloroethane, is a target compound. One of the mass fragments of 1,1,1,2-tetrachloroethane is mass 117, which is the recommended quantitation ion for chlorobenzene-d5. The use of the secondary ions should be used for quantitation in such cases when the lab can clearly demonstrate matrix problems. Mass 58 is recommended for quantitation of acetone due to the elution of a hydrocarbon at the same retention time.

4.4 The analysis of highly contaminated samples (>1mg/L or >1mg/kg) can affect succeeding analyses. Carry-over can occur when low concentration samples are analyzed after high concentration samples. Trap replacement and purging of the entire purging system may be necessary when carry-over is suspected. Reagent blanks must be analyzed when carryover is suspected to demonstrate that the system is free from contamination.

4.5 The Teflon seals of the purge and trap device can absorb and outgas many of the compounds that are included in this method. These Teflon fittings should be periodically checked for integrity. If contamination of the fittings is suspected, the fittings may be heated at 105 C for one hour or replaced.

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

5.1 Liquid samples are collected with no headspace in 40mL vials equipped with Teflon-lined caps. The samples are acidified at the time of collection with about 0.10mL of concentrated HCl per 40mL of sample. The acid prevents the biological degradation of the aromatic compounds and prevents the dehydrohalogenation of some of the chlorinated alkanes. The sample must be iced at the time of collection and refrigerated at 4C (less than 6C with no frozen samples) in the lab until analysis.

Check each sample vial at the time of receipt for the presence of "bubbles". If the bubbles are less than 3mm in diameter, the vial is acceptable. If the bubble is greater than 3mm, use another vial. Notify the department supervisor or project manager if there are no acceptable vials for analysis.

A "sacrificial" vial or the vial used for screening analysis is used to check the sample pH. If the sample pH is greater than 2, notify the department supervisor or project manager. If directed by supervisor or project manager, hydrochloric acid may be added through the septum to bring the pH <2. Do not add more than 400uL (0.40mL) of 1:1 HCl to a VOC vial. If pH cannot be adjusted to <=2 without destroying the integrity of the sample, the sample must be analyzed within 7 days of collection.

The holding time for samples preserved with HCl is 14 days for all target compounds. The holding time for un-preserved samples is 7 days.

5.2 Soils: Soils are routinely collected in duplicate in Encore samplers. A "bulk" sample is also routinely collected in a 125-mL jar fitted with a Teflon-lined cap. The bulk sample can be used for the methanol extraction if the concentration of the sample collected in the Encore exceeds the working range of the analytical system.

Soils collected in Encore samplers must be analyzed within 48 hours of collection or must be transferred within 48 hours of collection to sealed vials containing sodium bisulfate solution or methanol. If the sample contains high levels of carbonates, the sample is preserved with water and frozen until the time of analysis. The procedure for preparing soil samples is given in Section 9.2.

The hold time of the preserved sample is 14 days from the date of collection. The hold time for frozen samples is 14 days from the date of collection.

5.3 High level soil and waste samples are collected in glass containers (usually 125-mL clear glass) equipped with Teflon-lined caps. Soil samples may also be submitted as core samples contained in Encore samplers, metal or plastic "tubes", or in 40-mL VOA vials. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples). The holding time for soil and waste samples subjected to methanol extraction is14 days from date of collection; that is, the extraction and analysis must be completed within 14 days of collection.

5.4 TCLP leachate samples are collected with no headspace in Tedlar bags or syringes. The leachate samples are acidified at the time of collection (after the leaching procedure) with about 0.10mL of concentrated HCl per 40mL of sample and stored at 4C (less than 6C with no frozen samples) from the time leaching is completed until the analysis. The acidified leachate sample must be analyzed within 14 days of the leaching procedure. If the sample is not acidified, the leachate must be analyzed within 7 days of the leaching procedure.

NOTE: Samples that are suspected of having very high concentrations of VOC should be segregated from the "routine" samples and stored in a manner that will minimize sample and laboratory contamination. See STL-SL SOP AN70. If possible, keep the field QC in the same storage refrigerator as the samples.

6.0 APPARATUS AND MATERIALS

The apparatus and materials listed in this section may vary from lab to lab. The items listed are to give guidance and to provide a general overview of the equipment employed in this analysis.

6.1 Mass spectrometer: equipped with a capillary direct interface and a split/splitless injector or molecular jet separator

6.2 Gas chromatograph, compatible with the MS and purge and trap systems. If the GC is equipped with an injector that is operated in the split mode, the exit vent must have a carbon trap in-line to collect the volatile compounds that are vented during the transfer from the purge and trap device. The carbon traps should be changed a minimum of every three months.

6.3 Purge and trap device Tekmar 3000 Liquid Concentrator or equivalent

6.4 Supelco Vocarb 3000 trap or equivalent, Other traps may be used as long as the target compounds can be detected at the required quantitation limit.

6.5 Archon soil analyzer for low level soils, compatible with Tekmar purge and trap instruments. The instrument must be capable of automatically adding water and internal standard to the container while maintaining the septum seal, heating the sample to 40C, and spinning the stir bar to mix the sample during the purging step.

6.5 Data System compatible with the analytical system

6.6 Microsyringes: 10ul, 25ul, 50ul, 100ul, 250ul, 500ul, 2.5mL

6.7 Gastight syringe: 5mL, 25mL with luerlock tip

6.8 Volumetric flasks: 1.0mL, 10mL, 100mL

6.9 Recommended Columns

J&W DB-624: 60m x 0.32mm ID, 1.8um film
J&W DB-624: 20m x 0.18mm ID, 1.8um film

7.0 REAGENTS

Reagents must be tracked in accordance with STL-SL SOP AN44: *Reagent Traceability.*

7.1 Reagent water-free of volatile contaminants (obtained by purging with inert gas or carbon filtration)

7.2 Methanol-Burdich and Jackson, Purge and Trap grade

7.3 Sodium bisulfate-reagent grade. This salt is hydroscopic and should be stored in a dessicator.

7.4 Soil preservation solution- Slowly add, while stirring, 200g of sodium bisulfate to a 1.0-L volumetric containing about 700mL of reagent water. After the salt has dissolved, dilute to volume with reagent water, transfer to a storage container, and store the solution in an area free from VOC-especially water-soluble solvents such as acetone. The reagent should be tested prior to use by the analysis of a blank containing 5mL of the solution. The reagent is acceptable if it meets the same criteria as a method blank.

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions purchased from vendors or from stock standards prepared from neat materials. Certificates of analysis or purity must be received with all stock solutions or neat compounds. All preparation steps must be in accordance with STL-SL SOP AN41: *Standard Material Traceability.*

8.1 Preparation of **Stock Standards** from Neat Compounds

The lab should attempt to obtain a certified primary standard or secondary standard before preparing stock standards from neat materials. If primary stock standards must be prepared in-house, the target concentration range is from 2000ug/mL to 10000ug/mL. SL-SOP AN43: *Standard Preparation* gives the general instructions for the preparation of the stock solutions from neat materials.

8.2 Preparation of the **Working Standard** from Stock Standards

The working standard is prepared from the primary stock standards that are either prepared from neat compounds or purchased as certified solutions. The working standard contains one or more of the target compounds at a concentration suitable for preparing the calibration standards, generally 10-200ug/mL. A known volume of the working standard is then added to a known volume of reagent water to make the calibration standard.

The standards and standard concentrations listed in Table 1 are the suggested for routine use. If other "recipes" are used, the lab must document the standard preparation procedures in the standard traceability log.

8.3 Preparation of the **Calibration Standards** from the Working Standards

The calibration standards are the standards that are analyzed on the instrument. The calibration standard is made by adding a known volume of the working standard to a known volume of reagent water. The instrument must be calibrated using a minimum of five calibration standards. The lowest level standard must be at the reporting limit and the rest of the standards will define the working range of the analytical system.

8.3.1 Add 5.0mL of reagent water to a 5mL-glass syringe or 25ml of reagent water to a 25-ml glass syringe.

8.3.2 Add a known volume of the working standard to 5.0mL or 25ml of reagent water.

NOTE: The calibration standards for the low level soils are prepared using the same procedures as for the 5mL water purge except that the standards are purged at 40C. The lab has the option of using blank sand in the calibration standards.

The calibration standards listed in Table 1 are the suggested for routine use. If other "recipes" are used, the lab must document these standard preparation procedures in the standard traceablity log. A 5mL-purge volume may be used for low level (nominal RL of 1ug/L) if the instrument has sufficient sensitivity to detect the targets and the calibration criteria is met.

9.0 SAMPLE PREPARATION

Composite samples can be prepared using the guidance provided in STL-SL-SOP AN70.

9.1 **Aqueous samples** are analyzed directly by purge and trap/GC-MS. No sample preparation is necessary except to homogenize the sample prior to subsampling. The pH of liquid samples is checked and recorded prior to analysis to determine if the sample has been properly preserved.

9.2 Preparation of Soil Samples (5035)

9.2.1 Remove the Encore samples and the bulk sample from the storage area.

9.2.2 Test an aliquot of the bulk sample for the presence of carbonates.

- Transfer 5g of sample from the bulk sample to a 40mL vial..
- Add 5ml of the sodium bisulfate solution and shake the vial .
- If the sample exhibits effervescence, the Encore samples should be preserved as described above using 5mL of volatile-free water in place of the sodium bisulfate solution and placed in a freezer at –10C. The analytical hold time for frozen samples is 14 days from collection.
- If no effervescence is noted, the Encore samples may be preserved with 5mL soil preservation solution.

9.2.3 Add a stir bar to a vial and weigh the vial and record its tare weight(or tare the vial and stir bar weight by pressing the autotare button).

9.2.4 Transfer the sample from the Encore sampler to the tared vial and record the weight of the sample log.

If the sample effervesced during the carbonate test (9.2.2), add 5.0mL of reagent water and freeze at –10C. The hold time is 14 days from collection.

If not, add 5.0mL of the soil preservation solution, seal the vial, and store the sample at 4C until the time of analysis. The preserved sample must be analyzed within 14 days of collection.

NOTE: A preparation blank is prepared when Encore samples are transferred. The preparation blank contains the same reagents as the samples-either 5mL of reagent water or 5mL of soil preservation solution.

9.3 A methanol extraction is prepared when the concentration of the target compounds (by direct purge) exceeds the working range of the calibration curve. The bulk sample, collected in the 125-mL sample container, can be used to prepare the methanol extraction. Carry out the preparation quickly to minimize the loss of volatiles.

-Mix the sample with a stainless steel spatula and transfer 10g (+/- 0.5g) to a glass vial.

-Add 8uL of the surrogate spiking solution (2500ug/mL) to the sample and quickly add 10mL of purge and trap grade methanol. The theoretical concentration of the surrogates in the sample, assuming a sample weight of 10g and 100% percent solids, is calculated:

$$Ct(ug/kg,dw) = \frac{0.008mL \otimes 2500ug/mL}{0.010g \otimes solids} = 2000ug/kg,dw$$

-Shake the sample for two minutes. Allow the solvent to separate from the solids portion of the sample and transfer a 1-2mL aliquot of the extract to a storage vial. The vial should be sealed with no headspace. Store the methanol extract at 4C until the time of analysis. The extract must be analyzed within 14 days of sample collection.

-For each batch of twenty or fewer samples, prepare a method blank and a lab control standard. Prepare a matrix spike and matrix spike duplicate at a frequency of 5% of all samples.

The method blank is prepared by adding 8uL of the surrogate spiking solution to 10mL of purge and trap grade methanol. Assume a sample weight of 10g. Analyze 125uL of the extract.

The lab control standard is prepared by adding 8uL of the surrogate spiking solution and 8uL of the matrix spiking solution to 10mL of purge and trap grade methanol. Assume a sample weight of 10g. Analyze 125uL of the extract.

The matrix spikes are prepared by adding 8uL of the surrogate spiking solution (2500ug/mL) and 8uL of the matrix spiking solution (2500ug/mL) to 10-g aliquots of the sample selected for the MS/MSD. Quickly add 10mL of purge and trap grade methanol to each sample and shake for two minutes. Analyze 125uL of the extract or a smaller volume if the VOC concentration is high.

-Add 125uL of the extract (or a smaller volume if the VOC concentration exceeds the linear range of the system with 125uL) to 5.0mL of water (or to 25mL if the calibration is based on 25mL). Add the internal standard solution and analyze the sample using the ambient water calibration.

9.4 Methanol Extraction for Wastes

Carry out the preparation quickly to minimize the loss of volatiles.

9.4.1 Mix the sample with a stainless steel spatula and transfer 1g (+/- 0.2g) to a glass vial.

9.4.2 Add 10uL of the surrogate spiking solution (2500ug/mL) to the sample and quickly add 10mL of purge and trap grade methanol. If the sample is completely soluble in the methanol, dilute to a final volume of 10mL. The theoretical concentration of the surrogates in the sample, assuming a sample weight of 1.0g , is calculated:

$$Ct(ug/kg) = \frac{0.010mL \otimes 2500ug/mL}{0.0010g \otimes solids} = 25000ug/kg$$

9.4.2 Shake the sample for one minute. Allow the solvent to separate from the solids portion of the sample and transfer 1mL to 2mL of the extract to a storage vial. The vial should be sealed with no headspace. Store the methanol extract at 4C until the time of analysis. The extract must be analyzed within 14 days of sample collection.

For each batch of twenty or fewer samples, prepare a method blank and a lab control standard. Prepare a matrix spike and matrix spike duplicate at a frequency of 5% of all samples.

The method blank is prepared by adding 8uL of the surrogate spiking solution (2500ug/mL) to 10mL of purge and trap grade methanol. Assume a sample weight of 1.0g. Analyze 100uL of the extract.

The lab control standard is prepared by adding 10uL of the surrogate spiking solution (2500ug/mL) and 10uL of the matrix spiking solution (2500ug/mL) to 5.0mL of purge and trap grade methanol. Assume a sample weight of 5.0g. Analyze 100uL of the extract.

The matrix spikes are prepared by adding 10uL of the surrogate spiking solution (2500ug/mL) and 10uL of the matrix spiking solution (2500ug/mL) to 1g aliquots of the sample selected for the MS/MSD. Quickly add 10mL of purge and trap grade methanol to each sample and shake for one minute.

Add 100uL of the extract (or a smaller volume) to 5.0mL of water (or to 25mL if the calibration is based on 25mL). Add the internal standard solution and analyze the sample using the ambient water calibration.

NOTE: Waste samples may require significant dilution prior to analysis.

10.0 PROCEDURE

The following instrument conditions are recommended. The actual conditions may vary due to differences in instrumentation. The lab must document the instrument conditions in the maintenance log, the data system, or on the analysis log.

10.1 Instrument Conditions

10.1.1 GC Conditions
GC conditions may vary according to the environment and condition of each instrument. The lab must document the instrument conditions to assure consistent results and to aid in trouble-shooting the analytical system. Each lab is responsible for assuring that the conditions necessary to achieve adequate separation and sensitivity of the target analytes are maintained.

10.1.1.1 Example GC temperature program

Initial column temperature: 35 C for 3 minutes
Column temperature program 1: 20C per minute
Intermediate column temperature: 70C for 4 minutes
Column temperature program 2: 10C per minute
Final column temperature: 200C for 5.25 minutes

10.1.1.2 Column flow: Approximately 5-10mL/minute helium with a make-up of 20-25mL/minute helium. Total flow into the jet separator should be about 30mL/minute. The vacuum gauge on the jet separator will read about 0.5Torr.

If no jet separator is used and the column is plumbed directly into the source, the column flow should be adjusted to 0.5-1.0ml/min and a split ratio (desorb to column flow) of about 40:1 established. Smaller bore capillary columns (0.18 to 0.32mm) are required if the column is plumbed directly into the source

10.1.1.3 Mass Spectrometer and interface parameters

Jet separator temperature: 240C
Mass spectrometer interface: 240C
Mass spectrometer source temperature: factory set at 300C
range: 35-300amu, with a minimum scan cycle of 1 scan per second

10.1.2 Purge and Trap Conditions
The purge and trap conditions listed in this section are for guidance. The lab must document the actual conditions used. The purge time must be 11 minutes. Other parameters may be varied to optimize the detection of the target compounds.

10.1.2.1 "Three ring trap"-charcoal, Tenax, silica gel
Purge Time: 11 minutes
Purge temperature: aqueous-ambient; soils-heated 40C
Desorb time: 4 minutes
Desorb temperature: 180C
Bake time: 8 minutes at 225C
Purge flow: Approximately 20-30mL/minute
Valve temperature: 100C
Transfer line: 100C

10.1.2.1 VOCARB 3000 trap
Purge Time: 11 minutes
Purge temperature: aqueous-ambient; soils-heated 40C
Desorb time: 4 minutes
Desorb temperature: 225C
Bake time: 8 minutes at 250C
Purge flow: Approximately 20-30mL/minute
Valve temperature: 100C
Transfer line: 100C

The purge flow must be balanced for adequate sensitivity of the target compounds. If the purge flow is too high, the response of the gases will be low and not reproducible. The SPCC criteria for chloromethane may not be achieved if the purge flow is too high. If the purge flow is too low, the response of the more water-soluble targets-ketones, ethers, bromoform-may be low and the reporting limit may not be achieved on a routine basis.

10.2 BFB Tune Check

10.2.1 Fifty nanograms of 4-BFB must be analyzed at the beginning of each 12-hour clock as a check on the "**tune**" of the mass spectrometer. Meeting the tuning criteria ensures that the instrument is measuring the proper masses in the proper ratios. The 4-BFB analysis takes place under the same instrument conditions as the calibration standards and samples except that a different temperature program can be used to allow for the timely elution of 4-BFB. All other instrument conditions must be identical-the mass range, scan rate, and multiplier voltage. If the instrument is configured for direct injection, 50ng of 4-BFB may be injected directly on to the column. If the purge and trap is used to analyze the 4-BFB, the purge and trap conditions must be the same as for the calibration standards and samples.

10.2.2 Evaluation of the 4-BFB peak.

10.2.2.1 The chromatogram should exhibit acceptable baseline behavior and the 4-BFB peak should be symmetrical. A spectrum of the baseline that shows high abundances of mass 40 (Argon) and mass 44 (carbon dioxide) may indicate a leak or contaminated carrier gas.

10.2.2.2 The spectrum of the 4-BFB must meet the criteria listed in the attached SOP Summary. Background subtraction must be straightforward and designed only to eliminate column bleed or instrumental background. Scans +/- 5 scans from the apex can be evaluated for the 4-BFB criteria. Consecutive scans within this range can be averaged to meet the criteria.

10.2.2.3 The following records must be kept for each 4-BFB analysis that meets the criteria:
- the date, time, and data file of the analysis
- a spectrum of the scan or averaged scans
- a tabulation of the ion abundances of the scan

10.2.2.4 The 4-BFB analysis should be evaluated as to the relative size of the 4-BFB peak under the m/z 95 profile. A benchmark area window should be established for each instrument. Response outside of this window suggests instrumental problems such as a poor purge, clogged jet separator, leak in the Tekmar purging device, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open , or other anomalies.

10.2.2.5 If the 4-BFB fails to meet the acceptance criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the 4-BFB analysis, other corrective measures may include remaking the 4-BFB standard and/or cleaning the mass spectrometer source.

10.3 Initial Calibration

After the 4-BFB criteria has been met, the initial calibration standards are analyzed. Prepare the initial calibration standards according to the example recipes in the SOP appendices or lab-specific recipe. The lab must document the "recipe" used to prepare the calibration standards. The lowest level calibration standard must be at or below the routine RL and the other calibration standards will define the working range of the system.

10.3.1 Remove the plunger from the syringe and fill the barrel to overflowing with reagent water (syringe valve in the "red" position).

10.3.2 Replace the plunger, switch the syringe valve to "green", and force any airspace out of the syringe. Adjust the volume to the syringe volume(5mL or 25mL)

10.3.3 Briefly remove the syringe valve and inject the standards and internal standards into the syringe.

NOTE: Use the internal standard (IST) mix when preparing the calibration standards for analysis. The surrogates are already included in the standard mixes.

10.3.4 Load the standard(s) onto the purge and trap device and begin the analysis. All pertinent information concerning the standards must be recorded on the analysis log. The standards must be clearly identified and traceable to the preparation steps.

NOTE: The standards for low-level soil samples are prepared in the same manner as the 5mL standards. The standards for the low-level soils are purged at 40C. The lab has the option of using blank sand or soil in the calibration standards and the blank in the low level soil analysis.

10.3.5 After the acquisition has taken place, evaluate the calibration standards to ensure that each target compound, surrogate, and internal standard has been correctly identified. The analyst must be careful to complete this step before proceeding.

10.3.6 After each target compound, surrogate, and internal standard has been correctly identified, the relative response factor for each target compound and surrogate is calculated using the data system or using a PC spreadsheet as follows:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where
Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (see the attached quantitation report for a list of the compounds that are associated with the various internal standards)
Cx = concentration or mass on-column of the target compound being measured (ug/L or ug/kg OR ng or ug on-column)
Cis = concentration or mass on-column of the internal standard (ug/L or ug/kg OR ng or ug on-column)

The average relative response factor (RRFavg) is calculated for each target compound and each surrogate compound:

$$RRFavg = \frac{RRF1 + RRF2 + ... + RRFn}{n}$$

where n = number of calibration levels

Calculate the standard deviation (SD) for the target compounds and surrogates at all calibration levels:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RFi - RFavg)^2}{n-1}}$$

where
Rfi = response factor of a target compound in the individual calibration level
Rfavg = average response factor
n= number of calibration levels

10.3.7 Calculate the relative standard deviation (% RSD) of the calibration levels for each target:

$$\%RSD = \frac{standard\ deviation}{RRFavg} \otimes 100$$

10.3.8 The results of the initial calibration are evaluated against the Calibration Check Compound (CCC) criteria and the System Performance Check Compound (SPCC) criteria, which are listed below. The CCC and SPCC criteria must be met before samples can be analyzed.

Calibration Check Compounds – CCC Vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene

Initial Calibration	Continuing Calibration
<=30% RSD	<=20% difference from initial calibration

System Performance Check Compounds-SPCC

SPCC	Minimum RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Chlorobenzene	0.30
Bromoform	>0.10
1,1,2,2-Tetrachloroethane	0.30 (0.10 for 25mL purge volume)

NOTE: The CCC and SPCC criteria must be met even if the calibration curve option is used for quantitation. If the CCC and SPCC criteria do not pass, a new calibration curve must be prepared and analyzed.

10.3.9 After the initial calibration criteria (CCC and SPCC) have been met, each target is evaluated for linearity.

If the %RSD of the target compound is less than or equal to 15%, the average response factor can be used for quantitation of samples.

If the %RSD of the target compound is greater than 15%, a regression curve (linear, quadratic, etc) must be used for the quantitation of samples. A regression curve may also be used for the compounds that have %RSD less than 15%. The results can be used to plot a calibration curve of response ratios-Ax/Ais is plotted on the y-axis; Cx/Cis is plotted on the x-axis where

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (See attached quantitation report for a list of the compounds that are associated with the correct internal standard)
Cx = concentration or mass on-column of the target compound being measured (ug/L or ug/kg OR ng or ug)
Cis = concentration of the internal standard (ug/L or ug/kg OR ng or ug)

If the correlation coefficient of the regression curve is greater than 0.99, the curve can be used to quantify samples.. Regression curves may be forced through zero but it is recommended that the curve be evaluated without forcing through zero first and then with the curve forced through the origin. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire calibration range

When more calibration levels are analyzed than required, individual compounds may be eliminated from the lowest or highest calibration levels(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of the calibration curve be eliminated without eliminating the entire level.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPPs for other exceptions to using non-linear curve fitting.

8000B exception: evaluation of the "grand mean": If the average %RSD of ALL (all targets including CCC and SPCC) compounds in the initial calibration is less than 15%, the average response factor can be used for quantitation of all target compounds. The recommended course is to use regression curves, as described above, to quantify targets where the %RSD criterion (<=15%) is exceeded.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

10.3.10 After the initial calibration criteria has been met, the method blank is analyzed. 5.0mL or 25mL of reagent water is spiked with the internal standard/surrogate and analyzed. The concentrations of the target compounds in the method blank are calculated and the results are compared to the reporting limits (RL) in Table 5 of the STL-SL CQAP or other specified QAP.

If the concentrations of all target compounds are below the RL, analysis of client samples can take place. Note that all target compounds must meet the criteria.

If the concentration of any target compound is above the RL in Table 5 of the STL-SL CQAP, the method blank must be reanalyzed. The analytical system must be demonstrated to be free from contamination before the analysis of samples can take place.

If the method blank repeatedly fails to meet the criteria, contact the immediate supervisor to determine the cause of the problem and to determine a course of action. This action may include re-cleaning the sparging tubes (with soap, hot water, and methanol), purging the effected autosampler ports with heated methanol, flushing the purge and trap ALS concentrator with methanol, replacing the trap, changing the transfer line, and changing the column. A method blank is then analyzed after taking the corrective action to demonstrate that the contamination has been eliminated. Once the system is determined to be free from contamination; sample analysis may begin. Method blanks may be required after the analysis of samples that contain very high levels of VOC.

10.4 Continuing Calibration Verification

At the beginning of each 12-hour clock, the tune of the instrument must be checked by the analysis of 50ng of 4-BFB. This criteria must be met before the analysis of the calibration check standards can take place.

10.4.1 After the tune criteria has been met, a continuing calibration check standard(s) is analyzed. The continuing calibration standard should be at a nominal concentration of 50ug/L-kg for 5ml/5g samples and 10ug/L for 25mL with ketones and poor purgeables at higher concentrations. The CCC and SPCC criteria (Section 10.3.8) must be met before the analysis of the method blank and samples can take place. The percent difference (%D) is calculated as follows:

$$\%D = \frac{RRFavg - RRFccv}{RRFavg} \otimes 100$$

where
RRFavg = average response factor from initial calibration
RRFccv = response factor from the check (12-hour) standard-calibration verification

The percent drift (%Drift) may also be used to evaluate the change/deviation of the curve:

$$\%Drift = \frac{Ci - Cccv}{Ci} \otimes 100$$

where
Ci = Calibration Check Compound standard concentration
Cccv = measured concentration using the selected quantitation method

NOTE: The SPCC criteria (10.3.8) must be met even if the regression curve option is used for quantitation. If this criteria is not met, corrective action must be taken. The corrective action may include reanalysis of the calibration check standard or preparation of a new secondary stock standard and reanalysis of the calibration check standard. If subsequent analysis of the standard is still out of criteria, a new initial calibration curve must be analyzed and evaluated.

10.4.2 The calibration standard (CCV) must also be evaluated for internal standard retention time and response.

If the retention time of any internal standard changes by more than 30 seconds from the retention times of the internal standards in the initial calibration, the analytical system must be inspected for problems and corrective action instituted.

If the extracted ion current profile (EICP) area for any of the internal standards changes by more than a factor of two (-50% to +100%) from the last calibration check standard, the analytical system must be inspected for problems and corrective action instituted. If the CCV is the first one after the initial calibration, compare the ISTD response to the corresponding level in the ICAL.

10.4.3 After the continuing calibration criteria has been met, the method blank is analyzed. 5.0mL or 25mL of reagent water is spiked with the internal standard/surrogate and analyzed. The concentrations of the target compounds in the method blank are calculated and the results are compared to the reporting limits (RL) in Table 5 of the STL-SL CQAP.

If the concentrations of all target compounds are below the RL, analysis of client samples can take place. Note that all target compound must meet the criteria.

If the concentration of any target compound is above the RL in Table 5 of the STL-SL CQAP, the method blank must be reanalyzed. The analytical system must be demonstrated to be free from contamination before the analysis of client samples can take place.

10.5 Aqueous Sample Analysis-5.0mL to 25mL

The analyst must use the same volume as was used for the calibration standards-if a 5mL sample is used, it must be quanted off of the 5mL calibration curve; if a 25ml sample is used, it must be quanted off of the 25mL calibration curve. Samples are analyzed only after the tune criteria, the calibration (initial or continuing) criteria has been met, and the method blank criteria has been met. See the SOP Summary for the analytical sequence.

10.5.1 Remove the samples to be analyzed from the refrigerator and allow the samples to come to ambient temperature.

10.5.2 Put on a pair of gloves before transferring the sample from the vial to the syringe. The sample is most likely preserved with acid or may contain toxic or hazardous chemicals or biologically active components that may cause skin irritations. ***Gloves must be worn when handling samples.***

10.5.3 Mix the contents of the vial by inverting the vial several times. Check to see if there are air bubbles present in the sample. If air bubbles are present, use another vial if available. Make a note on the analysis log if the sample used contained bubbles and notify the supervisor and/or the project manager.

10.5.5 Remove the plunger from the glass syringe. Attach a syringe valve to the syringe Luer-tip to prevent sample from spilling out of the syringe when sample is added.

10.5.5 Open the vial of the well-mixed sample and gently pour the sample into the syringe barrel. The sample should fill the barrel of the syringe and overflow to allow trapped air bubbles to escape.

10.5.6 Replace the plunger into the syringe barrel. Try not to let air bubbles get into the barrel. If air bubbles are present, turn the syringe up, open the syringe valve , and expel the air while adjusting the volume to 5.0mL or 25mL. If no air bubbles were trapped, adjust the syringe to volume.

NOTE: For TCLP leachate samples, use 1.25mL of sample (1:4 dilution).

10.5.7 Open the syringe valve and inject the internal standard/surrogate (ISSU) mix into the sample.

10.5.8 Transfer the sample from the syringe to the purge and trap device. Record all of the sample identification information on the analysis log. Check the pH of the sample with pH paper and record the pH on the instrument log or other appropriate log..

10.5.9 Analyze the samples using the purge and trap and GC/MS conditions used for the initial and continuing calibration standards.

10.5.10 Determine the concentration of the samples and QC items. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

NOTE: Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client. For TCLP analyses, every reasonable effort should be made to achieve the regulatory level with out instrument overload.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with t the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower RLs.

A dilution is made when a volume of the sample is mixed with the reagent water to a final volume of 5.0mL or 25ml,depending on which curve is being used. The dilution factor is calculated by dividing the volume of sample into the volume used for the calibration curve.

$$DF = \frac{final\ volume\ of\ dilution(mL)}{volume\ of\ sample\ used(mL)}$$

For example, if 1.0mL of sample is diluted to final volume of 5.0mL, the dilution factor is 5. (5.0/1.0 = 5). If 1.0mL of sample is diluted to a final volume of 25mL, the dilution factor is 25 (25/1=25).

The following table gives some dilution factors:

Volume of Sample (mL)	Volume of Reagent Water (mL)	Final Volume (mL)	Dilution factor
5.0	0	5.0	1
2.5	2.5	5.0	2
1.0	4.0	5.0	5
0.5	4.5	5.0	10
0.10	4.9	5.0	50
25.0	0	25.0	1
5.0	20.0	25.0	5
2.5	22.5	25.0	10
1.0	24.0	25.0	25
0.50	24.5	25.0	50
0.10	24.9	25.0	250

NOTE: The same volume of internal standard/surrogate mix (ISSU) is added to the dilution as was added to the undiluted sample.

10.6 Low Level Soil Samples by Heated Purge and Trap (Method 5035)

The soil analytical system is calibrated using the same concentrations as the 5mL purge. The tune, initial and continuing calibration criteria, and the method blank criteria must be met before samples are analyzed. Standards and QC items must be analyzed under the same heated purge and trap conditions.

Remove the samples to be analyzed (Section 9.2) from the refrigerator or freezer and allow the sample to come to ambient temperature. Inspect the vial for cracks or obvious breaches in the septum. Load the samples on to the soil-purging unit and analyze according to the sequence described in Appendix B.

Liquid field QC for soils (trip blank, field blank, etc.) should be analyzed with the associated soil samples, using the same preparation and analytical procedures, including the heated purge. Report the results for liquid trip blanks as ug/L.

10.7 Analysis of Methanol Extracts of Soils and Wastes

The methanol extraction is used when the concentration of one or more target compounds exceeds the linear range of the low-level purge technique (>1000ug/kg). or if the concentration of VOC in the soil or waste samples is high. Samples are analyzed only after the 4-BFB criteria, the calibration criteria (initial and continuing), and the method blank criteria has been met. Medium level soil extracts are quanted using the ambient purge calibration curve. Sample preparation steps are included in Section 9.

10.7.1 Remove the plunger from the 5.0-mL syringe and fill the barrel to overflowing with reagent water(syringe valve in the "red" position). Replace the plunger, switch the syringe valve to "green", and force any airspace out of the syringe. Adjust the volume to the syringe volume(5mL)

10.7.2 Briefly remove the syringe valve and inject the sample extract and 5uL of the internal standard (IST) solution into the syringe. Use 125ul of the extract for soils and 100uL of the extract for wastes. Smaller aliquots are used if the concentration of target analytes exceed the working range of the system.

NOTE: Use the internal standard (IST) mix when preparing the medium level samples. Recall that the surrogates have already been added to the sample during the methanol extraction step (Section 9).

10.7.3 Load the sample on to the purge and trap device and begin the analysis. All pertinent information concerning the samples must be recorded on the analysis log. The samples must be clearly identified and traceable to the extraction log. These conditions must be the same as was used for the initial and continuing calibration standards-ambient purge for aqueous samples.

10.7.4 Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, a smaller aliquot of the methanol extract is reanalyzed to bring the highest target within the upper half of the calibration curve. Follow the guidelines in Section 10.4.10 for reporting dilutions.

NOTE: It is possible to dilute the surrogates in the sample extract below the linear range of the calibration curve. The minimum extract aliquot that can be used to provide a quantifiable result for the surrogates and matrix spikes is 0.0025mL (2.5uL).

SOIL: 10g to 10mL MeOH	WASTES: 1g to 10mL MeOH	Surrogates- Theoretical ng on-column
125uL(0.125mL)	100uL (0.100mL)	250
62.5uL(0.0625mL)	50uL(0.050mL)	125
25uL(0.025mL)	25uL(0.020mL)	50
12.5uL(0.0125mL)	10ul(0.010mL)	25
2.5uL(0.0025mL)	2.0uL(0.0020mL)	5.0-quantiation limit
<2.5uL(0.025mL)	<2.0uL(0.0020mL)	<5.0ng- below the quantitation limit-diluted out

NOTE: Some instrument quantitation limits may be higher than the limit listed in the table. The volume of extract should be adjusted accordingly.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Qualitative Analysis of Target Compounds

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from a reference spectrum of the target compound stored in a library generated on the same instrument or a standard spectral library such as the NIST/NBS.

11.1.1 Two criteria must be met in order to identify a target compound.

1) elution of the sample component within +/-0.06 RRT (relative retention time) units of the daily standard containing that compound.

$$RRT = \frac{\textit{retention time of the target compound}}{\textit{retention time of the associated internal standard}}$$

2) correspondence of the target compound spectrum and the standard component mass spectrum

11.1.2 All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion = 100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound will make the identification of the target compound more difficult. These ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

11.1.3 The relative intensities of the ions present in the sample component spectrum should agree within +/- 30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum.

11.1.4 If the above criteria are not met exactly, the analyst should seek help from a senior analyst or supervisor. If there is sufficient evidence to support the identification of the component, then the component is identified, quantified, and reported.

11.2 Tentatively Identified Compounds

For samples containing components not associated with the calibration standards, a library search on a reference library, such as the NIST/NBS, may be conducted in order to identify the non-target compounds. Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification. Tentative identifications of non-targets will be made only by analysts having completed the training specified in the training schedule.

11.2.1 Relative intensities of the major ions (masses) in the reference spectra (ions >10% of the most abundant ion) should be present in the sample spectrum.

11.2.2 The relative intensities of the major ions should agree within +/-30%.

11.2.3 Molecular ions present in the spectrum should be present in the sample spectrum.

11.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible subtraction from the sample spectrum because of over-lapping or co-eluting peaks.

11.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of coeluting peaks.

11.2.6 If, in the opinion of the analyst, there is enough evidence to support the tentative identification of a compound even though the above criteria is not met exactly, the peak may be considered tentatively identified. The analyst should consult other analysts or the mass spectral interpretation specialist if there are any questions concerning an interpretation of spectra.

11.2.7 The estimated concentration of the tentatively identified compound (TIC) is calculated using the total ion area of the tentatively identified peak and total ion area of the nearest internal standard that has no interferences. The calculation is

Aqueous

$$TIC(ug/L) = \frac{Cis}{AREAis} \otimes AREAtic \otimes DF$$

where
Cis = concentration of the internal standard, ug/L
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
DF = dilution factor

Soils by Heated P/T

$$TIC\,(ug/kg,dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{5.0g}{(W)(solids)}$$

where
Cis = concentration of the internal standard, ug/kg
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
W = weight of sample analyzed, g
solids = decimal equivalent of percent solids

Soils by Methanol Extraction

$$TIC\,(ug/kg,dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{Vcal}{(W)(solids)}$$

where
Cis = concentration of the internal standard, ug/kg
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
Vcal = volume that calibration curve is based on (5mL or 25mL)
solids = decimal equivalent of the percent solids(percent solids/100)
W = weight of sample added to the reagent water (g)

This weight is determined using the following equation:

$$W = \frac{Wext(g)}{Vf(mL)} \otimes Vext(mL)$$

where
Wext = weight of sample extracted (g)
Vf = final volume of the extract (mL)
Vext = volume of extract added to the water (mL)

11.3 Calculations for Samples-Internal Standard Technique

Aqueous Samples- relative response factor :

$$concentration(ug/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes DF$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/L)
RRFavg = average response factor of the compound being measured
DF = dilution factor

Aqueous Samples: regression curve

$$concentration(ug/L) = concentration(curve) \otimes DF$$

where
DF = dilution factor

The reporting limit (RL) is calculated:

$$RL(ug/L) = RLqap \otimes DF$$

where
DF = dilution factor. The SL CQAP Table 5 RL(RLqap) assumes a DF of 1.

Soils by Heated P/T- relative response factor :

$$concentration(ug/kg, dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{5.0g}{(W)(solids)}$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/kg)
RRFavg = average response factor of the compound being measured
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

Soils by Heated P/T: regression curve

$$conc(ug/kg, dw) = Ccurve(ug/kg) \otimes \frac{5.0g}{(W)(solids)}$$

where
Ccurve = concentration from curve(ug/kg)
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

The reporting limit (RL) is calculated:

$$RL = RLqap \otimes \frac{5.0g}{(W)(solids)}$$

where
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

The STL-SL CQAP assumes W= 5.0g and solids = 1.

Methanol Extraction Soils and Wastes- relative response factor

$$concentration(ug/kg,dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{Vcal}{(W)(solids)}$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/L)
RRFavg = average response factor of the compound being measured
Vcal = volume that calibration curve is based on (5mL or 25mL)
solids = (percent solids)/100)
W = weight of sample added to the reagent water (g)

This weight is determined using the following equation:

$$W = \frac{Wext(g)}{Vf(mL)} \otimes Vext(mL)$$

Wext = weight of sample extracted (g)
Vf = final volume of the extract (mL)
Vext = volume of extract added to the water (mL)

Methanol Extraction of Soils and Solids- regression curve:

$$conc(ug,kg,dw) = Ccurve(ug/L) \otimes \frac{Vcal}{(W)(solids)}$$

where
Vcal = volume that calibration curve is based on (0.005L or 0.025L)
W = weight of sample added to the reagent water (g)-defined above

The reporting limit (RL)is calculated:

$$RL = RLqap \otimes \frac{5.0g}{(W)(solids)}$$

where
W = weight of sample added to the reagent water (g)
solids = (percent solids)/100)

The STL-SL CQAP assumes W= 5.0g and solids = 1.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items that are analyzed together. The matrix spike and LCS frequency is defined in Section 3.1.3 of STL-SL SOP AN02: *Analytical Batching*. Note that the method blank for liquid samples and low-level soils is clock-specific and that the method blank for medium level soil samples is extraction batch-specific.

STL-SLSOP AN02: *Analytical Batching* describes the procedure for evaluating batch-specific QC. This criteria is summarized in the attached 8260 SOP Summary.

STL-SL SOP AN02 also contains the calculations for accuracy and precision and the calculations for the theoretical concentrations of surrogates, lab spikes, and matrix spikes.

12.2 Initial Demonstration of Capability (IDOC) to Generate Acceptable Accuracy and Precision

Each analyst must demonstrate competence in the analysis of samples by this procedure. The minimum criteria for this demonstration is the preparation and analysis of spiked reagent water. Section 8.3 of EPA Method 8260A gives the general procedure for the performance of the IDOC and Table 6 of EPA Method 8260A gives the acceptance criteria for the accuracy and precision.

12.3 Method Detection Limit

The method detection limit is determined in accordance with STL-SL SOP CA90.

13.0 PREVENTIVE MAINTENANCE

Preventive maintenance items will be added at a later date. Section 10 of the STL-SL QAPs provide guidance on preventive maintenance.

14.0 TROUBLE-SHOOTING

Trouble-shooting items will be added at a later time. See instrument manufacturers' manuals for guidance on locating and repairing instrument problems.

15.0 REFERENCES

1. *Savannah Laboratories' Comprehensive Quality Assurance Plan* and *Savannah Laboratories' Corporate Quality Assurance Plan*, current revisions.
2. Method s 5035, 8000B, and 8260B. *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846.including Update III.* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

Appendix A

VOLATILES BY GC/MS WORKING STANDARDS -EXAMPLE

These standards can be used to prepare the working standards for EPA Method 8260 to report the TCL (target compound list) compounds and the extended list of target compounds generally associated with EPA 8260. The standards are prepared in purge and trap grade methanol and are stored at 4C with minimum headspace.

Working Standard 1 (TCL WS-1)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA Cal #2	2000	12.5	25
VOA Cal #3	2000	12.5	25
VOA Cal #4	2000	12.5	25
1,2,-DCB	5000	5.0	25
1,3-DCB	5000	5.0	25
1,4-DCB	5000	5.0	25
2-CEVE	1000	125	125

Working Standard 2 (TCL WS-2)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA Cal #1	5000	25	125
8260 Surrogates	2500	10	25

Working Standard for GASES (TCL GASES)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
502.2 Cal 1	2000	12.5	25

Appendix A

Working Standard 3 (8260 WS-3)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
8260 Custom Mix #1	200	125	25
8260 Custom Mix #2	200	125	25
1,1,2,2-Tetrachloroethane	2000	12.5	25

Appendix A

Internal Standard (8260 ISTD)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
VOA ISTD	2500	20	50
1,2-DCE-d4	2000	25	50

Internal Standard/Surrogate (8260 ISSU)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA ISTD	2500	20	50
1,2-DCE-d4	2000	25	50
8260 Surrogate	2500	20	50

Tune Evaluation Standard (4-BFB)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
4-BFB	5000	10	50

Matrix Spike Standard (5-component subset)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
Matrix Spiking Solution	2500	20	50

TCLP matrix Spike Standard (5-component subset)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
TCLP Spiking Solution	2000	16	125

Appendix A

VOLATILES BY GC/MS CALIBRATION STANDARDS - EXAMPLES

The following calibration standards are prepared to define the working range of the EPA 8260 analysis for the target compound list (TCL) and the extended list of compounds generally associated with EPA 8260. The lowest level standard is at the reporting limit and the other standards define the working range. Samples with target analytes above the concentration of the highest calibration standard must be diluted and reanalyzed.

TARGET COMPOUND LIST

Working Level standards	Conc (ug/mL)	TCL-1 *	TCL-2 *	TCL-3 *	TCL-4 *	TCL-5 *	TCL-6 *
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 5.0mL of reagent water or to 5.0g of blank sand.

8260 EXTENDED LIST (TCL+ADDITIONAL COMPOUNDS)

Working Level standards	Conc (ug/mL)	8260-1 *	8260-2 *	8260-3 *	8260-4 *	8260-5 *	8260-6 *
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
8260 WS-3	25	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 5.0mL of reagent water or to 5.0g of blank sand.

CONCENTRATIONS OF THE CALIBRATION STANDARDS-5.0mL OR 5.0g

Cal Std	all targets except ketones, 2-CEVE	ketones, 2-CEVE
TCL-1,8260-1	5ug/l-kg	25ug/l-kg
TCL-2,8260-2	10ug/l-kg	50ug/l-kg
TCL-3,8260-3	25ug/l-kg	125ug/l-kg
TCL-4,8260-4	50ug/l-kg	250ug/l-kg
TCL-5,8260-5	100ug/l-kg	500ug/l-kg
TCL-6,8260-6	200ug/l-kg	1000ug/l-kg

Appendix A

VOLATILES BY GC/MS CALIBRATION STANDARDS-25mL Purge Volume-EXAMPLES

These calibration standards are prepared to define the working range of the EPA 8260 analysis for the target compound list (TCL) and the extended list of compounds generally associated with EPA 8260. The standards are based on a volume of 25mL to achieve lower quantitation limits for the target compounds. The lowest level standard is at the reporting limit and the other standards define the working range. Samples with target analytes above the concentration of the highest calibration standard must be diluted and reanalyzed.

TARGET COMPOUND LIST

Working Level standards	Conc (ug/mL)	25TCL -1*	25TCL-2*	25TCL-3*	25TCL-4*	25TCL-5*	25TCL-6*
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 25mL of reagent water.

8260 EXTENDED LIST (TCL+ADDITIONAL COMPOUNDS)

Working Level standards	Conc (ug/mL)	258260-1*	258260 -2*	258260-3*	258260-4*	258260-5*	258260-6*
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
8260 WS-3	25	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 25mL of reagent water.

CONCENTRATIONS OF THE CALIBRATION STANDARDS

Cal Std	all targets except ketones, 2-CEVE	ketones, 2-CEVE
25TCL-1,25-8260-1	1.0ug/l	5.0ug/l
25TCL-2,25-8260-2	2.0ug/l	10ug/l
25TCL-3,25-8260-3	5.0ug/l	25ug/l
25TCL-4,25-8260-4	10ug/l	50ug/l
25TCL-5,25-8260-5	20ug/l	100ug/l
25TCL-6,25-8260-6	40ug/l	200ug/l

Appendix B
8260 SOP SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage*	Container	Hold Time
Aqueous	None; 4C	40mL no headspace	7 days
	HCl pH<2; 4C	40mL-no headspace	14 days
Soil/solid(low level)	Iced at collection; 5mL sodium bisulfate added upon arrival in lab; store at 4C	5-g Encore Sampler	14 days
Soil/solid(low level) -high carbonates	Iced at collection; 5mL water added upon arrival in lab; store at –10C	5-g Encore Sampler	14 days
Soil/solid(high level)	None; 4C	Glass 125mL	14 days
TCLP	HCl pH<2; 4C	Tedlar bag or syringe	14 days

*storage temperature is 4C with a control criteria of less than 6C with no frozen samples.

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
4-BFB 50ng on column Clock starts at injection	4-BFB 50ng on column Clock starts at injection
Calibration standards- minimum of five cal levels	Mid point calibration verification (50ug/L or 50ug/kg)) RL Standard-low point on cal curve (if necessary)
Method blank	Method blank
Samples analyzed until the 12-hour clock expires	Samples analyzed until 12-hour clock expires

See SL SOP AN02, Section 3.1.3, for the batch/clock options for LCS and MS/MSD.

Recommended Internal Standards:
1,2-dichloroethane-d4; 1,4-difluorobenzene; chlorobenzene-d5; 1,4-dichlorobenzene-d4

Surrogates/System Monitoring Compounds:
dibromofluoromethane; toluene-d8; 4-bromofluorobenzene

LCS/MS: CQAP Subset:
1,1-dichloroethene; benzene; trichloroethene; toluene; chlorobenzene

Appendix B
8260 SOP SUMMARY

VOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION BROMOFLUOROBENZENE (BFB)	
m/e	**Abundance Criteria**
50	8.0-40.0% of mass 95
75	30.0-66.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0-9.0% of mass 95
173	< 2.0% of mass 174
174	50-120%% of mass 95
175	4.0-9.0% of mass 174
176	93.0-101.0% of mass 174
177	5.0-9.0% of mass 176

(1) *8260 criteria taken from CLP OLMO4.0 (January 1998)

CALIBRATION ACCEPTANCE CRITERIA

Calibration Check Compounds - CCC
Vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene

Initial Calibration	Continuing Calibration
Less than or equal to 30% RSD	Less than or equal to 20% difference or drift from initial calibration

System Performance Check Compounds-SPCC

SPCC	Minimum RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Chlorobenzene	0.30
Bromoform	>0.10
1,1,2,2-Tetrachloroethane	0.30 (0.10 for 25mL purge volume)

See Sections 10.3 and 10.4 for ICAL and CCV linearity checks and criteria.

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
MS Tune Check - 50ng 4-BFB	Before initial and continuing calibration standards - every 12 hours	Mass abundances within method acceptance criteria	-Evaluate chromatogram and spectrum - Reanalyze - Retune MS and reanalyze - Remake standard and reanalyze - Perform instrument maintenance and reanalyze
Initial Calibration – minimum five point curve with lowest point at or below the Reporting Limit (RL)	Initially; after major instrument maintenance; whenever continuing calibration check fails. Prior to analysis of method blank and samples	Method criteria for CCC/SPCC (see -Calibration Acceptance Criteria – Table presented earlier in this document)	- Evaluate chromatograms, spectra, and integrations - Reanalyze standard(s) - Remake and reanalyze standard(s) - Perform instrument maintenance and recalibrate
Continuing Calibration check - midpoint standard	Every 12 hours before analysis of method blank and samples	Method criteria for CCC/SPCC (see Calibration Acceptance Criteria - Table presented earlier in this document)	- Evaluate chromatogram, spectra, integrations - Reanalyze standard - Remake and reanalyze standard - Recalibrate - Perform instrument maintenance and recalibrate
Method Blank	Every 12 hours (per clock) before sample analyses	All reported targets <RL	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
Lab Control Sample (LCS) -subset of target compounds unless full target spike specified by client	Each batch	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Matrix Spike/Matrix Spike Duplicate (MS/MSD) -subset of target compounds unless full target spike specified by client	Each batch	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Surrogates	All samples, blanks, LCS, MS	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Internal Standard Area	Evaluate all standards and samples	-Areas in continuing calibration verification must be 50% to +200% of previous initial calibration sequence -Retention time of internal standard must be +/-30 seconds from internal standard in initial calibration -Areas in samples should be evaluated for gross error . Consult supervisor.	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
Reporting Limit Standard -1x to 2x the RL	(Optional) Daily. Required for Florida DEP	Detected with reasonable response	-Evaluate chromatogram, spectra, and integrations -Reanalyze -Remake standard and reanalyze -Retune and recalibrate -Perform instrument maintenance and recalibrate
Initial Demonstration of Capability	Per analyst	Method criteria	-Reanalyze targets that do not meet criteria
Method Detection Limit (MDL)	See STL-SL SOP CA90	See STL-SL SOP CA90	-Reanalyze and re-evaluate

Appendix C
EXAMPLE QUANTITATION REPORT

-*quantitation ions*
-internal standard and target compound association

SEVERN TRENT STL

SEMI-VOLATILE COMPOUNDS BY GC/MS
Method: 8270C

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Approved by:

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1.0 SCOPE AND APPLICATION

1.1 This method can be used to determine the concentration of various semi-volatile organic compounds (SVOC) in groundwater, TCLP and SPLP leachates, soils, sediments, wastes, and solid sample extracts. The attached quantitation report (Appendix B) lists the routine target compounds, the retention times of the target compounds, the characteristic ions of the target compounds, and the internal standard associated with each target compound.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision limits for the target compounds are given in Section 5 of the current revision of the Laboratory Quality Manual (LQM).

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample is extracted using an appropriate extraction procedure. The extract is dried, concentrated to a volume of 1.0mL, and analyzed by GC/MS. Qualitative identification of the target compounds in the extract is based on the retention time and the mass spectra determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

2.2 This procedure is based on the guidance provided in SW-846 Method 8270C.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The toxicity or carcinogenicity of each chemical used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, and lab glasses or face shield should be worn while handling extracts and standards. Standard preparation, addition of the internal standard solution, and sample extract dilution should be performed in a hood or well ventilated area.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst. These sheets specify the type of hazard that each chemical poses and the procedures that are used to handle these materials safely.

3.4 The exit vent of the splitless injector must have a carbon trap in-line to collect the semivolatile compounds that are vented during the injection of the extract. The traps should be changed every six months and disposed of in accordance with SOP CA70: *Waste Management.*

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, or glassware. Glassware and/or extraction vessels that have not been properly cleaned may contribute artifacts that make identification and quantification of the target compounds difficult. Elevated baselines may be due to oils, greases, or other hydrocarbons that may be extracted from improperly cleaned glassware or extraction vessels.

4.2 Matrix interferences may be caused by contaminants that are extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. Sample extracts that contain high concentrations of non-volatile material such as lipids and high molecular weight resins and polymers may require the optional GPC cleanup prior to analysis. The GPC cleanup is generally not effective in removing non-target material that is associated with common petroleum products like diesel.

4.3 Secondary ions may be used for quantification if there is interference with the primary quantitation ion. If a secondary ion is used for quantification, the concentration/response relationship of the secondary ion must be established. The secondary ion must meet the same calibration criteria as the primary ion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	none; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Waste	none; 4C	Glass	14 days	40 days
TCLP	none; 4C	1-L amber	7 days from TCLP leaching procedure	40 days

Refrigerator temperature acceptance criterion is less than 6C with no frozen samples.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph- Hewlett-Packard (HP) 5890 or equivalent with compatible autosampler, splitless injector, and direct capillary interface. The exit vent of the splitless injector must have a carbon trap in-line to collect the semivolatile compounds that are vented during the injection of extracts. The carbon traps should be changed every six months.

6.2 Mass spectrometer- HP5971, HP5972, HP5973 or equivalent

6.3 Recommended Capillary column-HP-5MS, 30m x 0.25mm ID x 0.25um film thickness or equivalent column

6.4 Data system- compatible with GC/MS system

6.5 Microsyringes- appropriate volumes

6.6 Volumetric flasks- Class A, appropriate volumes

6.7 Autosampler vials and crimper- compatible with autosampler

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability.*

7.1 Methylene chloride- pesticide residue grade, for preparation of standards

7.2 Acetone- pesticide residue grade, for preparation of standards

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with SOP AN41: *Standard Material Traceability*. General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation.*

The lab should purchase certified solutions from STL approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation from neat materials.

8.1 Preparation of the Stocks from Neat Standards

The steps for the preparation of primary stock standards from neat materials are given in SOP *AN43: Standard Preparation.* The standards should be prepared in methylene chloride but may require other solvents to dissolve the material.

8.2 Preparation the calibration standards from the stock standards

A minimum of five calibration standards are prepared. The concentrations of the stock standards are in the 1000-10000ug/mL range. The recommended standards are listed in Section 10.2. The lowest level standard should be at the equivalent of the reporting limit and the rest of the standards should define the working range of the detector. Note that six calibration levels are required for a second order regression curve. Internal standards should be added to each standard to give a final concentration of 40ug/mL.

Each lab should develop controlled recipes that can be posted or maintained in appropriate logbooks.

9.0 SAMPLE PREPARATION

9.1 The sample extraction procedures are given in the following SOPs:

Matrix	SOP	Extraction Technique
Aqueous, TCLP leachates	EX30	Continuous Liquid-liquid Extraction
Aqueous, TCLP leachates	EX35	Separatory Funnel
Soils/Sediments	EX40	Sonication
Wastes	EX42	Waste dilution

9.2 The sample concentration procedures are given in SOP EX 50: Zymark Nitrogen Concentration.

9.3 Gel permeation chromatography (SOP EX61) may help to eliminate or minimize matrix interferences in a limited number of samples. The GPC cleanup is generally not effective on samples containing petroleum products.

10.0 PROCEDURE

10.1 Instrument Conditions

Instrument conditions may vary according to the sensitivity of each instrument. The following conditions are provided for guidance. The lab must optimize and document the conditions used for the analysis of SVOC by GC/MS.

Recommended Column:
HP-5MS 30m x 0.25mm ID x 0.25um film thickness or equivalent

Column flow: Approximately 1mL/min helium

GC Oven temperatures:
Initial column temperature: 45 C for 3 minutes
Column temperature program: 10C per minute
Final column temperature: 300C (until at least one minute past the elution time of Benzo (g,h,i) perylene).

GC injector parameters
Injector temperature: 250-270EC
Injection type: split, approximately 1:10 or splitless injection
Injector liner: 4mm ID quartz or 4mm glass, deactivated (single "Gooseneck")
Sample injection volume: 1-2uL

Mass Spectrometer and interface parameters
Mass spectrometer interface: 300C
Mass spectrometer source temperature: Factory Set
Mass range: 35-500amu, with a scan time of 1.0 scans per second or greater

10.2 Calibration

A minimum of five calibration standards are prepared and analyzed. The recommended standards are 10, 20, 50, 80, 100, 200ug/mL. The lowest level standard should be at or below the equivalent of the reporting limit and the rest of the standards should define the working range of the detector. Note that six calibration levels are required for a second order regression curve.

10.2.1 Fifty nanograms of DFTPP must be analyzed at the beginning of each 12-hour clock as a check on the "tune" of the mass spectrometer. Meeting the tuning criteria demonstrates that the instrument is measuring the proper masses in the proper ratios. The DFTPP analysis takes place under the same instrument conditions as the calibration standards and samples except that a different temperature program can be used to allow for the timely elution of DFTPP. All other instrument conditions must be identical-the mass range, scan rate, and multiplier voltage.

10.2.1.1 Prepare a 50ng/uL solution of tune/column evaluation standard containing each of the following compounds at 50ug/mL in methylene chloride: DFTPP, pentachlorophenol, p,p'-DDT, and benzidine.

10.2.1.2 Analyze a 1uL aliquot of the tune/column evaluation solution.

10.2.1.3Evaluate the DFTPP peak.

-The chromatogram should exhibit acceptable baseline behavior and the DFTPP peak should be symmetrical.

-The spectrum of the DFTPP must meet the criteria listed in the SOP Summary (Appendix A). Background subtraction must be straightforward, that is, no scan within the elution window of DFTPP may be subtracted from another scan within the elution window, and designed only to eliminate column bleed or instrumental background. Scans +/- 2 scans from the apex can be evaluated for the DFTPP criteria. Consecutive scans within this range may be averaged to meet the criteria.

NOTE: The DFTPP analysis should be evaluated as to the relative size of the DFTPP peak under the m/z 198 profile. A benchmark area window should be established for each instrument and data system. Area outside of this window suggests instrumental problems such as a bad injection, clogged autosampler syringe, leaking injector, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open, etc.

If the DFTPP fails to meet the criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the DFTPP analysis, other corrective measures may include remaking the DFTPP standard, cleaning the mass spectrometer source, etc.

10.2.1.4Benzidine and pentachlorophenol should be present at their normal responses with minimal peak tailing visible. Peak tailing guidance is taken from EPA Method 625 which allows pentachlorophenol to be less than or equal to five and benzidine less than or equal to three. Refer to Figure 1for an example of [eak tailing factor calculation.

This is a good check on the system: if pentachlorophenol (a CCC) does not respond well, the calibration standard should not be analyzed. Injector port and column maintenance should be performed and the tune/column evaluation standard reanalyzed.

The percent breakdown of p,p'- DDT is calculated using the following equation. The percent breakdown should not exceed 20%.

$$\%Breakdown = \frac{(areaDDE + areaDDD)}{(areaDDT + areaDDE + areaDDD)} x\,100$$

Areas from the total ion chromatogram are used to calculate DDT breakdown.

10.2.2 After the DFTPP criteria and column evaluation criteria have been met, the initial calibration standards are analyzed.

10.2.2.1Prepare the initial calibration standards. The lowest calibration standard should be at the RL and the rest of the standards will define the working range. See section 10.2 for guidance regarding calibration levels.

10.2.2.2Set up a sequence and analyze the calibration standards. The injection volume must be the same for the calibration standards and all sample extracts.

10.2.3 Identify the internal standards, surrogates, and the target compounds. The data system must be updated with the proper retention times and ion data.

10.2.4 Calculate the relative response factor for each compound as follows:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured
(See the attached quantitation report for a list of the compounds that are associated with the correct internal standard)
Cx = concentration of the compound being measured (ug/mL)
Cis = concentration of the internal standard (40ug/mL)

Secondary ions may be used for quantification if there is interference with the primary quantitation ion. If a secondary ion is used for quantification, the concentration/response relationship of the secondary ion must be established. The secondary ion must meet the same calibration criteria as the primary ion.

10.2.5 Calculate the average relative response factor (RRF_{avg}) for each target compound and each surrogate compound:

$$RRF_{avg} = \frac{RRF1 + RRF2 + RRF3.... + RRFn}{n}$$

RRF1 = relative response factor of the first standard
RRFn = relative response factor of the last standard
n = number of calibration standards

10.2.6 Calculate the standard deviation (SD) for the initial calibration standards:

$$SD = \sqrt{\frac{\sum_{i-1}^{n_1} (RRF_i - RRF_{avg})^2}{n-1}}$$

10.2.7 Calculate the relative standard deviation (%RSD) of the target compounds in the calibration standards.

$$\%RSD = \frac{SD}{RRF_{avg}} x\ 100$$

10.2.8 Evaluation of the Initial Calibration

The initial calibration is evaluated specifically for the calibration check compounds (CCC) and the system performance check compounds (SPCC). The CCC and SPCC criteria are given in the SOP Summary (Appendix A). The %RSD criteria for CCC and minimum RRF for SPCC must be met before the analysis of sample extracts can begin.

If the CCC and SPCC criteria are not met, action must be taken to bring the analytical system into compliance with the criteria. This action may include injection port maintenance, source cleaning, changing the column, or replacement of injection port lines and assembly. In any case, if the criteria are not met, the initial calibration must be repeated. The analyst must be aware of the 12-hour clock for the DFTPP analysis. The DFTPP criteria must be met prior to the analysis of the calibration standards.

10.2.9 After the initial calibration criteria (CCC/SPCC) have been met, each target is evaluated for linearity. Refer to SOP AN67: *Evaluation of Calibration Curves* for guidance.

If the %RSD of the target compound is less than or equal to 15%, the average response factor can be used for quantitation of samples.

If the %RSD of the target compound is greater than 15%, a regression curve (linear, quadratic, etc) must be used for the quantitation of samples. A regression curve may also be used for the compounds that have %RSD less than 15%. The results can be used to plot a calibration curve of response ratios-Ax/Ais is plotted on the y-axis; Cx/Cis is plotted on the x-axis where:

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (See attached quantitation report for a list of the compounds and their associated internal standard)
Cx = concentration of the target compound being measured (ug/mL)
Cis = concentration of the internal standard (ug/mL)

A linear or quadratic curve may be used to define the concentration/response relationship. If r^2 is greater than 0.99, the curve can be used to quantify samples. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire concentration range.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPPs for other exceptions to using non-linear curve fitting.

When more calibration levels are analyzed than required, individual compounds may be eliminated from the lowest or highest calibration levels(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of the calibration curve be eliminated without eliminating the entire level.

8000B exception: evaluation of the "grand mean": If the average %RSD of ALL (all targets including CCC and SPCC) compounds in the initial calibration is less than 15%, the average response factor can be used for quantitation of all target compounds. The recommended course is to use regression curves, as described above, to quantify targets where the %RSD criterion (<=15%) is exceeded.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

10.3 Continuing Calibration Verification

At the beginning of each 12-hour clock, the tune of the instrument must be checked by the analysis of the tune/column evaluation solution (10.2.1.1). The tune and column evaluation criteria (10.2.1.3 and 10.2.1.4) must be met before the analysis of the calibration check standards can take place.

10.3.1 After the tune and column evaluation criteria have been met, a continuing calibration check standard(s) is analyzed. The continuing calibration standard should be at a mid-level concentration. The CCC and SPCC criteria (SOP Summary, Appendix A) must be met before the analysis of samples can take place. The percent difference (%D) is calculated as follows:

$$\%D = \frac{RRFavg - RRFccv}{RRFavg} \otimes 100$$

where
RRFavg = average response factor from initial calibration
RRFccv = response factor from the check (12-hour) standard-calibration verification

The percent drift (%Drift) may also be used to evaluate the change/deviation of the curve:

$$\%Drift = \frac{Ci - Cccv}{Ci} \otimes 100$$

where
Ci = Calibration Check Compound standard concentration (ug/mL).
Cccv = measured concentration using the selected quantitation method (ug/mL)

NOTE: The SPCC criteria (10.3.8) must be met even if the regression curve option is used for quantitation. If these criteria are not met, corrective action must be taken. The corrective action may include reanalysis of the calibration check standard or preparation of a new secondary stock standard and reanalysis of the calibration check standard. If subsequent analysis of the standard is still out of criteria, a new initial calibration curve must be analyzed and evaluated.

10.3.2 The continuing calibration verification standard (CCV) must also be evaluated for internal standard response.

If the extracted ion current profile (EICP) area for any of the internal standards in the CCV changes by more than a factor of two (-50% to +100%) from the last initial calibration sequence, the analytical system must be inspected for problems and corrective action instituted.

10.4 Samples are analyzed only after the DFTPP criteria, column evaluation criteria and the calibration verification criteria have been met. The analytical system must be evaluated every 12 hours by the analysis and evaluation of the tune/column evaluation standard and a mid-level calibration standard.

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
Tune/Column Evaluation Standard Clock starts at injection	Tune/Column Evaluation Standard Clock starts at injection
Calibration standards- Minimum of five cal levels	Mid point calibration verification Optional RL: Standard-low point on cal curve
Samples analyzed until 12-hour clock expires	Samples analyzed until 12-hour clock expires

10.4.1 Remove the sample extracts to be analyzed from the refrigerator and allow the sample to come to ambient temperature.

10.4.2 Add 20-uL of the internal standard mix (2000 ug/mL) to each 1.0mL aliquot of the sample extract. The concentration of the internal standard in the extract is 40 g/mL.

10.4.3 Mix the contents of the autosampler vial by inverting several times.

10.4.4 Analyze the samples using the same analytical conditions used for the initial and continuing calibration standard. Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

NOTE: Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client. For TCLP analyses, every reasonable effort should be made to achieve the regulatory level with out instrument overload.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with t the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower RLs.

10.4.5 The dilution factor is calculated by dividing the volume of sample extract in microliters into 1000. For example, if 100uL of a sample extract are diluted to final volume of 1.0mL, the dilution factor is 10. (1000/100 = 10). The following table gives some dilution factors:

Dilution Preparation

uL extract-Vext	uL MeCl2	volume of dilution (Vdil-uL)	uL ISTD (2000ug/mL)-Vistd	DF
1000	0	1000	20	1
500	500	1000	10*	2
200	800	1000	16*	5
100	900	1000	18*	10
50	950	1000	19*	20
20	980	1000	20*	50

*assumes dilution of a 1mL extract or 1mL aliquot of an extract that has been spiked with the internal standard at 40ug/mL using 20ul of a 2000ug/mL internal standard solution

The concentration of internal standards must remain constant for all extracts and extract dilutions at 40ug/mL. The following equation can be used to determine the volume of the 2000ug/mL internal standard solution to add to an extract when a dilution is prepared from an extract that has already been spiked with the internal standard solution:

$$Vistd(uL) = 20uL - \left(\frac{Vext}{Vdil} \otimes 20ul\right)$$

Vistd = volume of 2000ug/mL internal standard to add to the diluted extract (uL)
Vext = volume of extract used to prepare the dilution (uL)
Vdil = final volume of the dilution (uL)-1000uL (1.0mL)

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Qualitative Analysis

11.1.1 Target Compounds

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from the daily calibration standard or a reference spectrum of the target compound stored in a library generated on the same instrument or a standard spectral library such as the NIST/NBS.

11.1.1.1 Two criteria must be met in order to positively identify a compound.

1) elution of the sample component within +/-0.06 RRT (relative retention time) units of the daily standard containing that compound.

$$RRT = \frac{\textit{retention time of the target compound}}{\textit{retention time of the associated internal standard}}$$

2) correspondence of the target compound spectrum and the standard component mass spectrum

11.1.1.2 All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion = 100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound will make the identification of the target compound more difficult. Ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

11.1.1.3 The relative intensities of the ions present in the sample component spectrum should agree within +/- 30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum.

11.1.1.4 If the above criteria are not met exactly, the analyst should seek help from a senior analyst or supervisor. If there is sufficient evidence to support the identification of the component, then the component is identified, quantified, and reported.

11.1.2 Tentatively Identified Compounds (TICs)

For samples containing components not associated with the calibration standards, a library search on a reference library, such as the NIST/NBS, may be conducted in order to identify the non-target compounds. Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification.

The default procedure is to evaluate up to 20 compounds of greatest apparent concentration that are not included as target compounds or routinely reported volatile compounds. The unknown compounds are tentatively identified using a forward search of the reference library.

If the library search produces a match at or above 85%, report that compound. If the library search produces more than one compound at or above 85%, report the first compound (the highest match quality). If the library search produces no matches at or above 85%, report the compound as unknown. If possible, provide a general classification of the unknown – for example, unknown aromatic, unknown hydrocarbon, etc.

TICs should be evaluated within the retention time range from the first eluting target or surrogate (whichever is first in the target list) to three minutes after the elution of the last target compound.

11.1.2.1 Relative intensities of the major ions (masses) in the reference spectra (ions >10% of the most abundant ion) should be present in the sample spectrum.

11.1.2.2 The relative intensities of the major ions should agree within +/-20%.

11.1.2.3 Molecular ions present in the spectrum should be present in the sample spectrum.

11.1.2.4 Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible subtraction from the sample spectrum because of over-lapping or co-eluting peaks.

11.1.2.5 Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of coeluting peaks.

11.1.2.6 If, in the opinion of the analyst, there is enough evidence to support the tentative identification of a compound even though the above criteria is not met exactly, the peak may be considered tentatively identified. The analyst should consult senior analysts or the mass spectral interpretation specialist if there are any questions concerning an interpretation of spectra.

11.1.2.7 The estimated concentration of the tentatively identified compound (TIC) is calculated using the total ion area of the tentatively identified peak and total ion area of the nearest internal standard that has no interferences. The calculations assume that the same volume is injected for standards and samples.

Aqueous

$$TIC(ug/L) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{F}{V} \otimes DF$$

where:

Cis =	concentration of the internal standard (ug/mL)
AREAis =	total ion peak area of the internal standard
AREAtic=	total ion peak area of the TIC
F =	final volume of extract (mL)
V =	volume of sample extract (L)
DF =	dilution factor

Soils

$$TIC\ (ug/kg,dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{F}{(W)(solids)} \otimes DF$$

where:

Cis =	concentration of the internal standard, ug/mL
AREAis =	total ion peak area of the internal standard
AREAtic=	total ion peak area of the TIC
F =	final volume of extract mL
W =	weight of sample analyzed (kg)
solids =	decimal equivalent of percent solids

11.2 Calculations for Samples-Internal Standard Technique
These calculations assume that the same volume is injected for standards and samples and that the standards and samples have the same concentration of internal standard.

11.2.1 Aqueous Samples

11.2.1.1 If the relative response factor is used, the calculation for samples is :

$$concentration(ug/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{V} \otimes DF$$

where:

Ax =	area of the characteristic ion of the compound being measured
Ais =	area of the characteristic ion of the internal standard
Cis =	concentration of the internal standard (ug/mL)
RRFavg =	average response factor of the compound being measured
F =	final volume of extract (mL)
V =	volume of sample extracted (L)
DF =	dilution factor

11.2.1.2 If a regression curve is used, the concentration is given:

$$concentration(ug/L) = Ccurve \otimes \frac{F}{V} \otimes DF$$

where:

C_{curve} =	concentration from curve (ug/mL)
F =	final volume of extract (mL)
V =	volume of sample extracted (L)
DF =	dilution factor

11.2.1.3 The reporting limit (RL) for each sample is given:

$$RL(ug/L) = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Vqap}{V} \otimes DF$$

where:

F = final volume of extract (mL)
Fqap = 1.0mL
Vqap = 1.0L
V = volume of sample extracted
DF = dilution factor. The LQM RL assumes a DF of 1.

NOTE: If V = 800mL to 1200mL, assume that Vqap/ V = 1 in the calculation of the reporting limit.

11.2.2 Soils

11.2.2.1 If the relative response factor is used, the calculation for samples is :

$$concentration(ug/kg,dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/mL)
RRFavg = average response factor of the compound being measured
F = final volume of extract (mL)
W = weight of sample extracted (kg)
solids = (percent solids)/100
DF = dilution factor

11.2.2.2 If the regression curve is used, the concentration is given:

$$conc(ug/kg,dw) = Ccurve \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Ccurve = concentration from curve(ug/mL)
W = weight of sample extracted (kg)
F = final volume of extract (mL)
solids = (percent solids)/100)
DF = dilution factor

11.2.2.3 The reporting limit (RL) for each sample is given:

$$RL = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Wqap}{(W)(solids)} \otimes DF$$

where

F = final volume of extract (mL)
W = weight of sample extracted (kg)
solids = (percent solids)/100

The LQM assumes Wqap = 30g, solids = 1, Fqap = 1.0mL, and DF = 1.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items that are analyzed together. The matrix spike and LCS frequency is defined in AN02: *Analytical Batching.* SOP AN02 also describes the procedure for evaluating batch-specific QC. The QA/QC criteria are summarized in the SOP Summary (Appendix A).

12.2 Initial Demonstration of Capability (IDOC) to Generate Acceptable Accuracy and Precision

Each analyst must participate in the analysis of samples by this procedure in accordance with SOP CA92: *Evaluation of IDOCs.*

12.3 Method Detection Limit

The method detection limit is determined in accordance with SOP CA90: *Procedure for the Determination of the Method Detection Limit.*

13.0 PREVENTIVE MAINTENANCE & TROUBLESHOOTING

Refer to SOP AN53: *Preventive Maintenance Procedures for Laboratory Instruments* for guidance.

14.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Refer to SOP CA70: *Waste Management* for proper waste handling procedures.

15.0 REFERENCES

15.1 *STL Savannah Laboratory Quality Manual* current revision.

15.2 Method 8270C: *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846;* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

APPENDIX A
8270C SOP SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	none; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Waste	none; 4C	Glass	14 days	40 days
TCLP	none; 4C	1-L amber	7 days	40 days

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
Tune/Column Evaluation Standard Clock starts at injection	Tune/Column Evaluation Standard Clock starts at injection
Calibration standards- minimum of five cal levels	Mid point calibration verification standard RL Standard (lowest point on calibration curve if required by client or state-specific QAP)
Samples analyzed until the 12-hour clock expires	Samples analyzed until 12-hour clock expires

SEMIVOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION (DFTPP)	
m/e	**Ion Abundance Criteria (1)**
51	30-80% of mass 442
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	25-75% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of mass 198
275	10-30% of mass 198
365	Greater than 0.75% of mass 198
441	Present but less than mass 443
442	40-110% of mass 198
443	15.0-24.0% of mass 442

(1) 8270 criteria taken from CLP OLMO4.0 (January 1998). The use of alternate criteria is expressly allowed in SW-846 Method 8270C.

APPENDIX A
8270C SOP SUMMARY

CALIBRATION ACCEPTANCE CRITERIA

Calibration Check Compounds - CCC
Phenol, 1,4-Dichlorobenzene, 2-Nitrophenol, 2,4-Dichlorophenol, Hexachlorobutadiene, 4-Chloro-3-methylphenol, 2,4,6-Trichlorophenol, Acenapthene, N-Nitrosodiphenylamine, Pentachlorophenol, Fluoranthene, Di-n-octylphthalate, Benzo(a) pyrene

System Performance Check Compounds-SPCC
N-Nitrosodi-n-propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol, 4-Nitrophenol

Initial Calibration	Continuing Calibration*
CCC: <= 30% RSD	CCC: <= 20% difference from initial calibration
SPCC: RRFavg >= 0.050	SPCC: RRF>= 0.050

*If CCC and/or SPCC do not meet the stated criteria, all targets that are reported must meet the CCC criteria.

NOTE: The CCC and SPCC criteria must be met even if the calibration curve option is used for quantitation. If the CCC and SPCC criteria do not pass, a new calibration curve must be prepared and analyzed.

The results for all target compounds are evaluated for linearity. If the %RSD is less than 15%, the calibration is assumed linear through the origin and the average response factor can be used for quantitation. If the average response factor for the target exceeds 15% (including any CCC), the analyst must use the calibration curve option.

NOTE: The lab has the option of using a regression curve for all analytes.

A linear, quadratic, or higher order regression fit may be used to define the concentration/response relationship. If r^2 is greater than 0.99, the curve can be used to quantify samples. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire calibration range. The minimum number of calibration standards required for a regression curve are given in the following table:

Type of curve	Minimum Number of Calibration Points
Linear (first order)	5
Quadratic (second order)	6

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tune/Column Evaluation Standard DFTPP 50ng Pentachlorophenol - 50ng Benzidine – 50ng p,p'-DDT 50ng	Prior to analysis of calibration standards every 12 hours	DFTPP - within criteria	-Evaluate alternative scans -Reanalyze and evaluate -Retune and reanalyze -Clean source, retune, reanalyze
		Pentachlorophenol and benzidine - present at usual response with no peak tailing visible p,p'-DDT - %breakdown <20%	-Reanalyze -Perform injector port maintenance and reanalyze -Cut more than usual length of column and reanalyze -Replace column
Initial Calibration	After Tune Check and when calibration verification standard fails acceptance criteria. All initial calibration standards	CCC: %RSD < 30% SPCC: RRFavg > 0.050 Use regression curve for quantitation if %RSD for any target compound exceeds 15%	-Reanalyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standards -Retune and reanalyze standards -Replace column and reanalyze standards -Clean source and reanalyze standards
Continuing Calibration Verification	After tune check; every 12 hours prior to analysis of samples	CCC: %Difference <= 20% Or %Drift <= 20% SPCC: RRF >= 0.050	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate
Internal Standard Areas	Evaluate all standards and samples	Areas in continuing calibration verification must be 50% to +200% of previous initial calibration sequence Areas in samples should be evaluated for gross error. Consult supervisor Retention time of internal standard must be +/-30 seconds from internal standard in previous CCV.	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available -Recalibrate

QC Item	Frequency	Acceptance Criteria	Corrective Action
Surrogate recovery	Evaluate for all samples and QC items if extract is not diluted OR If diluted, where >RL	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract(s) -Re-extract and reanalyze if sufficient sample available
Method Blank	Per batch	All targets < RL in LQM	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL-SL SOP AN02
Lab Control Standard (LCS) - QAP subset	Per batch See SOP AN02	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL-SL SOP AN02
Matrix spike (MS) Matrix spike duplicate (MSD)	Per batch if sufficient sample volume/weight supplied See SOP AN02	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL-SL SOP AN02
RL Standard (reporting limit)	Daily (optional)-lowest point on calibration curve if required by client or state-specific QAP	Detected at reasonable sensitivity	-Evaluate integrations and spectra; -Reanalyze -Prepare new standard and reanalyze
Initial Demonstration of Capability (IDOC)	Each work group	Accuracy and precision within method specified criteria	-Evaluate data -Reanalyze extracts if warranted -Re-extract and reanalyze for targets that fail criteria
Method Detection Limit (MDL)	Annually for each routine matrix See SOP CA90	Evaluate according to SOP CA90	Evaluate according to SOP CA90

APPENDIX B- TARGET COMPOUNDS

ROUTINE TARGET LIST

PARAMETER	RT	Quant Ion	Secondary Ions		ISTD
1,4-Dioxane	1.894	88	58	45	1
Pyridine	2.123	79	52	51	1
N-Nitrosodimethylamine	2.102	42	74		1
Aniline	3.812	93	66		1
Phenol	3.796	94	66	65	1
Bis(2-chloroethyl)ether	3.854	63	93	95	1
2-Chlorophenol	3.908	128	130	64	1
1,3-Dichlorobenzene	4.025	146	148	111	1
1,4-Dichlorobenzene	4.073	146	148	111	1
Benzyl Alcohol	4.202	108	79	77	1
1,2-Dichlorobenzene	4.239	146	148		1
2-Methylphenol	4.314	107	108	77	1
bis(2-Chloroisopropyl)ether	4.335	45	121		1
N-Nitroso-di-n-propylamine	4.469	70	42	101	1
3&4-Methylphenol	4.447	107	108		1
Hexachloroethane	4.522	117	201	199	1
Nitrobenzene	4.602	77	123	65	2
Isophorone	4.837	82	95	138	2
2-Nitrophenol	4.923	139	109	65	2
2,4-Dimethylphenol	4.965	107	122	121	2
Bis(2-chloroethoxy)methane	5.067	93	123	95	2
Benzoic acid	5.115	105	122		2
2,4-Dichlorophenol	5.169	162	164	98	2
1,2,4-Trichlorobenzene	5.259	180	182	145	2
Naphthalene	5.323	128	129		2
4-Chloroaniline	5.409	127	129	65	2
Hexachlorobutadiene	5.532	225	223	227	2
4-Chloro-3-methylphenol	5.991	107	144	142	2
2-Methylnaphthalene	6.135	142	141		2
1-Methylnaphthalene	6.269	142	141		2
Hexachlorocyclopentadiene	6.429	237	235	272	3
2,4,6-Trichlorophenol	6.541	196	198	200	3
2,4,5-Trichlorophenol	6.590	196	198	200	3
2-Chloronaphthalene	6.760	162	164	127	3
2-Nitroaniline	6.958	65	92	138	3
Dimethylphthalate	7.268	163	194	164	3
2,6-Dinitrotoluene	7.353	165	89	63	3
Acenaphthylene	7.337	152	151	153	3
3-Nitroaniline	7.540	138	108	92	3
Acenaphthene	7.599	154	153	152	3
2,4-Dinitrophenol	7.685	184	63	154	3
4-Nitrophenol	7.824	65	109	139	3
Dibenzofuran	7.829	168	139		3
2,4-Dinitrotoluene	7.914	165	89	63	3
2,3,4,5-Tetrachlorophenol	8.064	232	230	131	3
2,3,4,6-Tetrachlorophenol	8.091	232	230	131	3
Diethylphthalate	8.310	149	177	150	3

Fluorene	8.336	166	165	167	3
4-Chlorophenyl-phenylether	8.363	204	141	206	3
4-Nitroaniline	8.454	138	108	92	3
4,6-Dinitro-2-methylphenol	8.513	198	105	121	4
N-Nitrosodiphenylamine	8.555	169	168	167	4
1,2-Diphenylhydrazine	8.593	77	105	182	4
4-Bromophenyl-phenylether	9.090	248	250	141	4
Hexachlorobenzene	9.293	284	142	249	4
Pentachlorophenol	9.581	266	264	268	4
Phenanthrene	9.784	178	176	179	4
Anthracene	9.854	178	176	179	4
Carbazole	10.137	167			4
Di-n-Butylphthalate	10.847	149	150	104	4
Fluoranthene	11.659	202	203	101	4
Benzidine	11.926	184	92	185	5
Pyrene	12.006	202	200	203	5
Butylbenzylphthalate	13.214	149	91	206	5
3,3'-Dichlorobenzidine	13.892	252	254	126	5
Benzo(a)Anthracene	13.866	228	229	226	5
Bis(2-ethylhexyl)phthalate	14.111	149	167	279	5
Chrysene	13.924	228	226	229	5
Di-n-octylphthalate	14.971	149	43		5
Benzo(b)fluoranthene	15.367	252	253	125	6
Benzo(k)fluoranthene	15.399	252	253	125	6
Benzo(a)pyrene	15.783	252	125	253	6
Indeno(1,2,3-cd)pyrene	17.284	276	139		6
Dibenzo(a,h)anthracene	17.317	278	139	279	6
Benzo(g,h,i)perylene	17.674	276	277	138	6
SURROGATES					
2-Fluorophenol	3.032	112	64		1
Phenol-d5	3.785	99	71		1
Nitrobenzene-d5	4.586	82	128	54	2
2-Fluorobiphenyl	6.643	172	171		3
2,4,6-Tribromophenol	8.732	330	332	141	3
Terphenyl-d14	12.332	244	122	212	5
INTERNAL STANDARDS					
1,4-Dichlorobenzene-d4	4.057	152	150	115	1
Naphthalene-d8	5.302	136	68		2
Acenaphthene-d10	7.556	164	162	160	3
Phenanthrene-d10	9.747	188	94	80	4
Chrysene-d12	13.887	240	236	120	5
Perylene-d12	15.858	264	265	260	6

APPENDIX B- TARGET COMPOUNDS

APPENDIX IX TARGET LIST

PARAMETER	RT	Quant Ion	Secondary Ions			ISTD
1,4-Dioxane	1.933	88	58	45		1
Pyridine	2.178	79	52	51		1
2-Picoline	2.664	93	66			1
1,4-Benzoquinone	**4.466**	54	108	82		1
N-Nitrosomethylethylamine	2.739	88	42	43	56	1
Methyl methanesulfonate	2.964	80	79	65		1
N-Nitrosodiethylamine	3.268	102	42	44	57	1
Ethyl methanesulfonate	3.503	79	109	97	45	1
N-Nitrosopyrrolidine	4.481	100	41	42		2
Acetophenone	4.486	105	77	51		2
N-Nitrosomorpholine	4.497	56	86			1
O-Toluidine	4.529	106	107	79		2
Phorate	9.123	75	121			4
N-Nitrosopiperidine	4.796	114	42	55	56	2
O,O,O-Triethyphosphorothioate	5.122	65	97	93		2
2,6-Dichlorophenol	5.469	162	164	98		2
Hexachloropropene	5.507	213	211	215	117	2
1,2,4,5-Tetrachlorobenzene	6.447	216	214	179		3
a,a-Dimethylphenethylamine	5.619	58	91	42		2
N-Nitroso-di-n-butylamine	5.875	84	57	41		2
1,4-Phenylenediamine	5.864	108	80	107		2
Safrole	6.094	162	104	135	103	2
Isosafrole	6.757	162	104	131		2
1,1-Biphenyl	6.805	154	76			3
1,4-Naphthoquinone	7.056	158	104	76		3
m-Dinitrobenzene	7.317	168	76	50		3
Pentachlorobenzene	7.916	250	248	252	215	3
1-Naphthylamine	8.001	143	115	116		3
2-Naphthylamine	8.113	143	115	116		3
2,3,4,6-Tetrachlorophenol	8.140	232	230			3
5-Nitro-o-toluidine	8.466	152	77	106		3
Thionazin	8.471	107	96	97		4
Sulfotepp	9.032	97	65			4
1,3,5-Trinitrobenzene	9.091	213	74	120		4
1-Diallate	9.118	86	43	234		4
Phenacetin	9.161	108	109	179		3
2-Diallate	9.235	86	43	234		4
Dimethoate	9.396	87	93	125		4
4-Aminobiphenyl	9.556	169	168	170		4
Pronamide	9.748	173	175	145		4
Pentachloronitrobenzene	9.748	237	295	142	214	4
Disulfoton	9.935	88	60			4
Dinoseb	9.957	211	163	147		4
Methyl parathion	10.517	109	125			4
4-Nitroquinoline-1-oxide	11.094	174	101	128	75	4
Parathion	11.158	109	97			4
Famphur	**13.178**	218	93	125		4

Methapyrilene	11.388	97	58	191		4
Aramite-1	12.435	185	191	319		5
Aramite-2	12.563	185	191	319		5
p-Dimethylaminoazobenzene	12.638	120	225	77		5
Chlorbenzilate	12.745	139	251	75		4
Kepone	**17.739**	272	270	237		5
3,3'-Dimethylbenzidine	13.167	212	196	106		5
2-Acetylaminofluorene	13.562	181	180	223		5
7,12-Dimethylbenz(a)anthracene	15.438	256	239	241		6
Hexachlorophene	15.747	196	198			6
3-Methylcholanthrene	16.324	268	252	253		6
INTERNAL STANDARDS						
1,4-Dichlorobenzene-d4	4.102	152	150	115		1
Naphthalene-d8	5.346	136	68			2
Acenaphthene-d10	7.601	164	162	160		3
Phenanthrene-d10	9.802	188	94	189		4
Chrysene-d12	13.926	240	236	120		5
Perylene-d12	15.902	264	265	260		6

FIGURE 1 – Tailing Factor Calculation

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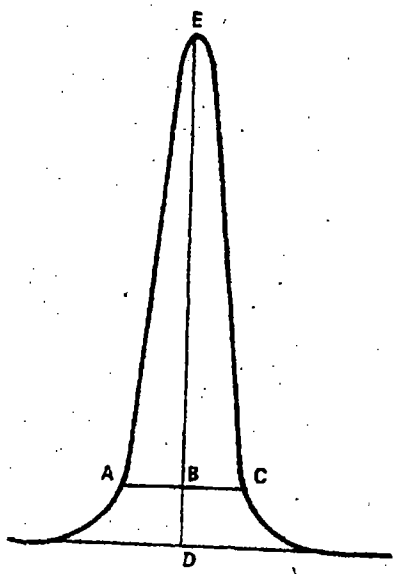

$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Tailing Factor} = \frac{12}{11} = 1.1$$

POLYCHLORINATED BIPHENYLS (PCBs) by GC/MS

(Method: EPA 680)

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1.0 SCOPE AND APPLICATION

1.1 This procedure is used to determine the concentration of polychlorinated biphenyls (PCBs) in groundwater, soils, sediments, wastes, and biological tissues by GC/MS. PCBs are reported by the level of chlorination: monochlorobiphenyls, dichlorobiphenyls, trichlorobiphenyls, etc., up to decachlorobiphenyl.

1.2 The routine target analytes, reporting limits (RL), method detection limits (MDL), and the accuracy and precision limits are given in the current revision of the *Laboratory Quality Manual* (LQM) prepared by and for STL Savannah.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Summary of Method

A measured volume or weight of sample is spiked with a surrogate and extracted using an appropriate extraction procedure. The extract is dried, concentrated to a volume of 1.0mL, and analyzed by GC/MS operated in the Selected Ion Monitoring Mode (SIM). Windows are established to monitor for the characteristic masses of the various PCB homologues. Qualitative identification of the target compounds in the extract is based on the presence of the peak within the SIM window and the mass ratio between the primary and confirmation ions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion. Results are reported as total monochlorobiphenyls, total dichlorobiphenyls, etc.

The default identification and quantitation procedure will be to use only the quantitation and confirmation ions for the PCB homologues. Interference check ions, as described in Section 11.2.3, will not be used routinely to evaluate peaks as PCB homologues unless specified in a client QAP or agency requirement or the sample concentration is near a critical quantitation limit. Samples evaluated according to the default quantitation procedures may be slightly high biased.

2.2 Definitions - Refer to SOP AN99: *Definitions, Terms, and Acronyms* for a complete listing of applicable definitions.

Congener: a member of a family or class of compounds such as polychlorinated biphenyls (PCBs). There are 209 congeners of PCBs
Homologue: a PCB isomer with the same level of chlorination; e.g., the monochlorobiphenyl isomers, the dichlorobiphenyl isomers, etc.

2.3 This procedure is based on the guidance provided in EPA Method 680.

2.4 Method Modifications

The method has been modified to include the use of a carbon-13 labeled analogue of decachlorobiphenyl (13C12-DCB) as the surrogate in place of the labeled BHC and DDT compounds. 13C12-DCB can be subjected to the optional acid cleanup (the unlabeled analogue, decachlorobiphenyl, is routinely used in SW-846 Method 8082). A window-defining mix containing the first and last eluting isomers of each level of chlorination is used as an aid to establish and verify that the SIM windows are properly set.

This SOP contains preparation and sample evaluation procedures for soils and biological tissues, which are not included in EPA Method 680. The CCV criteria for soils and biota have been broadened to 30%D due potential matrix interferences associated with these types of samples, which may affect end-capping standards.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Waste Disposal SOP, and this document.

3.1 Specific Safety Concerns or Requirements

The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized.

Hexane is a flammable solvent. It can cause irritation to the respiratory tract. Overexposure can cause fatigue, lightheadedness, headache, dizziness, and blurred vision.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, or glassware. Glassware and/or extraction vessels that have not been properly cleaned may contribute artifacts that make identification and quantification of the target compounds difficult. Elevated baselines may be due to oils, greases, or other hydrocarbons that may be extracted from improperly cleaned glassware or extraction vessels

4.2 Matrix interferences may be caused by contaminants that are extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. Sample extracts that contain high concentrations of non-volatile material such as lipids and high molecular weight resins and polymers may require the optional GPC cleanup prior to analysis. The GPC cleanup is generally not effective in removing non-target material that is associated with common petroleum products such as diesel or waste oil. GPC cleanup may be necessary for biological tissues. Acid cleanup may be employed as an additional cleanup tool.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

The following table lists the routine sample containers, storage conditions, and holding time associated with this procedure:

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time (1)	Extract Hold Time
Aqueous	none; 4°C	1-L amber	7 days	40 days
Soil/Sediment	none; 4°C	500-mL	14 days	40 days
Biological	Frozen	Glass or aluminum foil	6 months	40 days

[1] Holding times are advisory - no holding times are defined in method 680.

6.0 APPARATUS AND MATERIALS

6.1 GC/MS System with compatible data system, autosampler, splitless injector, and direct capillary interface.

6.2 Recommended Capillary column: HP-5MS, 30m x 0.25mm ID, 0.25um film thickness. Equivalent columns can be used.

6.3 Microsyringes: appropriate volumes

6.4 Volumetric flasks, Class A: appropriate volumes

6.5 Analytical balance

7.0 REAGENTS

The preparation of reagents must be performed in accordance with SOP AN44: *Reagent Traceability*.

7.1 Hexane – reagent grade

7.2 Acetone – reagent grade

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with SOP AN41: *Standard Material Traceability*. General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation*.

The lab should purchase certified solutions from STL-approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation from neat materials.

8.1 The recommended calibration standards are listed in Appendix A, Table 1. Prepare these standards at the stated concentrations in hexane.

8.2 The surrogate compound, 13C12-Decachlorobiphenyl, is prepared at a concentration of 2.5ug/mL. 1.0mL of this solution is spiked into all samples and QC items prior to extraction.

8.3 The matrix spiking solution contains one PCB congener of each chlorination level except for the nonachlorobiphenyls. The solution is prepared at the indicated concentrations in acetone. 1.0mL of this solution is spiked into all lab spikes and matrix spikes.

COMPOUND	CONCENTRATION (ug/mL)
2-Chlorobiphenyl	2.0
2,3-Dichlorobiphenyl	2.0
2,4,5-Trichlorobiphenyl	2.0
2,2',4,6-Tetrachlorobiphenyl	4.0
2,2',3,4,5'-Pentachlorobiphenyl	4.0
2,2',4,4',5,6'-Hexachlorobiphenyl	4.0
2,2',3,4',5,6,6'-Heptachlorobiphenyl	6.0
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	6.0
Decachlorobiphenyl	10

9.0 SAMPLE PREPARATION

9.1 The sample extraction procedures are given in the following SOPs:

Matrix	SOP Number	Extraction Technique
Aqueous	EX30	Continuous Liquid-liquid Extraction
Soils/Sediments and Biological	EX40	Sonication

9.2 The sample concentration procedures are given in SOP EX 50: *Zymark Nitrogen Concentration.*

9.3 Gel permeation chromatography may help to eliminate or minimize matrix interferences in a limited number of samples. The GPC cleanup is generally not effective on samples containing petroleum products. Acid cleanup (SOP EX60: *Acid, Permanganate, and Copper Cleanups for PCBs and Pesticides*) is recommended as a routine cleanup prior to analysis. Sulfur cleanup may be necessary if the sample extract contains high levels of sulfur.

10.0 ANALYTICAL PROCEDURE

10.1 Instrument Conditions
Instrument conditions may vary according to the sensitivity of each instrument. The following conditions are provided for guidance. The lab must document the conditions used for the analysis of SVOC by GC/MS.

Recommended Column:
HP-5MS 30m x 0.25mm ID, 0.25um film thickness or equivalent

Column flow:
Approximately 1mL/min helium

GC Oven temperatures:
- Initial column temperature: 45°C for 1 minute
- Column temperature program 1: 20°C per minute to 150°C, hold 1 minute
- Column temperature program 2: 10°C per minute to 310°C, hold until DCB and 13C12-DCB elute

GC injector parameters:
- Injector temperature: 250-260°C
- Injector: splitless
- Inlet purge time: 0.8 minutes
- Injector liner: 4mm ID quartz or 4mm glass, deactivated
- Sample injection volume: 1µL

Mass Spectrometer and interface parameters:
- Mass spectrometer interface: 300°C
- Mass spectrometer source temperature: Factory Set
- Mass range: SIM (see Table 3 in Appendix B for ions to monitor)
- Mass range for DFTPP analysis: 35-500amu at 1 scan per second or less.

10.2 Tune Criteria

Ten nanograms of DFTPP are analyzed at the beginning of each 12-hour clock as a check on the "tune" of the mass spectrometer. The DFTPP analysis is performed using scan analysis. The same tune parameters are used for the SIM analysis of the calibration standards and samples.

10.2.1 Prepare a 10ng/µL solution of DFTPP column evaluation standard. The standard must also contain p,p'-DDT (4,4'-DDT).

10.2.2 Analyze a 1µL aliquot of the 10ng/µL DFTPP solution using the same temperature program that is used for SIM analysis of the calibration standards, samples, and QC samples.

10.2.3 Evaluate the DFTPP peak.

-The chromatogram should exhibit acceptable baseline behavior and the DFTPP peak should be symmetrical.

-The spectrum of the DFTPP must meet the criteria listed in the SOP Summary. Background subtraction must be straightforward and designed only to eliminate column bleed or instrumental background. Scans ± 2 scans from the apex can be evaluated for the DFTPP criteria. Consecutive scans within this range may be averaged to meet the criteria.

NOTE: The DFTPP analysis should be evaluated as to the relative size of the DFTPP peak under the m/z 198 profile. A benchmark area window should be established for each instrument and data system. Area outside of this window suggests instrumental problems such as a bad injection, clogged autosampler syringe, leaking injector, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open, etc.

If the DFTPP fails to meet the criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the DFTPP analysis, other corrective measures may include remaking the DFTPP standard, cleaning the mass spectrometer source, etc.

10.3 Window-Defining Solution and SIM Parameters

10.3.1 Analyze 1µL of the window-defining solutions in the scan mode from 45amu to 500amu at > 1 scan per second. Use the same temperature program that will be used for the SIM analysis of PCBs. The window defining solutions may be analyzed separately or may be combined into a single solution.

10.3.2 Determine the retention times of the first and last eluting congeners at each level of chlorination. The quantiation and confirmation masses are listed in Table 3 of Appendix B.

10.3.3 Set the SIM parameters as follows. Refer to Table 3 of Appendix B for the ion sets.

-Begin data acquisition with ion set #1 before the elution of PCB congener #1, the first eluting CL-1-PCB
-Stop the acquisition of ion set #1 and begin acquisition of ion set #2 approximately 10 seconds before the elution of PCB congener #104, the first eluting CL5-PCB.
-Stop the acquisition of ion set #2 and begin the acquisition of ion set #3 approximately 10 seconds after the elution of PCB congener #77, the last eluting CL4-PCB.
-Stop the acquisition of ion set #3 and begin the acquisition of ion set #4 approximately 10 seconds after the elution of 4,4'-DDT. (The retention time of 4,4'-DDT is determined from the scan analysis of the DFTPP solution that is analyzed at the beginning of each 12-hour clock.)
-Stop the acquisition of ion set #4 and begin the acquisition of ion set #5 approximately 10 seconds before the elution of PCB congener #208, the first eluting CL9-PCB.

10.4 Initial Calibration
Initial calibrations are performed in accordance with SOP AN67: *Evaluation of Calibration Curves*. After the SIM windows are established and verified and the DFTPP criteria have been met, the initial calibration standards are analyzed. Note that a single PCB congener of each chlorination level is used for calibration and quantitation. Decachlorobiphenyl is used to quantify nonachlorobiphenyls.

10.4.1 Prepare the initial calibration standards. The lowest calibration standard should be at the RL, and the rest of the standards will define the working range.

10.4.2 Set up a sequence and analyze the calibration standards. The injection volume must be the same for the calibration standards and all sample extracts. The routine volume is 1µL.

~~10.4.3 Identify the internal standards, surrogates, and the target compounds. The data system must be updated with the proper retention times and ion data.~~

10.4.4 The relative response factor for each compound is calculated as follows:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where

Ax = area of the characteristic ion of the calibration congener
Ais = area of the characteristic ion for Chrysene-d10
Cx = concentration of the compound being measured (µg/mL)
Cis = concentration of the internal standard (40µg/mL)

NOTE: Use Chrysene-d10 as the internal standard unless matrix interferences are encountered. If phenthrene-d10 must be used, the calibration must be re-evaluated and verified using the second internal standard.

10.4.5 Calculate the average relative response factor (RRF_{avg}) for each target compound and each surrogate compound:

$$RRF_{avg} = \frac{RRF1 + RRF2 + RRF3 \ldots + RRFn}{n}$$

RRF1 = relative response factor of the first standard
RRFn = relative response factor of the last standard
n = number of calibration standards

10.4.6 Calculate the standard deviation (SD) for the initial calibration standards:

$$SD = \sqrt{\frac{\sum_{i-1}^{n_1} (RRF_i - RRF_{avg})^2}{n-1}}$$

10.4.7 Calculate the relative standard deviation (%RSD) of the target compounds in the calibration standards:

$$\%RSD = \frac{SD}{RRF_{avg}} x\,100$$

- If the %RSD of each target compound is less than or equal to 20%, the average response factor can be used for quantitation of samples.
- If the %RSD of the target compound is greater than 20%, the curve should be evaluated for errors and one or more standards re-analyzed. Take corrective action until the %RSD of each target is less than 20%.

10.4.8 Performance Criteria
In addition to meeting the calibration criteria, the following performance criteria must also be met for the mid-level standard.

-Mass abundance ratios of all calibration congeners within acceptance range (See Table 4 Appendix B)

-Baseline separation of PCB congener #87 from congeners #154 and #77, which may coelute.

-Signal-to-noise ratio of >=5 for decachlorobiphenyl ion 499 and chrysene-d12 ion 241

-decachlorobiphenyl mass abundance: mass 500 >=70% but <=95% of mass 498

10.5 Continuing Calibration Verification
Samples are analyzed only after the DFTPP criteria and the calibration acceptance criteria have been met. The analytical system must be evaluated every 12 hours by the analysis and evaluation of the DFTPP and a mid-level calibration standard prior to the analysis of samples and after the samples by the analysis and evaluation of a mid-level standard. The endcap standard must be analyzed within the 12 hour clock.

10.5.1 The percent difference or percent drift between the continuing calibration RRF and the average relative response factor (RRFavg) is calculated for each target compound and each surrogate compound:

$$\%difference = \left| \frac{RRF - RRFavg}{RRFavg} \right| \otimes 100$$

where
RRF = relative response factor from CCV
RRFavg = average relative response factor from initial calibration curve

If the percent difference is less than or equal to 20% for each target compound, the initial calibration is verified. If soils and/or biota are being evaluated, the CCV criteria have been broadened to 30%D due potential matrix interferences associated with these types of samples, which may affect end-capping standards.

If the continuing calibration criteria are not met, action must be taken to bring the analytical system into compliance with the criteria. This action may include injection port maintenance, source cleaning, changing the column, or replacement of injection port lines and assembly. In any case, if the criteria are not met, the analysis of the continuing calibration standard must be repeated. The analyst must be aware of the 12-hour clock DFTPP criteria must be met prior to the analysis of the calibration standards. If the continuing calibration standard repeatedly fails the calibration verification criteria, the initial calibration curve must be reanalyzed and reevaluated.

The performance criteria given in Section 10.4.8 must also be met prior to the analysis of samples.

10.6 Sample Analysis
Remove the sample extracts to be analyzed from the refrigerator and allow the sample to come to ambient temperature.

10.6.1 Add 30µL of the internal standard mix (25µg/mL) to each 1-mL aliquot of the sample extract. The concentration of the internal standard in the extract is 0.75ng/µL.

10.6.2 Mix the contents of the autosampler vial by inverting several times.

10.6.3 Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

10.6.4 The dilution factor is calculated by dividing the volume of sample extract in microliters into 1000. For example, if 100µL of a sample extract is diluted to final volume of 1.0mL, the dilution factor is 10 (1000/100 = 10). The following table gives some dilution factors:

Dilution Preparation

µL extract-Vext	µL MeCl2	volume of dilution (Vdil-µL)	µL ISTD (25µg/mL)-Vistd	DF
1000	0	1000	30	1
500	500	1000	15*	2
200	800	1000	24	5
100	900	1000	27	10
50	950	1000	28.5	20
20	980	1000	30	50

*assumes dilution of a 1.0mL extract or 1mL aliquot of an extract that has been spiked with the internal standard at 0.75µg/mL using 30ul of a 25.0µg/mL internal standard solution

The concentration of internal standards must remain constant for all extracts and extract dilutions at 0.75µg/mL. The following equation can be used to determine the volume of the 25.0µg/mL internal standard solution to add to an extract when a dilution is prepared from an extract that has already been spiked with the internal standard solution:

$$Vistd(uL) = 30\mu L - \left(\frac{Vext}{Vdil} \otimes 30\mu l\right)$$

Vistd = volume of 25.0ug/mL internal standard to add to the diluted extract (µL)
Vext = volume of extract used to prepare the dilution (µL)
Vdil = final volume of the dilution (µL)-1000µL (1.0mL)

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Qualitative Analysis

The default procedure will be to use only the quantitation and confirmation ions for identification and quantification of PCB congeners. Interference check ions, as described in Section 11.2.3, will not be used routinely to evaluate peaks as PCB congeners unless specified in a client QAP or agency requirement or the sample concentration is near a critical quantitation limit.

11.1.1 Examine the Selected Ion Current Profiles (SICP) for the internal standards. Confirm that the RT and response of the internal standards are within the acceptance criteria specified in the SOP Summary. If the internal standard retention times have changed significantly or the peaks cannot be located, stop and analysis and correct the problem. Reanalyze any associated samples.

11.1.2 Evaluate the peaks for candidates to be identified as PCBs. A peak is tentatively identified as a PCB if:

-The peak falls within the retention time range bordered by the first and last eluting isomer of that chlorination level

-The ratio of the quantitation and confirmation ions are present and the area ratios fall within the acceptance criteria in Appendix B, Table 4. The scans must maximize within one scan of each other. Examine the data for the presence of a coeluting PCB of higher chlorination if both ions and the M-70 ions are present and the ratio does fall within the acceptance limits.

-The areas for the quantiation and confirmation ions must be greater than three times the background noise and must fall within the working range of the calibration curve (must not saturate the detector

-At least one ion in the M-70 cluster must be present

11.1.3 Evaluate each PCB candidate in the Cl-3 to Cl-7 range for the presence of coeluting PCBs containing one or two additional chlorines. An intense M+35 ion at the retention time may indicate a PCB with one additional chlorine and the presence of an intense M+70 would indicate a co-eluting PCB containing two additional chlorines. Use the information in Tables 5 and 6 of Appendix B to correct for the interfering ion(s).

For example, if a Cl-7-PCB and a Cl-5-PCB coelute, the Cl-7-PCB will contribute to the quantiation and confirmation ions for the Cl-5-PCB. Cl-7-PCB produces a cluster of three ions by the loss of two chlorines-ions 322,324, and 326. Two of these ions, 324 and 326, are also ions contained in the molecular ion cluster of Cl-5-PCB. To determine the ion 326 and 324 areas produced only by the Cl-5-PCB, calculate the contribution to each and subtract it from the measured areas. See Tables 5 and 6 in Appendix B for the percentage of the interference peak to subtract from the quantiation and confirmation ions. In this example, 164% of the area measured for ion 322 should be subtracted from the area measured for ion 324 and 108% of the area measured for ion 322 should be subtracted from ion 326.

NOTE: A coeluting PCB with one more chlorine will affect only the quantiation ion (Table 6). The interference from a coeluting PCB containing one more chlorine, due to the natural abundance of 13C12, is small and can usually be neglected except when measuring the area of a small amount of a PCB coeluting with a large amount of a another PCB containing one more chlorine.

11.2 Calculations for Samples-Internal Standard Technique
These calculations assume that the same volume is injected for standards and samples.

11.2.1 Aqueous Samples

$$concentration(\mu g/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{V} \otimes DF$$

where

Ax =	sum of areas of the characteristic ion of the PCB chlorination level being measured
Ais =	area of the characteristic ion of the internal standard
Cis =	concentration of the internal standard (µg/mL)
RRFavg =	average response factor of the compound being measured
F =	final volume of extract (mL)
V =	volume of sample extracted (L)
DF =	dilution factor

The reporting limit (RL) for each sample is given:

$$RL(\mu g/L) = RL_{LQM} \otimes \frac{F}{F_{LQM}} \otimes \frac{V_{LQM}}{V} \otimes DF$$

where

F =	final volume of extract (mL)
F_{LQM} =	1.0mL
V_{LQM} =	1.0L
V =	volume of sample extracted
DF =	dilution factor. The LQM (RL_{LQM}) assumes a DF of 1.

NOTE: If V = 800mL to 1200mL, assume that Vqap/ V = 1 in the calculation of the reporting limit.

11.2.2 Soils

$$concentration(\mu g/kg, dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Ax =	sum of areas of the characteristic ion of the PCB chlorination level being measured
Ais =	area of the characteristic ion of the internal standard
Cis =	concentration of the internal standard (µg/mL)

RRFavg = average response factor of the compound being measured
F = final volume of extract (mL)
W = weight of sample extracted (kg)
solids = (percent solids)/100
DF = dilution factor

The reporting limit (RL) for each sample is given:

$$RL = RL_{LQM} \otimes \frac{F}{F_{LQM}} \otimes \frac{W_{LQM}}{(W)(solids)} \otimes DF$$

where

F = final volume of extract (mL)
W = weight of sample extracted (kg)
solids = (percent solids)/100

The LQM assumes W_{LQM} = 30g, solids = 1, F_{LQM} = 1.0mL, and DF = 1.

12.0 QUALITY CONTROL AND DATA ASSESSMENT

12.1 Analytical Batching

QC data must be evaluated against the precision and accuracy criteria set forth in the Laboratory Quality Manual and SOP AN02: *Analytical Batching and Evaluation of QC Data*. SOP AN02 also provides guidance for establishing and evaluating QC items to be included in an analytical batch.

The analytical batch consists of up to twenty client samples and the associated QC items that are analyzed together. The matrix spike and LCS frequency is defined in SOP AN02. The attached SOP summary provides guidance for evaluating sample data.

12.2 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP CA85: *Nonconformance and Corrective Action Procedures*. CA85 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures.

13.0 METHOD PERFORMANCE

The Reporting Limits (RL), the Method Detection Limits (MDL), and accuracy and precision limits associated with these methods are given in the current revision of the Laboratory Quality Manual prepared by and for STL Savannah.

13.1 Initial and Continuing Demonstration of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP *CA92: Procedure for Initial and Continuing Analyst Demonstration of Capability*.

13.2 Method Detection Limit

The method detection limit must be determined for each analyte in accordance with SOP CA90: *Procedures for the Determination of Method Detection Limit (MDL)*.

14.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

Refer to SOP AN53: *Maintenance Procedures for Laboratory Instrumentation* for routine preventive maintenance and the manufacturer's guides for trouble-shooting items.

15.0 WASTE MANAGEMENT AND POLLUTION CONTROL

All waste will be disposed of in accordance with Federal, State and Local regulations. Follow the guidance for disposal in SOP CA70: *Waste Disposal.* Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

15.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Excess samples, reagents, and standards must be disposed in accordance with SOP CA70: *Waste Management.*

- Flammable waste (hexane from extracts, rinsings, and standards) – Transfer to a satellite container designated for flammable waste and transfer to waste disposal department when the container is full.

- Excess samples. Dispose according to characterization on sample disposal sheets. If non-hazardous, dispose down drain/sewer. If hazardous, transfer to hazardous waste department for storage.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Excess oil samples – Transfer to waste department for storage/disposal.

16.0 REFERENCES

~~STL Savannah's *Laboratory Quality Manual (LQM),* current revision~~

Severn Trent Laboratories' *Quality Management Plan (QMP), current revision*

Method 680: Determination of Pesticides and PCBs in Water and Soils/Sediment by Gas Chromatography/Mass Spectrometry. November 1985. Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, USEPA, Cincinnati, OH

17.0 TABLES, DIAGRAMS, AND VALIDATION DATA

Appendix A, B, and C contain applicable tables including the SOP and QC Summary.

APPENDIX A

TABLE 1 CALIBRATION STANDARDS

CALIBRATION COMPONENTS	CAL 1	CAL 2	CAL3	CAL4	CAL5
Calibration Congener					
2-chlorobiphenyl (1)	0.10	0.50	1.0	2.0	5.0
2,3-dichlorobiphenyl(5)	0.10	0.50	1.0	2.0	5.0
2,4,5-trichlorobiphenyl(29)	0.10	0.50	1.0	2.0	5.0
2,2',4,6-tetrachlorobiphenyl(50)	0.20	1.0	2.0	4.0	10
2,2',3,4,5'-Pentachlorobiphenyl (87)	0.20	1.0	2.0	4.0	10
2,2',4,4',5,6'-hexachlorobiphenyl(154)	0.20	1.0	2.0	4.0	10
2,2',3,4',5,6,6'-heptachlorobiphenyl(188)	0.30	1.5	3.0	6.0	15
2,2',3,3',4,5,5',6,6'-octachlorobiphenyl(200)	0.30	1.5	3.0	6.0	15
Decachlorobiphenyl	0.50	2.5	5.0	10	25
Retention Time Congeners					
3,3',4,4-tetrachlorobiphenyl(77)	0.20	1.0	2.0	4.0	10
2,2',4,6,6'-Pentachlorobiphenyl (104)	0.20	1.0	2.0	4.0	10
2,2',3,3',4,5,5',6,7'-nonachlorobiphenyl(208)	0.40	2.0	4.0	8.0	20
Surrogate					
13C12-Decachlorobiphenyl	0.50	2.5	5.0	10	25
Internal Standards					
Phenathrene-d10	0.75	0.75	0.75	0.75	0.75
Chrysene-d12	0.75	0.75	0.75	0.75	0.75

TABLE 2 –First and Last Eluting Isomers

Congener	First Eluting Isomer	Last Eluting Isomer
Cl-1	2-chlorobiphenyl	4-Chlorobiphenyl
Cl-2	2,6-dichlorobiphenyl	4,4'-dichlorobiphenyl
Cl-3	2,2',6-trichlorobiphenyl	3,4,4'-trichlorobiphenyl
Cl-4	2,2',6,6'-tetrachlorobiphenyl	3,3',4,4'-tetrachlorobiphenyl
Cl-5	2,2',4,6,6'-pentachlorobiphenyl	3,3',4,4',5-pentachlorobiphenyl
Cl-6	2,2',4,4',6,6'-hexachlorobiphenyl	3,3',4,4',5,5'-hexachlorobiphenyl
Cl-7	2,2',3,4',5,6,6'-heptachlorobiphenyl	2,3,3',4,4',5,5'-heptachlorobiphenyl
Cl-8	2,2',3,3',5,5',6,6'-octachlorobiphenyl	2,3,3',4,4',5,5',6-octachlorobiphenyl
Cl-9	2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl

APPENDIX B
SIM IONS

Table 3-Ions for SIM Acquisition

ION Set 1 (a)	ION Set 2 (b)	ION Set 3 (c)	ION Set 4 (d)	ION Set5 (e)
152	186	248	240	356
153	188	249	241	358
186	220	254	288	360
187	222	256	290	390
188	254	288	322	392
189	255	290	324	394
190	256	322	326	424
220	258	323	356	425
221	288	324	357	426
222	289	326	358	428
224	290	328	360	430
255	292	357	362	432
256	294	358	391	462
258	323	360	392	464
290	324	362	394	466
292	326	392	396	496
294	328	394	398	498
	358	396	428	499
	360	398	430	500
	362		432	502

(a) CI-1 to CI-4 and Phenthrene-d10
(b) CI-3 to-CI-6
(c) CI5 to CI-7
(d) CI-6 to CI-8 and Chrysene-d12
(e) CI-8 to CI-10 and 13C12-DCB

TABLE 4-Approximate Retention Times for PCB Isomer Groups and Calibration Congeners

PCB Isomer Group	Approximate RRT Range	Calibration Congener	Approximate Calibration Congener RRT
~~CI-1~~	~~0.30-0.35~~	~~2-chlorobiphenyl (1)~~	~~0.30~~
~~CI-2~~	~~0.38-0.50~~	~~2,3-dichlorobiphenyl(5)~~	~~0.43~~
CI-3	0.46-0.64	2,4,5-trichlorobiphenyl(29)	0.54
CI-4	0.55-0.82	2,2',4,6-tetrachlorobiphenyl(50)	0.56
CI-5	0.64-0.92	2,2',3,4,5'-entachlorobiphenyl (87)	0.80
CI-6	0.75-1.1	2,2',4,4',5,6'-hexachlorobiphenyl(154)	0.82
CI-7	0.88-1.2	2,2',3,4',5,6,6'-heptachlorobiphenyl(188)	0.88
CI-8	0.99-1.21	2,2',3,3',4,5,5',6,6'-octachlorobiphenyl(200)	1.03
CI-9	0.16-1.28	Decachlorobiphenyl	1.3
CI-10	1.3	Decachlorobiphenyl	1.3

RRT = retention time relative to Chrysene-d12

Table 4 Quantitation and Interference Check Ions

PCB Isomer Group	Quant ION	Confirmation ION	Expected Ratio(a)	Acceptable Ratio(a)	M-70 Confirmation ION	Interference Check ION M+70	Interference Check ION M+35
Cl-1	188	190	3.0	2.5-3.5	152	256	222
Cl-2	222	224	1.5	1.3-1.7	152	292	256
Cl-3	256	258	1.0	0.8-1.2	186	326	290
Cl-4	292	290	1.3	1.1-1.5	220	360	326
Cl-5	326	324	1.6	1.4-1.8	354	394	360
Cl-6	360	362	1.2	1.0-1.4	288	430	394
Cl-7	394	396	1.0	0.8-1.2	322	464	430
Cl-8	430	428	1.1	0.9-1.3	356	498	464
Cl-9	464	466	1.3	1.1-1.5	390		498
Cl-10	498	500	1.1	0.9-1.3	424		
Chrysene-d12	240	241	5.1	4.3-5.9			
Phenathrene-d10	188	189	6.6	6.0-7.2			
13C12-DCB (surrogate)	510	512					

(a) ratio of quantitation ion to confirmation ion

TABLE 5-Corrections for Interference of PCB Containing Two Additional Chlorines

PCB Isomer Group	Quant ION	Confirmation ION	Ion Measured to Determine Interference	Percent Ion area to be subtracted from QUNAT ION Area	Percent Ion area to be subtracted from CONFIRMATION ION Area
Cl-3	256	258	254	99	33
Cl-4	292	290	288	65	131
Cl-5	326	324	322	108	164
Cl-6	360	362	356	161	71
Cl-7	394	396	390	225	123

TABLE 6-Corrections for Interference of PCB Containing One Additional Chlorine

PCB Isomer Group	Quant ION	Ion Measured to Determine Interference	Percent Ion area to be subtracted from QUNAT ION Area
Cl-2	222	221	13.5
Cl-3	256	255	13.5
Cl-4	292	289	17.4
Cl-5	326	323	22.0
Cl-6	360	357	26.5
Cl-7	394	391	30.9
Cl-8	430	425	40.0

APPENDIX C
680 SOP SUMMARY

HOLD TIME & PRESERVATION SUMMARY

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time (1)	Extract Hold Time
Aqueous	none; 4°C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4°C	500-mL	14 days	40 days
Biological	Frozen	Glass or aluminum foil	6 months	40 days

[1] Holding times are advisory - no holding times are defined in method 680.

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
DFTPP 10ng on column Clock starts at injection	DFTPP 10ng on column Clock starts at injection
Calibration standards- minimum of five cal levels	Mid point calibration verification
Samples and the capping standard must be analyzed within 12 hours of the start of the clock	Samples and the capping standard must be analyzed within 12 hours of the start of the clock
Capping standard	Capping standard

DFTPP CRITERIA

m/z	Ion Abundance Criteria
127	40-60% of mass 198
197	<1.0% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass443
442	>40% of mass 198
443	17-23% of mass 442

CALIBRATION ACCEPTANCE CRITERIA

Initial Calibration	Continuing Calibration
RRFavg <= 20% RSD	Percent difference <= 20% difference from initial calibration for aqueous samples; <=30% for soils and biota

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tune/Column Evaluation Standard DFTPP 20ng	Prior to analysis of calibration standards every 12 hours	DFTPP - within criteria	-Evaluate alternative scans -Reanalyze and evaluate -Retune and reanalyze -Clean source, retune, reanalyze
Initial Calibration-minimum of five calibration standards	After Tune Check and when calibration verification standard fails acceptance criteria.	%RSD <= 20%	-Reanalyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standards -Retune and reanalyze standards -Replace column and reanalyze standards -Clean source and reanalyze standards
Performance Criteria	Evaluate mid level calibration standard each clock	-Mass abundance ratios of all calibration congeners within acceptance range (see Appendix B) -Baseline separation of PCB congener #87 from congeners #154 and #77 -Signal-to-noise ratio of >=5 for decachlorobiphenyl ion 499 and chrysene-d12 ion 241 -decachlorobiphenyl mass abundance: mass 500 >=70% but <=95% of mass 498	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate
Continuing Calibration Verification	After tune check; every 12 hours prior to analysis of samples and at the end of the analytical sequence	%Difference <= 20% for aqueous samples; <=30% for soils and biota	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate

QC Item	Frequency	Acceptance Criteria	Corrective Action
Internal Standard Areas	Evaluate all standards and samples	Areas in continuing calibration verification must be within 30% of the previous CCV or within 50% of the initial calibration Areas in samples should be evaluated for gross error . Consult superior	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available
Surrogate recovery	Evaluate for all samples and QC items if extract is not diluted OR If diluted, where >RL	Within LQM limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract(s) -Re-extract and reanalyze if sufficient sample available
Method Blank	Per batch	All targets < RL in LQM	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in SOP AN02
Lab Control Standard (LCS) - LQM subset	See AN02	All spiked targets within the accuracy criteria in LQM	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in SOP AN02
Matrix spike (MS) Matrix spike duplicate (MSD)	Per batch if sufficient sample volume/weight supplied See AN02	All targets within the accuracy and precision criteria in LQM	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in SOP AN02
Demonstration of Capability (DOC)	Initially and then annually per analyst	Accuracy and precision within method specified criteria	-Evaluate data -Reanalyze extracts if warranted -Re-extract and reanalyze for targets that fail criteria
Method Detection Limit (MDL)	Annually	Evaluate according to SOP CA90	Evaluate according to SOP CA90

STL

SOP SUMMARY FORM

SOP#: SM07.05.28.04.2	**SOP Description:** POLYCHLORINATED BIPHENYLS (PCBs) by GC/MS

Revisions:

___Minor _X_ Significant ___Complete Re-write ___New SOP

Summary of Revision(s).

- Revised format to be consistent with current STL Savannah SOP format and NELAC requirements
- Revised safety information to be consistent with current STL format
- Clarified method modification section to include CCV requirements for soils and biota, section 2.4
- Removed reference to separatory funnel extraction procedure. No longer performed, section 9.1
- Changed injection volume from 2uL to 1uL, section 10.1
- Clarified SIM parameters in section 10.3.3
- Added 30% CCV criteria for soils and biota, section 10.5.1
- Added requirement to analyze endcap within 12-hour clock, section 10.5
- Added quality control, method performance, and waste management information
- Revised cal level 3 concentration in Table 1

IDOCs Required:	___Yes	_X__ No	___ NA
MDLs Required:	___Yes	_X__ No	___ NA

SOP Implementation Date. 06.28.04

Target Training Completion Date. 06.28.04

Approved by: Andrea Jal

Title: QA Manager

Date: 05/28/04

Division Approval: [illegible]

Title: Laboratory Director

Date: 5/28/04

EXTRACTABLE ORGANIC HALIDES (EOX)

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Approved by:

R. Wayne Robbins — Dec 2, 1999

Title: STL-SL QA Manager — Date

1.0 SCOPE AND APPLICATION

1.1 This procedure can be used to determine the concentration of extractable organic halides (EOX) in soils and solids. Organically bound halides (chlorine, bromine, and iodine) are measured as equivalent concentrations of organic chloride.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria are given in Section 5 of the current revision of the STL-SL LQM.

2.0 SUMMARY OF METHOD

2.1 The organic halides present in soils and solids are extracted with ethyl acetate. An aliquot of the extract is injected into the pyrolysis oven of the TOX instrument where the OX is converted to hydrogen halide. The hydrogen halide is swept into the titration cell of a calibrated micro-coulometric detector and the concentration of the organic halide detected is reported as an equivalent concentration of organically bound chloride.

2.2 This method is based on the guidance in SW-846 Method 9023. This SOP contains a modification from the referenced method. 2,4,6-trichlorophenol is used as the standard in place of 1,2,4-trichlorobenzene. 1,2,4-trichlorobenzene is volatile and does not extract efficiently under the method conditions.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or will put yourself or others in a potentially unsafe situation. When handling samples and standards for analysis, the analyst must wear a lab coat or apron, safety glasses, and latex gloves.

3.2 Care must be taken when handling 2,4,6-trichlorophenol, which is used to prepare the stock calibration standards. This material is a suspected carcinogen and may be harmful if inhaled.

3.3 Glacial acetic acid can cause nose and throat irritation upon inhalation. Handling of this material must take place under a ventilated fume hood.

3.4 Field samples may have high concentrations of volatile compounds. Open the samples under a ventilated fume hood if the nature of the sample is not known.

3.5 The analyst must be familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in this procedure. The MSDS denote the type of hazard that each reagent poses and provide guidance for safely handling these compounds.

4.0 INTERFERENCES

4.1 Reagents and gases must be of the highest purity to minimize contamination. The lab should be free from halogenated solvents (such as chloroform and methylene chloride) which will cause a positive interference.

4.2 Contamination of glassware is diminished through scrupulous cleaning. If the reagent blanks show no detectable organic halide (OX), the cleaning steps are sufficient. If not, all glassware must be cleaned as soon as possible after use with a Nochromix solution. After the Nochromix cleaning, glassware must be washed with detergent (Liquinox) in hot water. Rinse glassware thoroughly with tap water, rinse

thoroughly with DI water, and allow to dry.

4.3 Loss of volatile components is diminished if sample is taken with zero headspace in the sampling container. Minimum handling of the sample also avoids loss of volatile organohalides (OX) as well as reduces the possibility of contamination.

4.4 Some inorganic salts, such as mercuric chloride, may be soluble in the ethyl acetate and cause a positive interference.

5.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

Soils and solid sample are collected in glass containers equipped with Teflon-lined caps. The samples should be collected and stored with minimum headspace to minimize the loss of volatile OX. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples) in the lab until the time of extraction and analysis. The samples must be extracted and analyzed within 28 days of collection.

6.0 APPARATUS AND MATERIALS

6.1 TOX microcoulometric analyzer: Dohrmann MC-3, or equivalent TOX/EOX analyzer

6.1.1 Sample boat

6.1.2 Pyrolysis furnace

6.1.3 Microcoulometric detector with integrator

6.1.4 Titration vessel

6.2 Top loading balance

6.3 Analytical balance

6.4 Microsyringes-various volumes with extended syringe bodies so that standards can be added under the surface of the liquid in volumetric flasks.

6.5 Centrifuge

6.6 15-mL conical centrifuge tubes

6.7 Sonicator

6.8 Scintillation or VOA vials

7.0 REAGENTS

Reagents must be tracked in accordance with STL-SL SOP AN44.

7.1 Reagent water - lab generated deionized (DI) water

7.2 Glacial acetic acid (CH_3COOH) - reagent grade.

7.3 Acetic acid, 70% (Titration cell electrolyte) - Transfer 70mL of glacial acetic acid to a 100mL volumetric flask. Dilute to volume with DI water. Transfer to a glass container with a Teflon lined cap.

CAUTION: GLACIAL ACETIC AICD WILL CAUSE EYE, NOSE, AND THROAT IRRITATION. THIS REAGENT MUST BE PREPARED UNDER A WELL VENTILATED HOOD.

7.4 Oxygen: 99.9% pure

7.5 Carbon dioxide: 99.9% pure

7.6 Ethyl acetate-residue grade. This solvent is used to extract organic halides from the sample matrix and must be protected from potential sources of halogenated organic materials such as chloroform and methylene chloride.

8.0 STANDARDS

The preparation of standards must be documented in accordance with STL-SL SOP AN41:*Standard Material Traceability.*

8.1 Sodium chloride-reagent grade

8.2 Sodium chloride stock standard (1000mg/L)-Weigh 0.1648g of sodium chloride into a 100-mL volumetric flask and dilute to volume with reagent water. This solution is used to calibrate the titration cell prior to the analysis of EOX.

8.3 Sodium chloride calibration standard (100mg/L)-Dilute 10mL of the 1000mg/L sodium chloride stock to 100mL in a 100-mL volumetric flask.

8.4 Sodium chloride calibration standard (10mg/L)-Dilute 1.0mL of the 1000mg/L sodium chloride stock to 100mL in a 100-mL volumetric flask.

8.5 2,4,6-Trichlorophenol-reagent grade

8.6 EOX/TCP Stock standard-10000 mg Cl /L. Transfer 1.856 g 2,4,6-trichlorophenol to a 100-mL volumetric flask containing 80mL of ethyl acetate. Dilute to volume with ethyl acetate. Transfer the stock standard to 40-mL VOA vials equipped with Teflon-lined septa. The stock standard is stored with minimum headspace to minimize the volatilization of the solvent and standard material. Store the solution at 4C in the dark.

NOTE: If the weight of 2,4,6-trichlorophenol is not exactly 1.856 g, the concentration of the stock (Cstock) can be calculated from the following equation:

$$Cstock(mg/L) = \frac{Wtcb \otimes \frac{106.5g}{197.4g}}{0.100L} \otimes 1000mg/g$$

where
Wtcb = weight of 2,4,6-trichlorophenol added to the volumetric flask(g)

8.7 EOX /TCP Spiking Solution, 400mgCl /L. Add 1 mL of the 10000 mg Cl /L EOX stock to 24 mL ethyl acetate. Transfer the stock standard to 40-mL VOA vials equipped with Teflon-lined septa. The stock standard is stored with minimum headspace to minimize the volatilization of the solvent and standard material. Store the solution at 4C in the dark.

NOTE: If the concentration of the stock solution is not 10000 mg Cl /L, the volume of stock required to prepare 25 mL of the 400mgCl /L working standard can be determined from the following equation:

$$Vs(mL) = \frac{25mL \otimes 400mg/L}{Cs(mg/L)}$$

where
Vs (mL) = volume of stock required in mL
Cs (mg/L) = concentration of the stock solution in mg Cl/L

9.0 SAMPLE PREPARATION

9.1 Remove the samples from the storage refrigerator and allow the samples to equilibrate to room temperature. Collect the required glassware and reagents and complete as much of the analysis log as possible while the samples are warming up.

9.2 Homogenize the samples by stirring with a stainless steel spatula. Stir in any water that has collected on top of the samples. Perform this step quickly to minimize loss of volatile compounds.

9.3 Using a stainless steel spatula or glass pipette, weigh 2g +/-0.1g of each soil or waste sample into separate 40mL VOA vial. Record the weight to the nearest 0.1g. For each batch of twenty or fewer samples, prepare two additional aliquots of the sample selected as the MS and MSD.

9.4 Prepare the method blank and LCS by weighing 2g of blank sand or blank soil into each of two extraction vials. (Assume that the weight of the method blank and LCS are 2g even if the weight is slightly different from 2g.)

9.5 Add 0.25mL (250uL) of the EOX spiking solution to the LCS, the MS, and the MSD. The theoretical concentration of the spike for a 2g sample is:

$$Ct(mg/kg,dw) = \frac{0.25mL \otimes 400mg/L}{2.0g \otimes solids} = \frac{0.25mL \otimes 400ug/mL}{2.0g \otimes solids} = \frac{100ug}{2g \otimes solids} = \frac{50mg}{kg \otimes solids}$$

9.6 Add 10mL of ethyl acetate to each sample, blank, LCS, and MS/MSD.

9.7 Close each vial and shake vigorously for 30 seconds.

9.8 Place the vials in an ultrasonic bath containing about 1 inch of water and sonicate for 15 minutes.

9.9 After the sonication, allow the samples to sit for 10 minutes. The particulates will settle out.

9.10 Decant the upper layer of extract into a 15-mL conical centrifuge tube. The water, soil, and solvent remaining in the vial can be discarded.

9.11 Centrifuge each sample and QC item at half power for 10 minutes.

9.12 Transfer the extract (upper layer) into a labeled scintillation vial equipped with a Teflon-lined cap and store at 4C in the dark until the time of analysis.

10.0 PROCEDURE

10.3 Routine Start-up and Cell Equilibration for EOX

10.3.1 Prepare the analyzer for use in the direct injection mode for TOX according to the directions in the Dorhmann instruction manual.

10.3.2 Turn the instrument on and open the CO2 and O2 tanks. Both regulators should be preset at 25psi.

10.3.3 While the furnace is heating up to 800C, perform the following checks:

-the FUNCTION select button on the front of the panel is set to STANDBY
-the GAIN control button on the front of the instrument is set at 30.
-the BIAS control button on the front of the instrument is set at 250
-ensure that the titration cell electrodes and the heater tape leads are properly connected
-ensure that the clamp on the titration cell ball joint is forming a tight seal
-verify that the input CO2 and O2 gas pressures are at 25psi.
-observe the gas bubbles in the titration cell. If no bubbles are observed, see Section 13 of STL-SL SOP BA12 or BA14 for guidance in troubleshooting the problem.

10.3.4 Flush the titration cell twice with 70% acetic acid.

10.3.5 Fill the titration cell with electrolyte to the fill line.

10.3.6 Check the baseline reading on the front panel. If a negative reading is displayed, continue to flush the titration cell with 70% acetic acid until a positive reading is displayed.

10.3.7 If the cell is flushed more that three times and a negative reading is still displayed, refer to Section 13 of STL-SL SOP BA12 or BA14 for guidance on troubleshooting the problem. If the problem cannot be resolved quickly, contact the immediate supervisor for assistance.

10.3.8 When a positive baseline is achieved, set the FUNCTION button to DET and the MODE button to POX.

10.3.9 Allow the baseline to stabilize. The baseline is stable when it varies by less than 2 digits.

-if the baseline fails to stabilize within 2-3 minutes, increase the GAIN adjustment slightly.

-if the baseline continues to fluctuate more than 2 digits, see Section 13 of this SOP for guidance in troubleshooting the problem. If the problem cannot be resolved quickly, contact the immediate supervisor.

10.3.10 After the baseline has stabilized, set the MODE button to the EOX mode and the FUNCTION setting to INT.

10.3.11 Set the analysis time to five minutes and verify that the READY lamp on the front panel is illuminated. *If the READY lamp is not on, press the CANCEL button once or twice to reset.*

10.4 EOX Sample Analyses

ANALYTICAL SEQUENCE

Initial Calibration	Direct injection of sodium chloride standards into titration cell at 0.10, 0.20, 0.50, 1.0, 2.0, 4.0 and 8.0ug Cl
System Blank (Method Blank)	40uL blank extract
Calibration Verification (LCS)	40uL of 50 mg/kg EOX/TCP Calibration Standard
Sample Analyses-twenty sample analyses	All samples are analyzed in duplicate at 40uL.

NOTE: Cell maintenance or other changes to the analytical system that affect the system performance may not be performed during sample analysis. The calibration must be verified by the analysis of the LCS standard and system blank after instrument maintenance is performed.

10.4.1 Calibrate the TOX analyzer by injecting various amounts of the 10mg/L sodium chloride stock and 100mg/L sodium chloride calibration solutions directly into the titration cell. The analyzer is operated in the POX mode during the cell calibration.

Calibration Standard	Stock	Volume (uL) Injected	ng Cl	ug Cl
EOX-1	10mg/L	10	100	0.10
EOX-2	10mg/L	20	200	0.20
EOX-3	10mg/L	50	500	0.50
EOX-4	100mg/L	10	1000	1.0
EOX-5	100mg/L	20	2000	2.0
EOX-6	100mg/L	40	4000	4.0
EOX-7	100mg/L	80	8000	8.0

10.4.1.1 Calculate the response factor for each calibration standard using the following equation:

$$RF = \frac{\text{concentration from the analysis of the cal std (ug/L)}}{\text{true concentration of the cal std (ug/L)}}$$

10.4.1.2 Calculate the average response (or calibration) factor for the initial calibration standards:

$$RF_{avg} = \frac{RF_1 + RF_2 + \ldots + RF_n}{n}$$

where n = number of standards in the initial calibration

10.4.1.3 Calculate the standard deviation of the five calibration levels for each target.

$$Standard\ Deviation = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RFavg})^2}{n-1}}$$

where

RF_i = response factor of the individual calibration level

RFavg = average response factor

n = number of calibration standards in the initial calibration

10.4.1.4 Calculate the relative standard deviation (% RSD):

$$\%\ RSD = \frac{standard\ deviation}{RFavg} \otimes 100$$

If the % RSD is less than 20% in the initial curve, the calibration is considered linear and the average response factor (or calibration factor) is used for quantitation.

10.4.1.5 After the initial calibration has been evaluated, each calibration standard is recalculated using the average response factor from the curve:

$$C(recal - ug/L) = \frac{\text{concentration from the analysis (ug/L)}}{RFavg}$$

The "recalculated concentration" for each calibration point must be within 5% of the true concentration or within 50 ng of the true value.

10.4.2 Verify the calibration by analyzing three 40uL aliquots of the EOX /TCP calibration standard. All three standards must be ±40% of the true value.

10.4.3 Remove the extracts from the storage refrigerator and allow the extracts to come to room temperature.

10.4.4 Draw 45uL of the extract into a 50uL microsyringe. If air bubbles are introduced into the syringe, expel the extract and draw up another aliquot of the extract. Adjust the volume to the 40uL mark. Pull the plunger out until all of the extract is contained in the body of the syringe.

10.4.5 Press START. The READY light should go out and the INT light should be illuminated. Wait four seconds for baseline memorization.

10.4.6 Inject the extract through the septum at the end of the glass-to-ball connector at a rate of about 5uL/sec.

10.4.7 When the READY light on the front panel comes on, record the reading on the EOX log. Note that the reading is in nanograms. If the reading exceeds 9999 nanograms, the display will blink and zeros will be displayed, indicating that the weight of OX in the extract has exceeded the capacity of the titration cell and that the extract will require dilution and reanalysis.

11.0 CALCULATIONS

11.4 Soils (EOX)

$$EOX(mg/kg,dw) = \frac{TX}{\frac{W \otimes solids}{Vext} \otimes Vinj} \otimes DF$$

where
TX = weight of halogen detected in the extract (ng)
W = weight of sample extracted (g)
solids = (percent solids)/100
Vext = volume of solvent used to extract the sample (mL)
Vinj = volume of extract (mL)
DF = dilution factor (if dilution of the extract is required)

11.1 Matrix spike recovery

$$\%recovery = \frac{Cms - Csample}{T} \otimes 100$$

where
Cms = concentration of the spiked sample (mg/kg,dw)
Csample = concentration of the unspiked sample (mg/kg,dw)
T = true value of the spike (mg/kg,dw)

The equation can also be used to calculate the recovery of the LCS where Csample = 0.

The true value (concentration) of the spike is calculated:

$$T = \frac{Cs \otimes Vs}{W \otimes solids}$$

where
Cs = concentration of the spiking solution(ug/mL)
Vs = volume of the spiking solution added to the sample(mL)
W = weight of sample spiked (g)
solids = (percent solids)/100

(recall that mg/L = ug/mL)

11.5 Precision as %RPD

$$\%RPD = \left| \frac{Cms - Cmsd}{\frac{Cms + Cmsd}{2}} \right| \otimes 100$$

where
Cms = concentration of MS
Cmsd = concentration of MSD

12.0 QUALITY ASSURANCE/QUALITY CONTROL

12.1 See STL-SL SOP AN02: *Analytical Batching* for guidance in establishing and evaluating batch QC. MS and MSD must be performed at a minimum frequency of 5% of samples. Each batch will have a minimum of a method blank and a LCS.

12.2 Each analyst must demonstrate the ability to generate acceptable results using this procedure-the initial demonstration of capability (IDOC).

-Weigh five 2-g aliquots of a blank sand or soil into extraction vessels.

-Add 0.25 mL of the 400mg/L TCP standard to four of the vials. The theoretical concentration is

$$Ct(mg/kg) = \frac{400mg/L \otimes 0.25mL}{2.0g} = \frac{400ug/mL \otimes 0.25mL}{2.0g} = 50ug/g = 50mg/kg$$

-Add 10mL of ethyl acetate to each spiked sample and the blank.

-Extract the samples as described in Section 9 and analyze the samples as described in Section 10.

-Calculate the concentration of each sample, the average recovery, and the standard deviation. The following criteria should be met to demonstrate capability:

Average recovery (mg/kg)	Standard Deviation(mg/kg)
44-56	<5

This criteria is based on the recovery of the CCV specified in Method 9023 and represents a recovery range of 88-112%. The standard deviation criteria was selected at 10% of the true value.

12.3 The method detection limit (MDL) must be determined annually in accordance with STL-SL SOP CA90.

13.0 MAINTENANCE, TROUBLESHOOTING, AND GENERAL CONCEPTS

13.1 Microcoulometric Titrations

13.1.1 Theory of Microcoulometry

In the titration cell, the acid halide species are titrated within the cell with an internally generated titrant. There are two pair of electrodes contained in the titration cell. The generating pair of electrodes generates the titrant (silver ions). These electrodes are called the working and auxiliary electrodes. The sensor/reference pair of electrodes monitors the concentration of the titrant at all times. All of the electrodes with the exception of the generator auxiliary are made of solid silver. The generator auxiliary electrode is platinum wire. The cell electrolyte is 70% acetic acid.

13.1.2 Principles of Operation of the Titration Cell and Microcoulometric Detector

13.1.2.1 The titration cell is designed to maintain a constant titrant (silver ion) concentration. When a halide such as chloride, bromide, or iodide enters the titration cell, the silver halide is formed so the silver ion concentration decreases. This decrease in silver ion is detected by the reference and sensor electrodes.

13.3.2.2 The mV output is directly related to the silver ion concentration.

13.3.2.3 The reference electrode is mounted in silver acetate. This electrode generates a constant mV output used as the reference voltage within the cell.

13.3.2.4 The silver sensor electrode is positioned directly above the gas stream coming from the pyrolysis tube, to ensure that the halides present pass over it.

13.3.2.5 The working generator electrode is also positioned directly above the gas stream coming from the pyrolysis tube, to ensure that the halides present pass over it.

13.3.2.6 The sensor electrode and the working electrode are coated with a silver chloride coating. Silver ions are continuously released into the electrolyte to maintain a constant silver ion concentration when halides are not present.

13.3.2.7 The working electrode and the auxiliary electrode work together to generate or remove silver ions in the stirred electrolyte which permits the restoration of the silver ion to its original concentration whenever a change is detected by the reference/sensor electrode pair.

13.3.2.8 The microcoulometric detector will detect zero OX when the voltage at the reference electrode is exactly equal to the voltage determined at the sensor electrode. A change in the voltage at the sensor electrode (a decrease in silver ion concentration) is translated by the detector as a positive TOX result.

13.2 Cell Maintenance and Troubleshooting

13.2.1 Cell Performance Check

13.2.1.1 The cell performance check must be performed daily after the cell has been flushed and filled with fresh electrolyte. The results of the performance check should be recorded into the TOX or EOX analysis log.

13.2.1.2 Prepare a 1000ppm sodium chloride (NaCl) solution by dissolving 0.1648g of NaCl in approximately 80mL of DI water placed in a 100mL volumetric flask. Mix. Dilute to 100mL with DI water.

13.2.1.3 Set the FUNCTION knob to POX, and set the MODE to DET, and the output units to ng.

13.2.1.4 With the titration cell connected to the pyrolysis tube, verify that the baseline is stable.

13.2.1.5 Change the FUNCTION knob to INT.

13.2.1.6 Press START and wait 4 seconds for baseline memorization.

13.2.1.7 Remove the glass cap from the top of the titration cell. Using a 100uL or 50uL syringe, inject 5uL of the 1000ppm sodium chloride (NaCl) solution directly into the top of the titration cell. Replace the titration cap.
**NOTE--The syringe tip should be submerged in the electrolyte when the NaCl is injected.

13.2.1.8 The halide measurement should fall within 2% of the true value injected.

13.2.1.9 The true value of the standard is calculated as follows:

Ideal reading = (1000ng/uL) x 5uL = 5000ng

(Recall that 1000mg/L = 1000ng/uL)

13.2.1.10 If the true value of the chloride standard is not within 2%, the cell must be flushed and the performance check should be performed again.

13.2.2 Flushing the Cell and Disposal of Electrolyte

A drain vessel is placed below the titration cell which is large enough to hold approximately 200mL of electrolyte. Place about 2 teaspoons of sodium carbonate in to the bottom of the vessel to neutralize the acetic acid. When flushing the titration cell, allow the acetic acid to drain into this vessel and neutralize. Once the solution is neutralized it may be disposed of in a sink while running plenty of water behind.

13.2.3 Whenever the titration cell is connected to the pyrolysis tube and NO gas stream is flowing through the cell inlet, the heater tape must ALWAYS be de-energized. This can be done by switching the FUNCTION knob to "STANDBY".

13.2.4 The titration cell must ALWAYS be stored with electrolyte. The electrodes must not be allowed to dry.

13.2.5 The analyst should be checking for bubbles in the titration sidearms continuously throughout sample analysis. The presence of air bubbles in the sidearms will cause erratic and consistent results since the continuity of the electrical charge will potentially be broken.

13.2.6 Bubbles in the titration sidearms (except in the reference sidearm) can be dislodged by opening the stopcock closest to the sidearm containing the bubble, while tilting the cell so the stopcock is pointing upward. Gently tap the cell body until the bubble becomes dislodged and passes through the stopcock. Close the stopcock and reposition the cell.

13.2.7 A negative baseline reading can be from an excess of ions in the cell solution. Flush the cell with fresh electrolyte and perform the cell performance check with the NaCl. The cell performance check should be +/- 2% of the true value.

A negative baseline can also be from contaminated gas or low gas pressure. Replace gas source.

13.2.8 If the baseline is too high or too noisy, check for air bubbles which may be lodged in the electrode sidearms. Dislodge any bubbles according to 13.4.6.

13.2.9 A high or noisy baseline may also be caused by a dirty titration cell, or a titration cell which is low on electrolyte. Clean (13.5) the titration cell and do the performance check.

13.3 Titration Cell Cleaning

13.3.1 Empty the cell of electrolyte and disconnect from the pyrolysis tube. Remove the heater tape.

13.3.2 Unplug all BUT the reference electrodes from their ports. Replug these three ports with a silicone plug.

13.3.3 Open the reference sidearm stopcock briefly to lodge a pocket of air in the capillary and prevent any other material other than electrolyte from coming into the reference arm. Then rinse the cell body and reservoir with DI water. Fill the cell body with 5 to 10mL of Nochromix solution.

13.3.4 Using a suction bulb, draw the acid up and down the capillary inlet until clean.

13.3.5 Rinse the cell thoroughly with DI water.

13.3.6 Re-install the three electrodes in their proper ports.

13.3.7 Flush the cell thoroughly with electrolyte, then restore the electrolyte to the proper level.

13.3.8 Eliminate any bubbles in the sidearms, including the bubble in the reference sidearm.

13.3.9 If the cell performance check yields values greater than +/- 2% of the true value, check or replace the o-rings at the exit tube. Once the o-rings are replaced, verify a constant gas flow.

13.4 Cleaning and Reconditioning the Cell Electrodes.

13.4.1 Drain the cell electrolyte and remove the black and green electrodes.

13.4.2 Clean the sensor and working (green and black, respectively) electrodes: Pull electrodes through the red/white septa. Sand the electrodes lightly with 4/0 emery cloth or immerse exposed silver parts in NH4OH solution, under a hood, until the silver gets shiny, then rinse thoroughly with DI water.

13.4.3 Reinsert sensor (green) and working (black) electrodes into their red/white septa and install the sensor and working electrodes in their normal ports in the cell body.

13.4.4 Turn on gases.

13.4.5 Mount the cell on the combustion tube.

13.4.6 Fill the cell with electrolyte. Make sure gas is bubbling through the cell.

13.4.7 The sensor (green) electrode will be coated first. Plug the white and red electrodes into their corresponding white and red jacket positions. Plug the green and blank electrodes into the REVERSE jacket positions (green to black and black to green).

13.4.8 Switch the function knob to DET. Wait for the baseline to somewhat stabilize.

13.4.9 Inject 5uL of 1000mg/L NaCl directly into the cell electrolyte. Integrate the result and record the data. (Five minute analysis time is sufficient).

13.4.10 Repeat 13.6.9 until the recovery of the NaCl stabilizes close to 100%.

13.4.11 Switch the function knob to STANDBY. Drain electrolyte and restore the sensor (green) electrode and the working (black) electrode to their normal ports and restore the green-green and black-black pin connectors.

13.4.12 Fill the cell with electrolyte and repeat steps 13.6.9 and 13.6.10.

13.4.13 Flush the cell and begin analysis.

13.5 Repacking the Reference Electrode Chamber

13.5.1 Drain, then disconnect the cell by unclamping it from the pyrolysis tube. Unplug the heater tape and four electrode leads. Take off the heater tape.

13.5.2 Gently remove the reference electrode and its septum from the cell, keeping the assembly intact.

13.5.3 Remove and discard the quartz wool and silver acetate from the reference electrode chamber.

13.5.4 Rinse the cell with electrolyte and clean if necessary.

13.5.5 Place a small tuft of quartz wool in to the reference electrode chamber. Add electrolyte to the cell body so that it just covers the quartz wool. Drain some electrolyte through the reference arm, if necessary, to establish fluid continuity between the cell body and the reference arm. Carefully poke the quartz wool with a small diameter rod to release any bubbles trapped in the wool. Make sure there are no bubbles in the capillary leading to the reference chamber.

13.5.6 Fill the reference chamber with silver acetate to a level which will nearly cover the entire electrode when inserted.

13.5.7 Completely fill the cell with electrolyte. Note that this will cause the electrolyte to overflow through the reference chamber. Wearing gloves for this procedure is strongly recommended.

13.5.8 Eliminate any bubbles which may be present in the reference chamber by stirring the silver acetate packing gently with the reference electrode. When bubbles are gone, be sure electrolyte is overflowing through the reference chamber, then slowly insert the reference electrode septum followed by the reference electrode.

13.5.9 Flush the cell and begin analysis.

13.6 Removing Bubbles from Reference Electrode

13.6.1 Fill the titration cell so that the electrolyte level is above the reference electrode chamber. Drain a small amount of electrolyte from the reference arm, if necessary, to establish fluid continuity between the cell body and the reference chamber.

13.6.2 Slide the reference electrode out of its septum, then remove the septum from the chamber. Using the electrode, gently stir or probe the silver acetate and quartz wool to dislodge any bubbles from the electrode chamber.

13.6.3 Once the chamber is free of bubbles, add a few drops of electrolyte to fill the chamber, reinsert the septum, rinse the electrode with DI water, and then reinsert electrode through the septum.

13.6.4 Inspect the chamber to ensure that no bubbles are present. Remove any spilled electrolyte.

13.7 Filling the Titration Cell

13.7.1 Remove the white reference electrode and septum as a unit from the reference chamber. Pyrex wool and silver acetate are already in place in the reference chamber so care should be taken in removing the white reference electrode. Open the reference stopcock. Slowly fill the cell with electrolyte through the main cell body. When the reference arm is full of electrolyte and there are no bubbles present in the arm, close the stopcock.

13.7.2 Continue filling the cell slowly until the fluid level is above the top of the reference chamber. As the chamber fills with electrolyte, the silver acetate may have to be stirred gently with a clean stainless steel syringe needle. When the electrolyte level reaches the top of the chamber, replace the reference electrode.

13.7.3 Look for bubbles. Remove any bubbles sitting on top of the silver acetate by repeating 13.9.2. Then confirm that no bubbles exist under the Pyrex wool or in the reference capillary. To remove existing bubbles, carefully tip the cell so that the top points towards you with the reference stopcock uppermost. Gently push on the reference electrode to pump the bubble out of the capillary.

CAUTION**DO NOT FORCE THE ELECTRODE THROUGH THE PYREX WOOL.

13.7.4 The cell is ready for initial startup.

13.8 Pyrolysis Tube

13.8.1 The exit tube and quartz wool should be visually checked daily for signs of coking (dark residue). If coking is present clean the exit tube, and replace the quartz wool and the o-rings.

13.8.2 The exit tube may be cleaned by soaking the tube in Nochromix for several hours then rinsing thoroughly with tap water. Finally rinse three times with DI water, and allow the exit tube to air dry prior to reinstallation.

14.0 TROUBLESHOOTING

This section has been incorporated into section 13 in this SOP.

15.0 REFERENCES

15.1 *Savannah Laboratories' Comprehensive Quality Assurance Plan* and Savannah Laboratories' *Corporate Quality Assurance Plan*, current revisions

15.2 *Test Methods for Evaluating Solid Waste, Third Edition with Revisions and Updates, SW-846*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC. (Update III)

Method Summary- 9023-EOX (Extraction for soils and wastes)

HOLD/STORAGE

Container	500mL amber glass with Teflon-lined cap to seal the bottle with minimum headspace
Preservative	None
Storage*	4C from collection until analysis
Hold Time	The analysis must be completed within 28 days of collection

*The control temperature is less than 6C with no frozen samples

SAMPLE PREPARATION

Extraction, 2g to 10mL with ethyl acetate, followed by direct injection of the extract into the pyrolysis chamber.

ANALYTICAL SEQUENCE

Initial Calibration	Direct injection of sodium chloride standards into titration cell at 1,5,10,50, and 80ug Cl
System Blank (Method Blank)	40uL ethyl acetate extraction blank
Calibration Verification (LCS)	40 uL of extracted lab control standard
Sample Analyses-twenty sample analyses	All samples are analyzed in duplicate at 40uL.

QC Batch

Method blank
LCS
MS/MSD at a frequency of 5% of samples

QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Initially and when CCV fails	Less than 5% difference or within 0.05ug of the true value (against the average response)	-evaluate instrument and repeat analysis of one or more calibration standards
Method blank (ethyl acetate)	After LCS	<10 mg/kg	-evaluate instrument and repeat analysis of method blank -evaluate according to STL-SL SOP AN02
Calibration verification (LCS)	After initial calibration and once per batch	44-56 mg/kg %RSD: <5%	-evaluate instrument and repeat analysis of CCV -re-calibrate -maintenance instrument and re-calibrate
MS/MSD	At a frequency of 5% of samples	Within STL-SL QAP limits	-evaluate according to STL-SL SOP AN02
Initial demonstration of Capability (IDOC)	Initially and when new analysts are trained	Section 12	-evaluate instrument and repeat IDOC
Method Detection Limit (MDL)	Annually	See CA90	CA90

SOP SUMMARY FORM

SOP#: BA13:11.30.99:2	SOP Description: Extractable Organic Halides (EOX)

Revisions:

___Minor _X__Significant ___Complete Re-write ___New SOP

Summary of Revision(s):
-Section 8.5 through 8.7 - standard preparation revised to reflect change in calibration compound from tirchlorobenzene to trichlorophenol.
-Section 9.3 - Sample weight increased to 2 g ± 0.1 g.
-Section 9.5 - equation revised. Spiking level is 50 mg/kg (50ug/g).
-Section 10.4 - analytical sequence revised.
-Section 10.4.2 - revised calibration verification to method criteria.
-Section 12.2 - revised IDOC spiking solution and weight of sample. Revised recovery and precision criteria to method requirements.
-SOP Summary - revised analytical sequence; revised LCS frequency and acceptance criteria; revised method blank criteria to <10 mg/kg.

IDOCs Required:	_X__Yes	___No
MDLs Required:	_X__Yes	___No
SOP Implementation Date:	12.30.99	
Target Training Completion Date:	1.13.99	

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Date: Dec 2, 1999

Division Approval: [signature]

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Date: 12-13-99

FAN057:08.03.99:1

Savannah Laboratories

PERCENT SOLIDS DETERMINATION

(Methods: SW-846 3050 & 3550, and EPA 160.3)

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1.0 SCOPE AND APPLICATION

This SOP describes the procedures for the determination of the percent solids in soils, sediments, sludges, and other solid materials that must be reported on a "dry weight basis".

This SOP was written by and for STL Savannah.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 A well-mixed sample is transferred to a tared aluminum weighing pan or crucible. The sample is placed in an oven maintained at 103°C-105°C. The residue that remains after the liquid has been evaporated is the solids portion of the sample. The solids portion is routinely expressed as the percent solids, but it can also be expressed as the percent moisture. Equations for both the percent moisture and percent solids determination are described in Section 11 of this SOP.

2.2 This procedure is based on the percent solids determination in SW-846 Methods 3050 and 3550 and EPA 160.3.

2.3 Definitions – Refer to SOP AN99: *Definitions, Terms, and Acronyms* for a complete listing of applicable definitions.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Waste Disposal SOP, and this document.

3.1 Specific Safety Concerns or Requirements

All samples must be treated as if they are hazardous. The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested for percent solids may contain hazardous chemical compounds or biological organisms. The analyst must wear protective clothing (lab coat or apron), eye protection (glasses or face shield), and disposable gloves when handling these samples.

The analyst should handle samples that have been dried at 103C - 105C with caution. This temperature can cause skin burns.

4.0 INTERFERENCES

The primary cause of interferences comes from glassware or other containers that have not been properly cleaned or prepared prior to the analysis. The basis of this procedure is the difference in the weight of the aluminum pan or crucible containing the residue and the tare weight of the crucible. Thus, care must be taken to ensure the aluminum pan or crucible is not treated in such a manner as to add or lose weight.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Aliquots of samples for the determination of percent solids are routinely sub-sampled from the 100-mL to 500-mL widemouth containers collected for metals or organic extractable analyses. The samples

are iced at the time of collection and are maintained at 4°C ± 2°C until the time of analysis. The percent solids should be determined as soon as possible.

6.0 APPARATUS AND MATERIALS

6.1 Aluminum pans

6.2 Top-loading balance: capable of weighing to the nearest 0.01g

6.3 Drying oven: capable of maintaining a temperature of 103°C - 105°C

6.4 Spatula or other utensil for transferring sample

7.0 REAGENTS

No reagents are required for this procedure.

8.0 STANDARDS

Calibration and check standards are not required for this procedure.

9.0 SAMPLE PREPARATION

Sample preparation steps are included in Section 10.

10.0 ANALYTICAL PROCEDURES

10.1 Calibrate and verify that the top loading balance is working within the proper parameters in accordance with SOP AN10: *Balance Calibration and Use*.

10.2 Label an aluminum pan with an identification number. Weigh the pan on the top loading balance. Record the ID and the weight (to the nearest 0.01g) of the aluminum pan on the bench sheet.

10.3 Tare the balance by pressing the auto tare button. This will zero the balance.

10.4 Thoroughly mix the sample with a stainless steel spatula or glass rod. It is important to obtain a homogeneous mixture prior to sub-sampling so that the sub-sample will accurately reflect the composition of the sample. Leaves, rocks, and other foreign materials should not be included in the sub-sample.

NOTE: If there is any doubt as to how to treat a given sample, contact the immediate supervisor to determine the proper course of action. SOP AN70: *Compositing, Homogenization, and Segregation Samples* provides guidance for homogenizing samples.

10.5 Add a 9.95 - 10.05g aliquot of the well-mixed sample to the tared aluminum pan. Record the sample identification and weight to the nearest 0.01g on the analysis log.

NOTE: The LIMS percent solids program assumes 10.0g initial weight.

10.6 Place the sample in the drying oven, maintained at 103-105°C, for at least 12 hours.

10.7 Remove the aluminum pan from the oven and allow to cool. Remember not to place the aluminum pan on a surface that can cause dirt or other foreign objects to adhere to the pan. Ensure that the surface that the pan is placed on can handle the temperature of the aluminum pan without damage.

10.8 Weigh the aluminum pan containing the sample residue on the top-loading balance and record the weight to the nearest 0.01g.

11.0 DATA ANALYSIS AND CALCULATIONS

The LIMS program automatically calculates the results according to the equations listed below:

11.1 The percent solids is calculated using the following equation:

$$percent\ solids = \frac{A - B}{W} x\ 100$$

where

A = weight of sample residue and aluminum pan (g)
B = weight of aluminum pan (g)
W = weight of sample used to determine the percent solids (g)

To express the percent solids as a decimal equivalent ("solids") for calculating sample results on a "dry weight basis":

$$\text{Soilds} = \frac{\text{percent solids}}{100}$$

To express the percent solids as percent moisture:

$$\text{Percent moisture} = 100 - \text{percent solids}$$

11.2 The LIMS program prints out a log containing the percent solids results. This log is kept in a 3-ring binder.

12.0 QUALITY CONTROL AND DATA ASSESSMENT

12.1 The balance must be checked in accordance with ~~SL~~-SOP AN10: *Balance Calibration and Use* prior to use.

12.2 Refer to the analytical SOPs for quality control and data assessment information.

13.0 METHOD PERFORMANCE

13.1 Refer to the analytical SOPs for method performance information.

14.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

Refer to SOP AN53: *Maintenance Procedures for Laboratory Instrumentation* for routine preventive maintenance and the manufacturer's guides for trouble-shooting items.

15.0 WASTE MANAGEMENT AND POLLUTION CONTROL

All waste will be disposed of in accordance with Federal, State and Local regulations. Follow the guidance for disposal in SOP CA70: *Waste Disposal.* Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

15.1 Waste Streams Produced by the Method

Excess samples, reagents, and standards must be disposed in accordance with SOP CA70: *Waste Management.*

The following waste streams are produced when this method is carried out.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets

16.0 REFERENCES

16.1 STL Savannah's *Laboratory Quality Manual (LQM),* current revision.

16.2 *Test Methods for Evaluating Solids Waste, Third Edition*, SW-846; USEPA Office of Solids Waste and Emergency response, Washington, D.C.

17.0 TABLES, DIAGRAMS, AND VALIDATION DATA

There are no tables, diagrams, or validation data included in this SOP.

STL

SOP SUMMARY FORM

SOP#: BA51:02.18.04:2	**SOP Description**: PERCENT SOLIDS DETERMINATION

Revisions:

___Minor _X_Significant ___Complete Re-write ___New SOP

Summary of Revision(s):

- Changed title of SOP
- Revised format to be consistent with current STL Savannah SOP format and NELAC requirements
- Revised safety information to be consistent with current STL format
- Added requirement for samples to be dried at 103-105°C for at least 12 hours
- Added waste management information

IDOCs Required:	___Yes	_X_ No	___NA
MDLs Required:	___Yes	_X_ No	___NA

SOP Implementation Date: 03.18.04

Target Training Completion Date: 03.18.04

Approved by: Andrea Teal

Title: Quality Assurance Manager

Date: 02/20/04

Division Approval: [illegible]

Title: Lab Director

Date: 2/25/04

STANDARD OPERATING PROCEDURE
PARTICLE-SIZE ANALYSIS OF SOILS
ASTM D422-63

Applicable Matrix: Soil

APPROVAL SIGNATURES

Laboratory Director:	Michael F. Wheeler, Ph.D.	Date: 1/28/05
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1.0 SCOPE AND APPLICATION

1.1. This SOP describes the laboratory procedure for the determination of particle size distribution in soil samples that contain sand, silt, clay and gravel.

2.0 SUMMARY OF METHOD

2.1. A soil sample submitted for particle size analysis is prepared according to laboratory SOP LM-SL-D421 *Dry Preparation of Soil for Particle Size Analysis* or LM-SL-D2217 *Wet Preparation of Soil Samples for Particle Size Analysis*. Particles greater than 75um (gravels to fine sands) are determined by sieve analysis while particles less than 75um (silts and clays) are determined by sedimentation using a hydrometer followed by sieve analysis.

After wet or dry sample preparation, the sample is passed through No.10 sieve. The particles retained on the No.10 sieve (greater than 2.00mm) are further separated by sieve analysis. A portion of the sample that passed through the No.10 sieve is transferred to a glass sedimentation cylinder to which distilled water has been added. Seven hydrometer readings are taken over 24 hours. After the final hydrometer reading, the suspension is rinsed over a No. 200 (75 um) sieve, dried, and further separated by sieve analysis.

Particle size determinations for each sieve measurement and hydrometer reading are calculated and corrected for hygroscopic moisture and specific gravity. Unless a separate analysis for specific gravity is requested, the specific gravity is s assumed to be 2.65.

2.2. This procedure is based on ASTM D422-63.

3.0 DEFINITIONS

Not Applicable

4.0 INTERFERENCES

Not Applicable

5.0 SAFETY

5.1. Care should be taken to avoid exposure to the sample matrix since all environmental samples are potentially hazardous. Protective clothing, eye protection and disposable gloves should be worn when handling samples. All laboratory personnel must be familiar with the environmental health and safety plan described in the STL Chemical Safety Manual.

6.0 EQUIPMENT AND SUPPLIES

6.1. Top-Loading Balance sensitive to 0.01 g

6.2. Mechanical Stirring Apparatus and Dispersion Cup

6.3. Sedimentation Cylinder(s) 1000 mL

6.4. Hydrometer: ASTM 151H in specification E 100.

6.5. Thermometer: Accurate to 0.5°C

6.6. Mortar and Rubber Tipped Pestle

6.7. Sieves of the following size(s):

3.0 in (75.00mm)	No. 20 (850.0um)
2.0 in (50.00mm)	No. 40 (425um)
1.5 in (37.50mm)	No. 60 (250.0um)
1.0 in (25.00mm)	No. 80 (180.0um)
3/4 in (19.00mm)	No. 100 (150.0um)
3/8 in (9.50mm)	No. 200 (75.0um)
No. 4 (4.75mm)	
No. 10 (2.00mm)	

6.8. Oven with temperature range of 60° C to 110° C

6.9. Timing Device with second hand and capable of counting up to 25 hours

6.10. Stainless steel spatulas, spoons, metal and bristle brushes

6.11. Ro-tap machine

7.0 REAGENTS AND STANDARDS

7.1. Reagents

Deionized (DI) Water: Milli-Q System

Sodium Hexametaphosphate Solution: Combine 2940 g of DI water with 120 g of sodium hexametaphosphate in an appropriate container. Mix until the solution is homogeneous. Assign an expiration date of 30 days from date of preparation.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1. At least 500 grams of soil sample should be collected in glass or polyethylene jars. Immediately following collection the sample should be sealed and cooled to 4°C in order to preserve the moisture content of the sample.

8.2. Samples are stored from the time of receipt in the laboratory until 30 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or

client-specific protocol, samples are disposed of after 30 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

Not Applicable

10.0 CALIBRATION AND STANDARDIZATION

10.1. Calibrate the balance on each day of use, prior to use.

10.2 Calibrate the hydrometers every two years following the procedure given in LM-SL-001.

11.0 PROCEDURE

11.1 Sample Preparation

Prepare the sample following either laboratory SOP LM-SL-D421 (Dry Preparation) or LM-SL-D2217 (Wet Preparation).

11.2 Sample Analysis

11.2.1 Hydrometer Test

Transfer the sample/sodium hexametaphosphate mixture into a dispersion cup ensuring a quantitative transfer using DI water. Fill the dispersion cup ~half full with DI water. Mix the sample for one minute using the immersion blender.

Pour the contents of the dispersion cup through a #10 sieve into a 1000 mL sedimentation cylinder (1000 mL graduated cylinder). Rinse the cup with DI water, to ensure that the entire sample is transferred to the sedimentation cylinder.

Add DI water to the sedimentation cylinder until the volume is 1000 mL then cover the cylinder with a sheet of parafilm. Allow the sample to stabilize to ambient temperature.

Transfer the material retained on the No. 10 sieve to a labeled medium-size aluminum dish, and place the aluminum dish into an oven maintained at a temperature of 105ºC for a minimum of 16 hours.

After up to 12 sedimentation cylinders have been prepared, ensure that each cylinder is filled to the reference line with DI water, covered with parafilm, and that there is sufficient clean DI water available to rinse the hydrometer.

Record the ID of the hydrometer that you intend to use. Record the start time and set the timer for elapsed time.

Use the hydrometer reading table used to perform the activities as indicated (shake, place or read) for each 1000 mL cylinder.

To shake, rotate the flask up and down for one minute approximating at least 60 turns (one turn upside down and then right side up constitutes two turns).

To take a reading, gently insert the hydrometer into the cylinder then wait ~ 20 seconds. Read the hydrometer at the top of the meniscus to the nearest 0.0005. Enter the hydrometer reading into the appropriate cell on the benchsheet. Clean the hydrometer by twisting and dropping into a clean DI water bath.

Insert a temperature sensor into the cylinder to the depth the hydrometer reached. Read the temperature to the nearest 0.5°C. Enter the temperature reading into the appropriate cell on the benchsheet. After reading, rinse the sensor in a DI water bath.

Take readings every 2, 5, 15, 30, 60, 240 and 1440 minutes. Record each reading on the benchsheet, then transfer this information into the appropriate cell of the EXCEL worksheet.

11.2.2 Large Sieves

Tare the balance and weigh an aluminum dish. Enter the weight measurement in the non-material section of the EXCEL worksheet in the cell labeled "Pan, g".

Carefully transfer the non-soil material (e.g.- sticks, grass, wood, plastic) from the drying dish to the pre-weighed dish and enter the weight measurement in the non-soil material section of the EXCEL worksheet in the cell labeled "Pan/Dry Sample, g".

Enter a brief description of the type of non-soil material (e.g.- sticks, grass, wood, plastic) in the non-soil material section of the EXCEL worksheet in the cell labeled "Description".

Tare the balance and weigh each of the 3/4", 3/8", #4 and #10 sieves. Record the weight measurements in the EXCEL worksheet in the cells labeled "Sieves (Tares)". Also weigh any larger sieves if necessary.

Stack the sieves then transfer the soil material retained on the #10 sieve into the sieve stack. Shake for 2 minutes. If there is greater than ~30 g of material, place the sieve stack into the Ro-tap machine and shake for 10 minutes.

Weigh each sieve along with the material retained on it. Enter these weight measurements in the "Sieve + Sample Weights" section of the Excel worksheet.

Determine the average hardness of the particles retained on the #10 sieve by dropping a hammer on the particle from a height of approximately one foot. Hardness qualifiers are hard, soft or brittle. Record the hardness qualifier in the "Description of >#10 Particles" section of the Excel worksheet.

Observe and record the shape of the particles in the "Description of >#10 Particles" section of the Excel worksheet. Shape qualifiers are well rounded, rounded, subrounded, subangular, and angular.

11.2.3 Small Sieves

When the hydrometer test is complete, transfer the soil from the sedimentation cylinder to a #200 wet wash sieve.

Wash the soil through the #200 sieve until the water from the bottom of the sieve runs clear. Carefully transfer the material retained on the sieve to a labeled 250 mL glass beaker.

Place the beaker into the oven. Dry at a temperature of 105ºC for at least 16 hours. After 16 hours, remove the beaker from the oven and allow it to cool.

Gently mix the dried contents of the beaker with a rubber-tipped pestle to break any soil aggregates that may have formed during the drying stage.

Tare the balance and weigh each of the sieves between #20 and #200. Record the weight measurements in the EXCEL worksheet in the cells labeled "Sieves (Tares)".

Transfer the dry sample into the sieve stack, ensuring that all material is transferred. Use hair or wire brushes to clean the beaker.

Place the sieve stack on the Rotap machine and shake for ten minutes.

Weigh each sieve along with the material retained on it. Enter these weight measurements in the "Sieve + Sample Weights" section of the Excel worksheet.

Determine particle size using the following formula.

12.0 CALCULATIONS

12.1. Sample Used (SU)

<u>Wet Method</u>

$$SU = (pan + wet\ sample - pan) \otimes PS$$

Where:

PS = Percent solids

Note: for hydrometer SU, subtract the dry weight of any material retained on the No. 10 sieve.

Dry Method

$$SU = (pan + dry\ sample - pan) - (pan + non - soil\ material - pan) \otimes HMCF$$

Where:

HMCF = Hygroscopic moisture correction factor

12.2 Sieve Analysis (Percent Finer = PF)

Large Sieves:

3 inch: PF = 100-100 (Sieve and Sample (3 inch) - Sieve (3 inch))/SU*

2 inch: PF = PF (3 inch) - 100(Sieve and Sample (2 inch) - Sieve (2 inch))/SU and so on through the #10 Sieve.*

Small Sieves:

#20: PF = PF(#10) - 100(mass passing #10/sample mass (Hyd))*(sieve and sample (#20) - sieve(#20))/sample used*

#40: PF = PF (#20) - 100(mass passing #10/sample mass (Hyd))*(sieve and sample (#40) - sieve (#40))/sample used and so on up through #10 sieve.*

12.5 Hydrometer Analysis

Particle size, Micron

1000*sqrt [930*viscosity/980*(SG-1))*(effective depth/time)]

Viscosity at sample temperature, poises
Effective Depth, cm = 16.29-264.5*(actual Hydrometer reading - 1) above equation for effective depth based on equation found with table 2 in method, in which 16.29 = 0.5*(14.0-67.0/27.8)+10.5 and 264.5 = (10.5-2.3)/0.031
Time, minutes = Time of hydrometer reading from beginning of sedimentation
Sqrt - square root
SG - Specific Gravity of soil
Viscosity - is the resistance of a liquid to flow

12.6 Percent Finer (PF):

PF = Constant*(actual hydrometer reading - hydrometer correction factor - 1)

Where:

Constant = (100,00/W)*SG/(SG-1)
W = (Total sample used *sample used for hydrometer analysis*HMCF)/Amount of total sample passing #10 sieve
Hydrometer Correction = slope*sample temperature + Intercept
Slope = ((low temp. reading -1)-(high temp. reading -1)/(low temp. - high temp.))
Intercept = (low temp. reading -1) - (low temp. * slope)

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.0. Complete the sample preparation benchsheet and EXCEL spreadsheet. Document any problems encountered during sample analysis so they may be properly addressed in the project narrative. Perform primary and secondary data review following the guidance given in laboratory SOP LP-LB-003 *Data Review*.

14.0 METHOD PERFORMANCE

Not Applicable

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1. The laboratory optimizes technology to minimize pollution and reduce the production of hazardous waste whenever possible.

15.2. The laboratory procedures for waste management comply with applicable federal, state and local regulations and are described in SOP LP-LB-001HAZWD.

16.0 REFERENCES

16.1. Standard Test Method for Particle-Size Analysis of Soils, ASTM D422-63, Volume 04.08 Soil and Rock, American Society for Testing and Materials, Philadelphia, Pa., 1998.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

17.1 Table 1: Hydrometer Reading Table

Table 2: Hydrometer Reading Table (For up to 12 Sedimentation Cylinders)

Elapsed Time (hr:min)	Task	Cyl. No.	Actual Time (min)	Elapsed Time (hr:min)	Task	Cyl. No.	Actual Time (min)
0:00	Shake			1:01	Read	10	5
0:01	**Place**	**1**		1:02			
0:01	Shake	2		**1:03**	Place	11	
0:02	Place	2		1:04	Read	9	15
0:03	Read	1	2	1:05	Read	11	2
0:04	Read	2	2	1:06	Read	7	31
0:06	Read	1	5	1:07	Read	3	58
0:07	Read	2	5	1:08	Read	11	5
0:08	Shake	3		1:09	Shake	12	
0:09	**Place**	**3**		**1:10**	Place	12	
0:09	Shake	4		1:11	Read	10	15
0:10	Place	4		1:12	Read	12	2
0:11	Read	3	2	1:13	Read	4	63
0:12	Read	4	2	1:14	Read	8	32
0:14	Read	3	5	1:15	Read	12	5
0:15	Read	4	5	1:18	Read	11	15
0:16	Read	1	15	1:19	Read	9	30
0:17	Read	2	15	1:21	Read	5	60
0:20	Shake	5		1:25	Read	12	15
0:21	Place	5		1:26	Read	10	30
0:23	Read	5	2	1:27	Read	6	59
0:24	Read	3	15	1:33	Read	11	30
0:25	Read	4	15	1:34	Read	7	59
0:26	Read	5	5	1:41	Read	12	31
0:27	Shake	6		1:42	Read	8	60
0:28	Place	6		1:52	Read	9	63
0:30	Read	6	2	1:53	Read	10	57
0:31	Read	1	30	2:06	Read	11	63
0:32	Read	2	30	2:07	Read	12	57
0:33	Read	6	5	4:17	Read	1	256
0:34	Shake	7		4:18	Read	2	256
0:35	Place	7		4:19	Read	3	250
0:36	Read	5	15	4:20	Read	4	250
0:37	Read	7	2	4:21	Read	5	240
0:38	Read	3	29	4:22	Read	6	234
0:39	Read	4	29	5:00	Read	7	265
0:40	Read	7	5	5:01	Read	8	259
0:41	Shake	8		5:02	Read	9	253
0:42	Place	8		5:03	Read	10	247
0:43	Read	6	15	5:04	Read	11	241
0:44	Read	8	2	5:05	Read	12	235
0:47	Read	8	5	24:01	Read	1	1440
0:48	Shake	9		24:02	Read	2	1440
0:49	Place	9		24:03	Read	3	1434
0:50	Read	7	15	24:04	Read	4	1434
0:51	Read	9	2	24:05	Read	5	1424
0:52	Read	5	31	24:06	Read	6	1418
0:54	Read	9	5	24:07	Read	7	1412
0:55	Shake	10		24:08	Read	8	1406
0:56	Place	10		24:09	Read	9	1400
0:57	Read	8	15	24:10	Read	10	1394
0:58	Read	10	2	24:11	Read	11	1388
0:59	Read	6	31	24:12	Read	12	1382
1:00	**Read**	**1**	**59**				
1:00	**Read**	**2**	**58**				

Source: Laboratory Prepared Reference Document

STANDARD OPERATING PROCEDURE
HYDRAULIC CONDUCTIVITY OF SATURATED POROUS MATERIALS USING A FLEXIBLE WALL PERMEAMETER
ASTM 5084

Applicable Matrix: Clay, Silt

APPROVAL SIGNATURES

Laboratory Director:	Michael F. Wheeler, Ph.D.	Date: 5/5/05
QA Manager:	Kirstin L. McCracken	Date: 5-5-05
Department Manager:	Jon K. Jagmuntowicz	Date: 5/6/05
Technical Director: Geotechnical Lab	Matthew R. Duquette	Date: 5-5-05

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of the coefficient of hydraulic conductivity (permeability) of water-saturated porous materials with a flexible wall permeameter. It is applicable to silts and clays with a hydraulic conductivity less than or equal to 1×10^{-5} m/s that are collected in a Shelby tube or other method which maintains the soil in an undisturbed state. The procedure may be performed for disturbed soil samples, after the soil is compacted into a mold to represent a minimum or maximum density. More permeable soils should be tested using ASTM D 2434.

2.0 SUMMARY OF METHOD

2.1 Hydraulic conductivity is measured as flow of water over time through a sample. The sample is assembled in a hydraulic conductivity apparatus, and water permeates through under pressure. Burette readings are taken to measure the amount of water flowing through the soil.

2.2 This procedure is based on ASTM Method D5084.

3.0 DEFINITIONS

Not Applicable

4.0 INTERFERENCES

Not Applicable

5.0 SAFETY

5.1. Care should be taken to avoid exposure to the sample matrix since all environmental samples are potentially hazardous. Protective clothing, eye protection and disposable gloves should be worn when handling samples. All laboratory personnel must be familiar with the environmental health and safety plan described in the STL Chemical Safety Manual.

6.0 EQUIPMENT AND SUPPLIES

6.1 ELE/Soiltest Tri-Flex 2, Permeability Test System

6.2 ELE Master control panel

6.3 Trautwein Standard panel M100000

6.4 Trautwein Standard Add-on panel M116000

6.5 De-aired, deionized water

6.6 Flexible-Wall Permeability test cell

6.7 Filter paper

6.8 Latex membranes

6.9 Vacuum pump membrane assembly

6.10 High-vacuum grease

6.11 Sample extractor

6.12 Stainless steel spatulas/spoons

6.13 3" Shelby Tube Mold

7.0 REAGENTS AND STANDARDS

Not Applicable

8.0 SAMPLE HANDLING AND PRESERVATION

8.1 Samples should be collected using a Shelby tube or equivalent, of 3" diameter and at least 6" in length. Alternatively, a sample volume of approximately 500 g (dry weight) should be collected in a container that will maintain the soil's moisture content.

8.2 Samples are stored from the time of receipt in the laboratory until 30 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or client-specific protocol, samples are disposed of after 30 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

Not Applicable

10.0 CALIBRATION AND STANDARDIZATION

10.1. Calibrate the balance on each day of use prior to use.

10.2. Check the calibration of the mold apparatus annually following the procedure given in Appendix A.

11.0 PROCEDURE

Determine the soil moisture content of the sample following laboratory SOP LM-SL-D2216. Enter the moisture content value into the Excel spreadsheet as "Initial Moisture content (%)".

Place the porous end pieces of the chamber in deionized water during sample preparation.

If the sample is undisturbed (in Shelby Tube), prepare the test specimen by cutting a length of Shelby tube at least 6 times greater than the largest particle size in the sample.

If the sample is disturbed (other sample container), compact the sample in a 3" Shelby Tube Mold, building layers of soil and scarifying each previous layer with a stainless spatula or fork.

Using the sample extractor, carefully push out the soil cores, trimming the ends if voids cause the length to vary by more than 5%

Measure the initial length of the soil (cm) and enter the value into the Excel spreadsheet as "initial length (cm)".

Measure the initial width of the soil, and enter the value into the Excel spreadsheet as "initial width (cm)".

Weigh the sample, and record the weight as "initial mass, (g)" in the Excel spreadsheet.

Lightly grease the base plate, place a porous end piece on the base of the chamber, and a circle of filter paper on top. Set the sample core on the filter paper, top the sample with filter paper, porous end piece, and the lightly greased top cap.

Using the vacuum pump membrane assembly, carefully surround the sample with the latex membrane. Secure the latex membrane with rubber o-rings. Affix both top cap water lines. Lightly grease the chamber o-rings, top and bottom. Assemble the chamber and tighten retaining rods hand-tight.

Using a drain line, vent the top valve of the chamber to a catch basin. Attach the lower cell line to the water port on the master panel. Fill the cell with water, checking top and bottom seals for leaks.

Note: Ensure that there is no air in the system after venting the top valve. If a leak occurs, it may be necessary to reassemble the apparatus.

Re-attach the cell line to the appropriate chamber controls on the master panel, and check to ensure that all pipettes are approximately ½ full with de-aired water.

With all chamber valves closed, set the cell to a confining pressure, usually 20psi. Establish a pressure gradient across the sample, usually 15psi lower, 10psi upper.

First open the cell chamber valve, then open the lower valve, and then open the upper valve. Again, check for leaks. If a leak occurs at this point, reassemble the apparatus.

Remove the air from the sample lines by attaching the drain line to the drain valves, and opening the drain valves. Only de-air one line at a time, and take care to not allow the water in the pipette to empty.

Allow the sample to saturate with water for at least 24 hours. After saturation, de-air the lines again, and set the water levels in the panel pipettes to prepare for readings. Drain most of the water out of the "upper" pipette, and fill the "lower" pipette.

Turn all three control panel valves to "pipette", take a base reading of pressures (PSI) and pipette levels (mL), and start a count-up timer (hr/min/sec). Pressures may have to be adjusted to prevent leaks, if pressures are changed, reset pipette levels and timer, and re-establish the baseline reading.

Record the room temperature as "initial Temperature (ºC)" in the Excel spreadsheet.

Take readings as conditions permit (i.e. when there is an appreciable difference (>1/10 mL) in pipette levels). The time intervals between will vary greatly between samples but a minimum of 6 readings must be taken.

Enter the burette readings for each pipette into the Excel spreadsheet as "Burette, mL". Pressure readings for each reading should be recorded as "Pressure, psi" in the Excel spreadsheet. Times for each reading are entered into the spreadsheet in hours, minutes and seconds.

Calculate hydraulic conductivity using the equation given in Section 12.0.

The test is considered complete when the Hydraulic conductivities of 4 trials are within 25% of the mean hydraulic conductivity.

Upon completion of the testing, record the room temperature as "Final Temperature (ºC)" in the Excel spreadsheet.

After completion of the hydraulic conductivity testing, disassemble the chamber using the reverse procedure of the set-up.

Using a sharp razor blade, cut and remove the rubber membrane from around the sample. Remove the filter paper and porous disks from the sample as well.

Measure the final length of the soil (cm) and enter the value into the Excel spreadsheet as "final length (cm)".

Measure the final width of the soil, and enter the value into the Excel spreadsheet as "final width (cm)".

Weigh the sample, and record the weight as "final mass, (g)" in the Excel spreadsheet.

Determine the soil moisture content of the sample following laboratory SOP LM-SL-D2216. Enter the moisture content value into the Excel spreadsheet as "final Moisture content (%)".

12.0 CALCULATIONS

12.1 Hydraulic Conductivity (k):

$k = QL/Ath$

Where
Q = quantity of water discharged
L = distance between manometers
A = cross-sectional area of specimen
t = total time of discharge
h = difference in head on manometers

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Perform primary review of your work following the procedures given in the laboratory SOP for data review. All data undergoes secondary review by a senior analyst or a data review analyst. Problems encountered during analysis are documented and reported in the case narrative provided with the data package report. For additional guidance regarding the laboratory's protocol and required elements for each level of data review (primary, secondary, and tertiary) refer to laboratory SOP LP-LB-003 *Data Review*.

14.0 METHOD PERFORMANCE

Not Applicable

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably possible technology changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 No waste streams are produced when this method is carried out.

16.0 REFERENCES

16.1 Standard Test Method Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter, ASTM D5084-03, volume 04.08 Soil and Rock, American Society for Testing and Materials, Philadelphia, PA.

16.2 Tri-Flex 2 Permeability Test System Owner's Manual, ELE/Soiltest, Revision 2, September 1995.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

Not Applicable

APPENDIX A: Calibration Check for Mold Apparatus

The volume of the compaction mold is checked annually using a water-filled method checked by linear measurement.

Equipment & Supplies

- Vernier or Dial Caliper with a range of at least 0-6 in. (0-150 mm). Readable to at least 0.001 in. (0.02 mm).
- Inside micrometer with a range of at least 2-12 in. (50-300 mm). Readable to at least 0.001 in. (0.02 mm).
- Plastic or glass plate approximately 8 in. square by ¼ in. thick (200 by 200 mm by 6 mm).
- Thermometer 0-50°C range, 0.5°C readability.
- Stopcock or high vacuum grease.
- 4 in. compaction mold
- Top loading balance

Procedure

Water Fill Method

1) Lightly grease the bottom of the mold, assemble the base plate and mold, and secure the mold to the base plate.
2) Lightly grease the top of the mold.
3) Weigh the greased mold and glass plate to the nearest 1 g and record.
4) Place the mold on a firm, level surface and fill the mold with water to slightly above the rim.
5) Slide the glass plate over the top surface of the mold so that the mold remains completely filled with water and air bubbles are not entrapped.
6) Completely dry any excess water from the outside of the mold and plates.
7) Weigh the mold, plate and water and record to the nearest 1 g.
8) Determine the temperature of the water in the mold to the nearest 1°C.
9) Repeat steps 1-8

Linear Measurement Method

1) Using the Vernier caliper, measure the inside diameter of the mold 6 times at the top of the mold and 6 times at the bottom of the mold. Record the values to the nearest 0.001-in. (0.02-mm)

2) Using the Vernier caliper, measure the inside height of the mold by making three measurements equally spaced around the circumference of the mold. Record the values to the nearest 0.001-in. (0.02-mm).

Calculations

Water Fill Method

$V = (M_1 - M_2)/D_1$

Where:
V = volume of mold
M_1 = mass of mold, plate and water
M_2 = mass of mold and plate
D_1 = density of water at recorded temperature (from table 1)

Linear measurement method

$$V = \frac{(\pi)(h)(d_t + d_b)^2}{(16)(1728)} \quad \text{(inch-pound)}$$

$$V = \frac{(\pi)(h)(d_t + d_b)^2}{(16)(10^3)} \quad \text{(SI)}$$

Where:
V = volume of mold, ft^3 (cm^3)
H = average height, in. (mm)
d_t = average top diameter, in. (mm)
d_b = average bottom diameter, in. (mm)
1/1728 = constant to convert in^3 to ft^3
$1/10^3$ = constant to convert mm^3 to cm^3

SEVERN TRENT STL

STANDARD OPERATING PROCEDURE
PERMEABILITY OF GRANULAR SOILS (CONSTANT HEAD)

Applicable Matrix: Soil

APPROVAL SIGNATURES

Laboratory Director:	Michael F. Wheeler, Ph.D.	Date: 5/6/05
QA Manager:	Kirstin L. McCracken	Date: 5/6/05
Department Manager:	Jon K. Zygmuntowicz	Date: 5/6/05
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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of the coefficient of permeability by a constant-head method for the laminar flow of water through granular soils. In order to limit consolidation influences during testing, this procedure is limited to disturbed granular soils containing not more than 10% soil passing the 75 um (No. 200) sieve.

2.0 SUMMARY OF METHOD

2.1 The sample's moisture content is determined following laboratory SOP LM-SL-D2216. A portion of sample is air dried and layered into a constant-head permeameter chamber. Water from the constant-head filter tank is allowed to flow through the test sample with the flow rate measured from the outlet port. The test is repeated five times increasing the constant head (hydraulic head) with each subsequent test. Average permeability is then calculated.

2.2 This procedure is based on ASTM Method D2434.

3.0 DEFINITIONS

Not Applicable

4.0 INTERFERENCES

Not Applicable

5.0 SAFETY

5.1. Care should be taken to avoid exposure to the sample matrix since all environmental samples are potentially hazardous. Protective clothing, eye protection and disposable gloves should be worn when handling samples. All laboratory personnel must be familiar with the environmental health and safety plan described in the STL Chemical Safety Manual.

6.0 EQUIPMENT AND SUPPLIES

6.1 Constant-head permeameter

6.2 Top loading balance

6.3 Aluminum measuring pans

6.4 Stainless steel spoons and spatulas

6.5 100 mL graduated cylinder

6.6 Assorted size funnels

6.7 Thermometer

6.8 ¾"Flat solid steel cylinder

7.0 REAGENTS AND STANDARDS

Not Applicable

8.0 SAMPLE HANDLING AND PRESERVATION

8.1. At least 500 grams of soil sample should be collected in glass or polyethylene jars. Immediately following collection the sample should be sealed and cooled to 4°C in order to preserve the moisture content of the sample.

8.2. Samples are stored from the time of receipt in the laboratory until 30 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or client-specific protocol, samples are disposed of after 30 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

Not Applicable

10.0 CALIBRATION AND STANDARDIZATION

10.1. Calibrate the balance on each day of use prior to use using 2 Class S weights that bracket the range of use. Record the check in the logbook designated for this purpose.

10.2 Check the calibration of the mold apparatus using the procedures given in Appendix A.

11.0 PROCEDURE

11.1 Analysis

Determine the moisture content of the sample following laboratory SOP LM-SL-D2216. Enter the results from analysis in the "Moisture Content" section of the Excel worksheet.

Select and air-dry a portion of sample equal to twice the amount needed to fill the permeameter chamber. Remove any particles larger than 19 mm (3/4 in.).

Place the permeability chamber in the base of the apparatus and assemble the lower porous disc and spacer.

Place the soil sample in the chamber, in uniform thin layers that are approximately equal in thickness to the maximum particle size, but not less than 15mm.

Using the steel cylinder, lightly tamp each layer uniformly over the surface of the soil until there is no visible motion of surface particles at the edges of the tamping foot.

Level the upper surface of the soil, place the top porous disc on the sample and assemble the permeameter.

Measure the final height of the sample (cm), and record as "Soil Length" in the Excel worksheet.

Using a vacuum pump, evacuate the sample for 15 minutes to remove any air that is adhering to soil particles and from the voids.

Slowly saturate with water the sample from the bottom upward, removing any remaining trapped air.

Stabilize the head in the inlet funnel by adjusting the inflow of water to equal the outflow. Record the initial head reading in the Excel spreadsheet as "H initial, cm."

Once the outflow has stabilized, start the timer and place a 100 mL graduated cylinder under the outflow port in order to measure the quantity of water discharged.

When at least 20 mL of water has been collected, record the time elapsed as "Time (t)(seconds)," the quantity of water collected as "Q, cm3 (mL)" and record the temperature(°C) of the water in the Excel spreadsheet.

Repeat the procedure 5 times, increasing the head ½ cm to 1 cm with each subsequent trial.

Calculate the coefficient of permeability using the equation given in Section 12.0.

12.0 CALCULATIONS

12.1 Moisture Content

$$w = [(M_{cws} - M_{cs})/(M_{cs} - M_c)] * 100$$

Where:
w = water content, %
M_{cws} = mass of container and wet sample, g
M_{cs} = mass of container and oven dry sample, g
M_c = mass of container, g

12.1 Coefficient of Permeability (k):

$$k = QL/Ath$$

Where
Q = quantity of water discharged

L = distance between manometers
A = cross-sectional area of specimen
t = total time of discharge
h = difference in head on manometers

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Perform primary review of your work following the procedures given in the laboratory SOP for data review. All data undergoes secondary review by a senior analyst or a data review analyst. Problems encountered during analysis are documented and reported in the case narrative provided with the data package report. For additional guidance regarding the laboratory's protocol and required elements for each level of data review (primary, secondary, and tertiary) refer to laboratory SOP LP-LB-003 *Data Review.*

14.0 METHOD PERFORMANCE

Not Applicable

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably possible technology changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 No waste streams are produced when this method is carried out.

16.0 REFERENCES

16.1 Standard Test Method for Permeability of Granular Soils (Constant Head), ASTM D2434 - 68, volume 04.08 Soil and Rock, American Society for Testing and Materials, Philadelphia, Pa., March, 2000.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

Not Applicable

APPENDIX A: Calibration Check for Mold Apparatus

Check the volume of the compaction mold annually using a water-filled method checked by linear measurement.

Equipment & Supplies

- Vernier or Dial Caliper with a range of at least 0-6 in. (0-150 mm). Readable to at least 0.001 in. (0.02 mm).
- Inside micrometer with a range of at least 2-12 in. (50-300 mm). Readable to at least 0.001 in. (0.02 mm).
- Plastic or glass plate approximately 8 in. square by ¼ in. thick (200 by 200 mm by 6 mm).
- Thermometer 0-50°C range, 0.5°C readability.
- Stopcock or high vacuum grease.
- 4 in. compaction mold
- Top loading balance

Procedure

Water Fill Method

1) Lightly grease the bottom of the mold, assemble the base plate and mold, and secure the mold to the base plate.
2) Lightly grease the top of the mold.
3) Weigh the greased mold and glass plate to the nearest 1g and record.
4) Place the mold on a firm, level surface and fill the mold with water to slightly above the rim.
5) Slide the glass plate over the top surface of the mold so that the mold remains completely filled with water and air bubbles are not entrapped.
6) Completely dry any excess water from the outside of the mold and plates.
7) Weigh the mold, plate and water and record to the nearest 1g.
8) Determine the temperature of the water in the mold to the nearest 1°C.
9) Repeat steps 1-8

Linear Measurement Method

1) Using the Vernier caliper, measure the inside diameter of the mold 6 times at the top of the mold and 6 times at the bottom of the mold. Record the values to the nearest 0.001-in. (0.02-mm)

2) Using the Vernier caliper, measure the inside height of the mold by making three measurements equally spaced around the circumference of the mold. Record the values to the nearest 0.001-in. (0.02-mm).

Calculations

Water Fill Method

$V = (M_1 - M_2)/D_1$

Where:
V = volume of mold
M_1 = mass of mold, plate and water
M_2 = mass of mold and plate
D_1 = density of water at recorded temperature (from table 1)

Linear measurement method

$$V = \frac{(\pi)(h)(d_t + d_b)^2}{(16)(1728)} \quad \text{(inch-pound)}$$

$$V = \frac{(\pi)(h)(d_t + d_b)^2}{(16)(10^3)} \quad \text{(SI)}$$

Where:
V = volume of mold, ft^3 (cm^3)
H = average height, in. (mm)
d_t = average top diameter, in. (mm)
d_b = average bottom diameter, in. (mm)
1/1728 = constant to convert in^3 to ft^3
$1/10^3$ = constant to convert mm^3 to cm^3

APPENDIX C

Chain of Custody

Chain of Custody Record

P.O. No.

PROJECT NUMBER | PROJECT NAME

SAMPLERS: (Signatures)

Sample No.	DATE	TIME	LOCATION	Number of Containers	Type of Analysis										Type of Preservation	Remarks

Relinquished By:	Received By:	Date	Remarks
Signature	Signature	/ /	
Printed Name	Printed Name	Time	
Company	Company		
Reason			
Relinquished By:	Received By:	Date	
Signature	Signature	/ /	
Printed Name	Printed Name	Time	
Company	Company		
Reason			

Page ____ of ____

IN-SITU MCB/DCB TREATABIILTY TESTS

Paper 2C-24, in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds—2002*. Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2002). ISBN 1-57477-132-9, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

CHLOROBENZENE NAPL OXIDATION USING POTASSIUM PERMANGANATE: BENCH- AND FIELD-SCALE DEMONSTRATION

John F. Horst (jhorst@arcadis-us.com); Kurt A. Beil; Frank C. Lenzo; and Suthan S. Suthersan, Ph.D. (ARCADIS G&M, Inc., Langhorne, Pennsylvania)

ABSTRACT: Potassium permanganate ($KMnO_4$) was selected for use in a short-term field demonstration of chemical oxidation at an active industrial site in the eastern United States. The demonstration was designed to evaluate the feasibility of using permanganate (MnO_4^-) to destroy separate-phase, adsorbed-phase, and dissolved-phase monochlorobenzene (MCB) and 1,2-dichlorobenzene (DCB) present in the saturated soils and groundwater beneath the Site. A bench-scale treatability study confirmed the suitability of the technology for application at the Site. During the field demonstration, approximately 1,540 pounds of $KMnO_4$ were delivered to the subsurface in the form of a three-percent solution (by weight) through a series of ten injection events completed over a period of 12 weeks. The results of groundwater monitoring conducted during the field demonstration indicate that 1) the selected delivery method is effective and 2) the $KMnO_4$ was able to overcome the natural reductive poise throughout the pilot test area. However, it appears that the ability of the permanganate to sustain reaction with the target compounds was limited by an insufficient concentration of permanganate in the subsurface. An attempt to overcome this limitation through the use of an alternate source of permanganate with a higher solubility, such as sodium permanganate ($NaMnO_4$), has been proposed.

INTRODUCTION:

The subject Site is an active industrial facility located in the eastern United States. Overburden at the Site is comprised of unconsolidated deposits of silty sands and gravels ranging in thickness from approximately 30 to 65 feet. Specifically, surficial soils are comprised of an approximately 5 foot thick layer of fill material. Beneath the fill material, a layer of ablation till (poorly sorted sand, silt, and gravel) extends to between 25 and 45 feet below land surface (bls) to a layer of dense basal till ranging from 5 to 20 feet in thickness. The basal till lies directly over the regional bedrock. Groundwater at the site occurs in both the unconsolidated deposits and the fractured bedrock, and is encountered at an average depth of approximately 4.5 feet bls.

Elevated concentrations of MCB and DCB in groundwater indicate the presence of non-aqueous phase liquid (NAPL) in localized areas throughout the Site. The elimination of NAPL in such areas would remove the continuing source of groundwater impacts, thus reducing the total duration and cost to achieve Site-wide remediation goals. In support of this objective, in-situ chemical oxidation was selected for application in the form of a pilot-scale demonstration. Following an evaluation of available oxidation techniques, permanganate (MnO_4^-) in the form of potassium permanganate ($KMnO_4$) was selected for use in the pilot demonstration. This oxidant was selected for several reasons, as follows: 1) commercial availability; 2) high comparative oxidation potential; 2) ability to oxidize compounds with carbon-carbon double bonds, such as those found in MCB and

DCB (LaChance, 1998; Meyers, 1998; Oberle, 2000); 3) ability to react under a wide range of pH conditions and at normal groundwater temperatures (Meyers, 1998; Oberle, 2000); 4) ability to diffuse into lower permeability zones in heterogeneous geologic environments, such as those encountered at the Site (LaChance, 1998); and, 5) the low-energy of the resulting chemical reactions as compared to other oxidation technologies, such as Fenton's reagent. The final pilot demonstration work plan provided for the following:

- A bench-scale treatability study to confirm the suitability of the selected oxidation technology for application at the Site.
- A well network including two injection wells, six monitoring wells, and two sets of three piezometers.
- Delivery of permanganate to the subsurface through a series of ten injections involving a dilute $KMnO_4$ solution.
- Groundwater monitoring, including a baseline-sampling event prior to the injections, five sampling events during the injections, and one sampling event one to two months following completion of the injections.

Evaluation of the treatability study results, the success of the selected delivery method, and the data from the groundwater monitoring activities would be evaluated to determine whether the pilot demonstration was successful and the technology should be retained for use at the Site.

TREATABILITY STUDY

Prior to initiating the field demonstration, a bench-scale treatability study was completed in a laboratory. The objective of the study was to estimate oxidant demand in the Site subsurface. In order to complete the test, a bulk saturated soil sample and a bulk groundwater sample were collected in the area selected for the pilot demonstration and submitted to the ARCADIS laboratory in Durham, North Carolina. Upon receipt of the soil, the bench-scale treatability study was initiated. The key elements of the study were as follows:

- At the laboratory, the Site soil was homogenized and analyzed for total organic carbon (TOC) content. A total of five samples were analyzed for TOC: four were analyzed using the Walkley-Black method, which does not detect elemental carbon (charcoal/coal); and one was analyzed using the Lloyd Kahn method, which does detect elemental carbon.
- The homogenized soil was spiked with 1,000 microliters of MCB and 500 microliters of DCB (this equates to approximately 1,210 milligrams of MCB and 655 milligrams of DCB). The spiked homogenate was left undisturbed for ten days to allow time for the MCB and DCB to achieve partitioning equilibrium. The homogenate was then used to fill three equal-volume glass test columns.

- Each test column was saturated with clean water. In a closed-loop, the water in each test column was circulated several times to assure that equilibrium conditions had been achieved. Pre-treatment desorption samples of the water were then collected and submitted for VOC analysis.
- 500 milliliters (ml) of a 3% $KMnO_4$ solution was then introduced into each test column. In each column, the initial dilution resulted in a 1.89% solution that was recirculated until the concentration of $KMnO_4$ stabilized.
- The $KMnO_4$ solution was then drained, and each column was flushed once with clean water. Post-treatment desorption samples were collected from this water and were submitted for VOC analysis.

Based on numerous published studies and the results of similar testing previously completed in the ARCADIS laboratories, it was assumed that the permanganate molecule could effectively oxidize dissolved-phase constituents with carbon-carbon double bonds (such as MCB and 1,2-DCB). In an effort to make the treatability study more cost-effective, concentrations of the constituents of concern (COCs) in the permanganate effluent were not measured. The treatability study focused on the total oxidant demand assuming that reductions in COC concentrations were the result of successful oxidation.

The overall oxidant demand is generally comprised of two elements: contaminant demand and matrix demand. The matrix demand is principally comprised of naturally occurring organic material in the soil that will consume the oxidant. Matrix demand is generally larger than contaminant demand, such that it controls the magnitude of the overall oxidant demand at a Site. Consequently, soils with high organic content can result in a matrix demand that is hundreds to thousands of times greater than the contaminant demand, making oxidation technology impractical due to cost. Conversely, soils with minimal organic content can result in a very low overall oxidant demand. Based on the results of the TOC analyses, the natural organic carbon content in the Site soil is minimal, less than 500 milligrams per kilogram (mg/Kg), confirming the Site as an ideal candidate for oxidation technology.

The VOC analytical results of the pre- and post-treatment samples collected during the study are summarized below:

Measurement	MCB		1,2-DCB	
	Dissolved (ug/L)	In Soil (mg/Kg)	Dissolved (ug/L)	In Soil (mg/Kg)
Pre-treatment concentration	61,667	34,333	32,667	30,333
Post treatment concentration	346	<38	650	140
Apparent reduction:	99.4%	99.9%	98.0%	99.5%

Notes:
ug/L Micrograms per liter
mg/Kg Milligrams per kilogram

Using the average concentrations of MCB and DCB detected in the desorption samples, a conservative estimate of the sorbed-phase concentration of MCB and DCB was developed using published organic carbon/water partitioning coefficients (USEPA 1996b; Montgomery and Welkom, 1990) and equilibrium relationship equations (USEPA, 1996a). Knowing the average mass of the soil matrix in each test column, the total sorbed-phase mass of MCB and DCB oxidized in each column could be then determined. By comparing these results to the average total $KMnO_4$ consumed by each column, Site-specific oxidant utilization ratios were determined for MCB and DCB, as follows:

- 35 pounds of KMnO4 required to oxidize 1 pound of MCB (35:1)
- 54 pounds of KMnO4 required to oxidize 1 pound of DCB (54:1)

The above utilization ratios take into consideration the matrix demand created by the naturally occurring organic material in the Site soil. Due to the lack of matrix demand, the utilization ratios determined through the treatability study are less than ten times the stoichiometric utilization ratio of approximately 6:1 for both MCB and DCB. As previously mentioned, matrix demand can range from hundreds to thousands of times greater than the contaminant demand. Consequently, the results of the treatability study confirm the suitability of the technology for application at the Site.

PILOT DEMONSTRATION WELL NETWORK

The well network associated with the pilot demonstration was installed in an area of the Site where sufficient impacts were known to be present. The well network was configured such that both the performance of the oxidation process and the extent of the resulting in situ reactive zone could be evaluated. The injection wells were configured to target two discrete lithologic zones in the Site subsurface, one shallow and one deep (just above bedrock). The monitoring wells were arranged radially around the injection points, and were configured to monitor the entire saturated interval across which the chemical oxidant would be injected. The layout and profile of the pilot demonstration well network are depicted on Figures 1 and 2, respectively.

FIELD ACTIVITIES

A total of 10 injection events were completed over a period of 12 weeks. Over the course of the injection events, a total of 1,540 pounds of $KMnO_4$ was delivered to the subsurface in approximately 6,000 gallons of solution (approximately 3 percent by weight). In conjunction with the injection events, a total of seven groundwater sampling events were completed (one baseline, five during the treatment period, and one post-treatment). Based on the data collected, the following observations can be made:

- Injection pressures were negligible through all ten events, indicating that precipitation of manganese dioxide (MnO_2, a by product of $KMnO_4$ oxidation reactions) had a minimal effect on the soil permeability in the pilot area. This validates the effectiveness of the delivery method selected for the pilot demonstration.

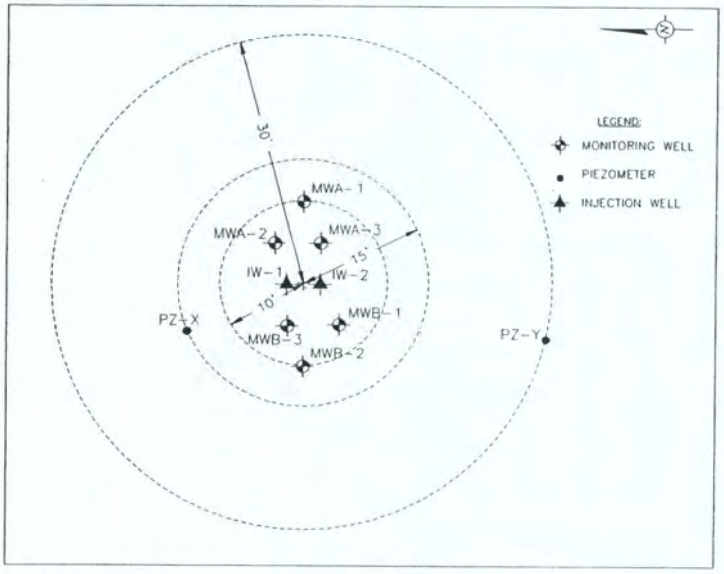


FIGURE 1: Pilot Demonstration Well Network, Layout

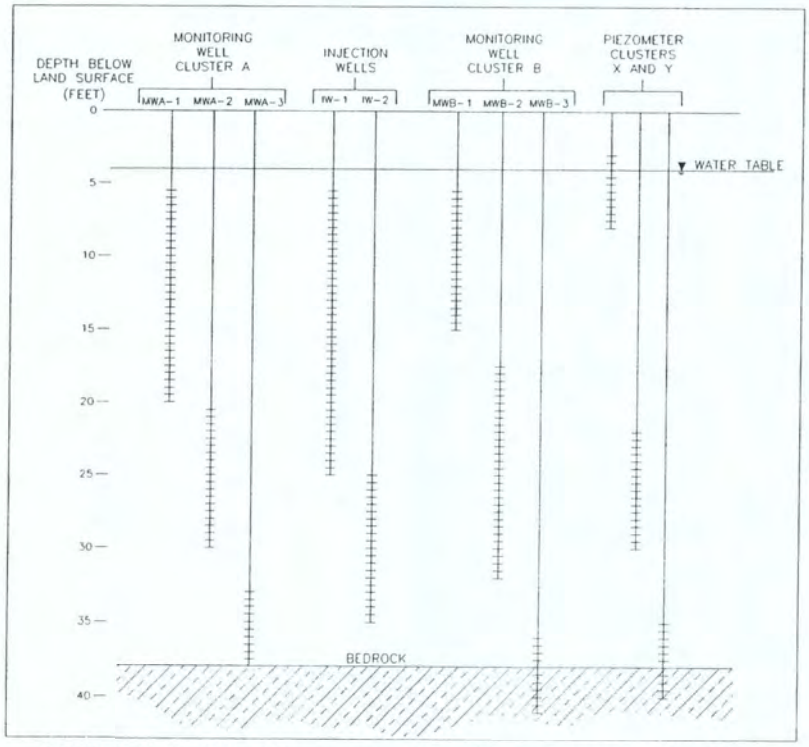
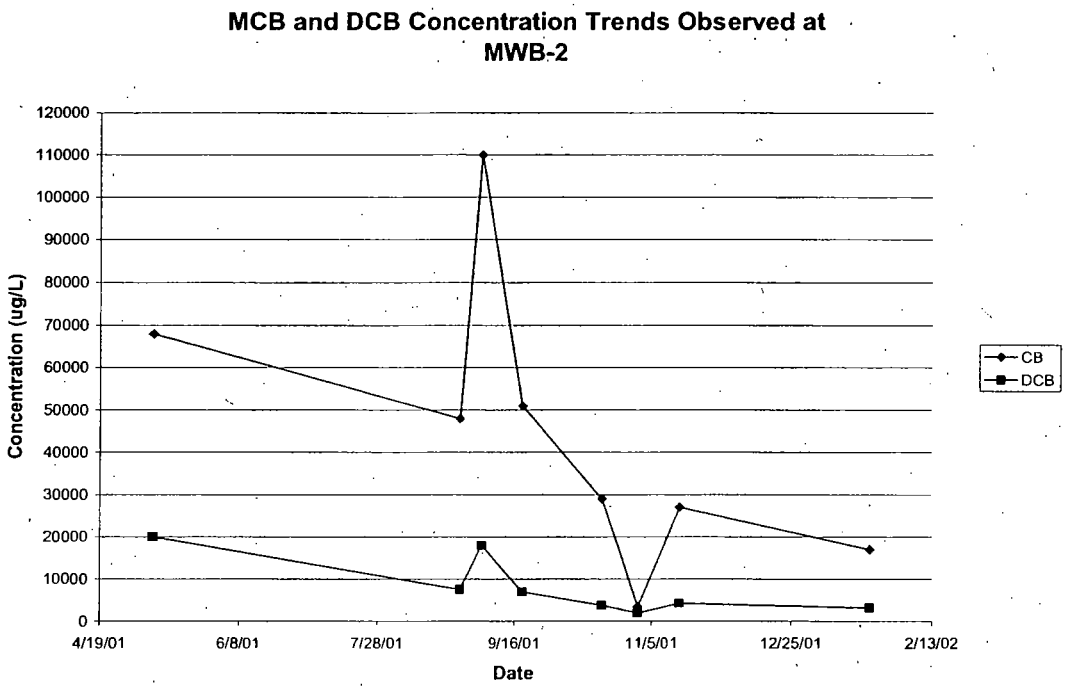


FIGURE 2: Pilot Demonstration Well Network, Profile

- The injected $KMnO_4$ was successfully delivered to the formation and distributed throughout the entire treatment area of the pilot demonstration. This is apparent based on the increase in dissolved potassium and manganese concentrations in groundwater samples collected from the monitoring wells, an increase in the specific conductivity of the groundwater at the monitoring locations, and the presence of unreacted $KMnO_4$ at the monitoring locations.
- The $KMnO_4$ was successful in overcoming the natural reductive poise (naturally occurring organic carbon and other sources of oxidant demand in the aquifer). This is evident by the significant increase in oxidation-reduction potential (ORP) throughout the treatment area.
- Evidence of the reaction between permanganate and the target compounds was observed in at least two of the monitoring well locations, as follows: 1) a 92% decrease in MCB concentration at MWB-1; and 2) a 75% decrease in MCB and 84% decrease in 1,2-DCB concentration at MWB-2 (see chart below). However, target compound concentrations in most of the pilot test monitoring wells exhibited stable to fluctuating trends, indicating that the ability of the permanganate to sufficiently react with the target compounds was limited.



CONCLUSIONS

Because the oxidation reaction associated with permanganate is dependant upon both the concentration of the target contaminant and the permanganate concentration (second order reaction), an insufficient concentration of permanganate in the subsurface would diminish its ability to react with the target compounds (Yan, 1998; Urynowicz,

2000). The low solubility of $KMnO_4$ only permitted the injection of a three percent by weight solution. Once injected, the three percent solution was further diluted in the treatment area after mixing with groundwater. This, in turn, appears to have limited the ability to sustain the desired reaction rates throughout the entire treatment area. We believe that the limited reaction between the oxidant and the target compounds can be overcome through the use of an alternate source of permanganate with a much higher solubility. Specifically, sodium permanganate ($NaMnO_4$) has a solubility ranging up to 50 percent by weight. By increasing the strength of the injected permanganate solution, the resulting in-situ permanganate concentrations should reach a point adequate to sustain sufficient reaction with the target compounds throughout the entire treatment area.

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PILOT-SCALE DEMONSTRATION OF IN-PILE THERMAL DESTRUCTION OF CHLOROBENZENE-CONTAMINATED SOIL

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Hugh McLaughlin (Groton, Massachusetts, USA)

ABSTRACT: At the Eastland Woolen Mill Superfund site in Corinna, Maine, decades of textile manufacturing led to contamination of approximately 75,000 cubic yards (57,300 cubic meters) of soil by mono-, di-, and trichlorobenzenes, which were components of the dyes used to add color to wool. In April 2000, Roy F. Weston, Inc. (Weston) completed demolition of the mill buildings, under the direction of the U.S. Army Corps of Engineers (USACE) pursuant to an Interagency Agreement with USEPA. Weston is now charged with implementing a Non-Time Critical Removal Action (NTCRA). Under the NTCRA, TerraTherm, Inc. performed a pilot test and evaluated the applicability of its In-Pile Thermal Destruction (IPTD) technology for treatment of contaminated soils in an aboveground soil pile. The soils requiring treatment are moist and derived from silty glacial till. TerraTherm's IPTD technology is an ex situ version of In Situ Thermal Destruction (ISTD), by which TerraTherm utilizes simultaneous application of thermal conduction heating and vacuum to treat contaminated soil without excavation. In IPTD, as with ISTD, the applied heat volatilizes both water and organic contaminants within the soil, enabling them to be carried in the air stream toward vacuum extraction wells for destruction within the soil and transfer of the remaining vapor to an air quality control (AQC) unit. It is anticipated that >95% of the contaminant mass will be destroyed in the heated soil.

INTRODUCTION

Eastland Woolen Mill owned and operated a textile mill in Corinna, Maine adjacent to the East Branch of the Sebasticook River between 1936 and 1996. Mill operations resulted in the release of chlorinated benzenes. In 1997, the Town of Corinna took title to the property for back taxes, and in 1999 the site was placed on the USEPA's National Priority List (NPL), designating it a Superfund Site. Under the direction of the U.S. Army Corps of Engineers (USACE), Roy F. Weston Inc., (Weston), pursuant to an Interagency Agreement with USEPA Region 1, completed demolition of the mill buildings in 2000. The major contaminants present in soils at the site are mono-, di-, and tri-chlorobenzenes. Table 1 provides a summary of the contaminants of concern, the observed range of concentrations, and their boiling points. The soils requiring treatment are moist and derived from silty glacial till excavated from locations next to the river.

Weston is currently implementing a Non-Time Critical Removal Action (NTCRA) for the Eastland Woolen Mill. Under the NTCRA, TerraTherm, Inc. performed a pilot test and evaluated the applicability of its In-Pile Thermal Destruction (IPTD) technology for treatment of the contaminated soils and sediments. TerraTherm's IPTD technology is an ex situ version of In Situ Thermal Destruction (ISTD), by which TerraTherm utilizes simultaneous application of thermal conduction

heating and vacuum to treat contaminated soil without excavation. In IPTD, as with ISTD, the applied heat volatilizes both water and organic contaminants within the soil, enabling them to be carried in the air stream toward thermal vacuum extraction wells for destruction within the soil and transfer of the remaining vapor to an air quality control (AQC) unit. It is anticipated that >95% of the contaminant mass will be destroyed in the heated soil.

TABLE 1. General Characteristics of Soil and Remedial Goals of Contaminants of Concern (COCs) at Eastland Woolen Mill, Corinna, Maine

Compound	Boiling Point (°C)	Stockpiled Soil Requiring Treatment			Pilot Test Soil Avg (ug/kg)	Cleanup Objective (ug/kg)
		Avg (ug/kg)	Maximum (ug/kg)	Minimum (ug/kg)		
Benzene	80.1	50	88	17 U	<53	30
Chlorobenzene	132.0	2,500	32,000	34 U	716	1,000
1,2-Dichlorobenzene	180.5	12,560	140,000	34 U	3,942	6,000
1,3-Dichlorobenzene	173.0	740	6,600	35 U	176	6,000
1,4-Dichlorobenzene	174.0	8,920	65,000	34 U	3,345	2,000
1,2,3-Trichlorobenzene	221.0	20,040	190,000	68 U	7,714	----
1,2,4-Trichlorobenzene	213.5	66,630	620,000	190	20,000	5,000

Source of BPs: Weast et al., 1985.
U indicates non-detect result. Result reported is the laboratory quantitation limit.

IPTD CONCEPT FOR EASTLAND WOOLEN MILL

TerraTherm's concept for using IPTD to treat the soils at the Eastland Woolen Mill (patents pending) would be to construct a series of rectangular soil piles, approximately 30 feet wide, 120 feet long and 12 feet high (10 m x 40 m x 4 m) on a liner placed on the concrete floor that remains of the former mill building. The fixed IPTD facility would be capable of treating many batches of soil. Figure 1 presents a conceptual cross-section through one of the soil piles. The end walls of the soil pile would consist of buttressed concrete slabs. A leachate collection system, consisting of a layer of gravel, collection pipes, and a liner would be installed beneath each soil pile prior to construction of the soil pile. This would allow removal and treatment of any drainage prior to treatment. The soil would be placed between the end walls and the surface sloped to maintain stability and covered with a temporary insulating cap and infiltration barrier. The soil pile would be constructed in lifts with the heating wells, heater/vacuum wells, and air intake wells installed as the lifts are placed.

Heat and vacuum would be applied simultaneously to the soil using an array of horizontal heater and heater/vacuum wells running the length of the soil pile (see Figure 1). A 30-foot wide by 12-foot high (10 m x 4 m) soil pile configuration would include 12 heater wells and 4 heater/vacuum wells arrayed in a triangular grid (see Figure 1). Each soil pile would also include an air-inlet well located in the center of the pile to provide a source of oxygen and to promote the migration of vapors through the pile to the heater/vacuum wells located at the outer corners of the pile (see Figure 1). Depending on the desired total IPTD treatment time (heat-up plus treatment), the spacing between the wells would typically be between 3 and 4 feet (0.9 and 1.2 m). The conceptual design for the Eastland Woolen Mill included a 4-foot (1.2 m) spacing between heater and heater/vacuum wells. With this spacing, the time to reach the desired treatment

temperatures (>150°C or >302°F) was estimated to be approximately 30 days (see below). Thermocouples and pressure transducers placed in the soil would track the progress of heating and the off-gas would be treated in an AQC unit consisting of a heat exchanger, condensate knockout, extraction blower, dry scrubber media and dual granular activated carbon (GAC) beds. Emissions from the AQC would be monitored during treatment. This conceptual full-scale treatment design was designed and evaluated by TerraTherm but not submitted to Weston and USACE for evaluation/consideration for use at the Eastland Woolen Mill Superfund site.

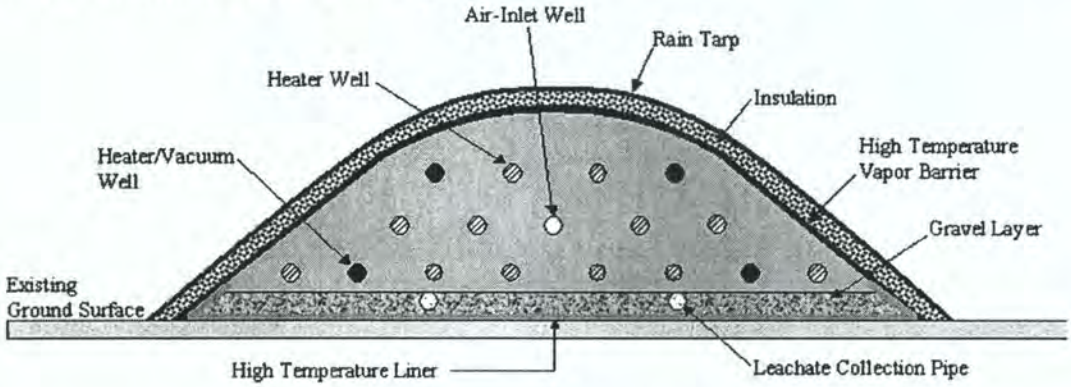

FIGURE 1. Conceptual Cross-Section Through IPTD System.

TARGET TREATMENT TEMPERATURES

The target treatment temperature was selected by considering: (1) the boiling points of the COCs (see Table 1), (2) ISTD processes, (3) the remedial goals, and (4) the desired treatment time. Based on boiling points alone, a temperature of 213.5°C (the highest boiling point of the COCs) would be required to boil off all of the primary COCs. Morever, in-situ distillation and steam stripping processes can result in significant removal of volatile and semivolatile organic compounds at temperatures around 100°C. For example, the boiling points of pure water and chlorobenzene are 100°C and 132°C, respectively. However, a mixture of water and chlorobenzene (present as non-aqueous phase liquid [NAPL] would boil at 90.2°C (i.e., the eutectic temperature of the azeotropic mixture) and the vapor would contain 71.6 percent by weight of chlorobenzene.

Theoretically, based on consideration of distillation and stream stripping processes alone, attaining 100°C in the coldest portions of the soil pile should result in sufficient treatment. However, potential non-uniform vapor flow through the soil pile and resulting mass transfer limitations could prevent attaining the cleanup goals uniformly throughout the soil pile. Thus, in order to ensure uniform treatment, a minimum target treatment temperature of 150°C was selected (i.e., the minimum temperature the coolest regions of the soil pile would attain). Experience from past ISTD projects indicates that after the water is boiled off, the superheated soil becomes desiccated, increasing its gas permeability by several orders of magnitude. In addition, at superheated temperatures below the boiling points of the COCs, their vapor pressures will rise sufficiently (e.g., to > 100 mm Hg) to ensure their rapid desorption from the soil matrix. Past research and field experience with other high-boiling compounds such as PCBs and PAHs (Stegemeier and Vinegar, 2001) suggests that the COCs at the Corinna

site will be completely removed after several days of the coolest portions of the soil volume having achieved 150°C.

Based on analytical modeling TerraTherm has conducted, adopting conservative input parameters for soil properties, it was expected that a target temperature of 150°C would be achieved throughout the soil pile within 30 days of heating with a 4-foot (1.2 m) spacing between thermal wells. The majority of the soil volume would have achieved considerably higher temperatures by that time, with maximum soil temperatures near the heaters approaching 700°C. Past research indicates that typically 95-99% of the contaminant mass is destroyed as the vapors are drawn through superheated soil in proximity to the heater-vacuum wells (Stegemeier and Vinegar 2001; Baker and Bierschenk, 2001).

PILOT TEST SETUP AND OBJECTIVES

In order to evaluate the applicability of TerraTherm's IPTD system to treat soils at the Eastland Woolen Mill, a pilot-scale test was conducted in two 55-gallon (208 L) drums located at the mill (see Figure 2). Band heaters were installed around the outside of the drums to simulate the heating from a thermal well. Drum 1 was filled with contaminated soil from the stockpiled soil requiring treatment and Drum 2 contained clean "cutback soil" excavated to access the contaminated soil.

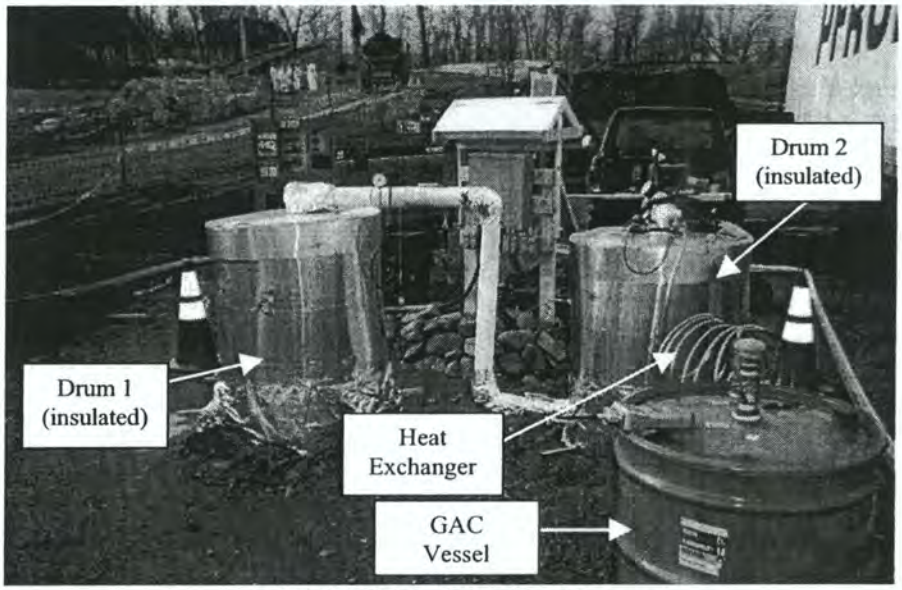

FIGURE 2. Pilot Test Layout

During the treatment phase of the pilot test the drums were connected in series with clean air entering Drum 1 and the vapors flowing from Drum 1, through Drum 2, and then on to the AQC unit (see Figure 2). The second drum was pre-heated to the target treatment temperature prior to initiating heating of the first drum.

The objectives of the pilot test were as follows: (1) Evaluate whether the soil in the pre-heated drum, representing a treated soil pile, could serve as an effective vapor pre-treatment medium while ending up with COC concentrations that achieve soil

cleanup objectives, i.e., showing that contaminants are not merely transferred from the contaminated soil to the clean soil; (2) Determine if the exhaust from the pre-heated soil drum has low levels of emissions; and, (3) Determine that emissions from the GAC drum are consistent with attainment of Maine Ambient Air Guidelines (MAAGs) at the fenceline.

Thermocouples were installed within the soil contained in each drum, one adjacent to the circumference of the drums in proximity to the band heaters, and one in the center of the drums which, being farthest from the band heaters, were the last locations to heat up. Data from the thermocouples therefore bracketed the range of soil temperatures experienced in the drums. Pre-treatment sampling of the soil designated for each drum was conducted and a composite sample from each drum was submitted to a USACE-certified lab for the following analyses: (1) Polychlorinated Dibenzo-Dioxins and Furans (PCDD/Fs) by EPA Method 8290, (2) DRO analysis by Method ME 4.1.25, and (3) Total Organic Carbon (TOC). In addition, 5 discrete soil samples from each drum were collected and submitted to an on-site lab, for volatile organic compounds (VOC) analyses of the soil by Modified EPA Method 8021B and soil moisture content analyses by EPA Method 160.3.

PILOT TEST OPERATION

Drum 2 was heated until its central thermocouple achieved a temperature of 150°C. This temperature represented soil in the cooler, interwell regions of a fully-heated soil pile. By this time, superheated soil in the proximity of the band heaters was considerably hotter. A source of fresh air was supplied to Drum 2 during pre-heating of the clean soil. The exhaust from Drum 2 was piped to an AQC system, which consisted of a small air-to-air heat exchanger and a 55-gal (208 L) drum of GAC. It took approximately 30 hours to pre-heat Drum 2 to the target temperature. Drum 1 was then connected between the air supply and the inlet port of Drum 2, and heating of Drum 1 began. As before, the exhaust from Drum 2 was piped to the AQC system. Vapor samples were collected from the inlet and outlet of Drum 2 and from the GAC discharge two times per day, over a 2-day heating period, for a total of 12 vapor samples. These samples were analyzed for VOCs by Modified EPA Method TO-15. After the target temperature of 150°C was maintained for approximately 24 hours in Drum 1, the heaters were shut off, the piping disconnected, and representative composite soil samples were collected from each drum. These samples were analyzed at a USACE-certified analytical laboratory for PCDD/Fs by EPA Method 8290. TerraTherm also submitted 5 discrete soil samples from each drum to an on-site lab, which conducted VOC analyses of the soil by Modified EPA Method 8021B and soil moisture content analyses by EPA Method 160.3.

PILOT TEST RESULTS

Figure 3 shows the temperature data collected from Drum 1 and 2 during the pilot test. There are several notable interactions evidenced in Figure 3, which will be individually discussed. First, Drum 1 (which was the drum containing the contaminated soil) was not heated until Drum 2 was preheated sufficiently. As such, Drum 1 heating began shortly after noon (10/30 12:00 PM on the temperature figures) on the second day of the pilot test. Following the preheating of Drum 2, the internal temperatures of

Drum 1 gradually increased over the first 18 hours, followed by the "steam drive" at 100°C (212°F), where the soil-bound water was driven off. The initial high temperatures exiting Drum 1 (D1 out) was attributed to a cartridge heater present in the exit of the Drum 1 line, which was intended to simulate the effect of the heater element in the vacuum well. The cartridge heater failed during the second day of operation, as indicated by the lower temperatures in the "D1 out" vapor stream later in the pilot test.

The temperature history of Drum 2 shows the relatively rapid heating of the drum initially, followed by the prolonged period of steam drive (see Figure 3). It is likely that the edge of the drum was desiccating ahead of the center, since the heat was provided by band heaters on the circumference of the drum at three heights.

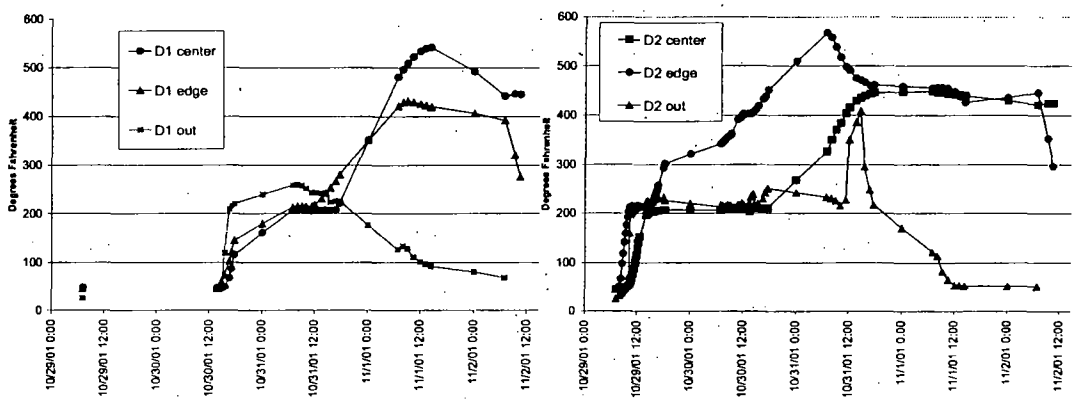

FIGURE 3. Temperature Histories for Drums 1 and 2

Figure 3 also shows an interesting temperature spike in the "D2 out" occurring the afternoon of 10/31, followed by a relatively rapid temperature decrease. This phenomenon is attributed to the effect of the stream drive from Drum 1 passing through Drum 2 and becoming superheated by the high temperatures in Drum 2. When the steam drive from Drum 1 ceased, the total vapor flow through Drum 2 decreased rapidly and the heat losses from the piping to the surroundings resulted in the cooler temperatures observed later in the Drum Test.

Figure 4 compares the level of chlorinated benzenes in the soils used in the test drums before and after the Drum Test. As expected, Drum 1 contained elevated levels of chlorinated benzenes, with a total of over 35,000 ppb of chlorinated benzenes. Prior to the Drum Test, even Drum 2 (filled with "cutback soil") measured roughly 2% of the level in Drum 1. After the Drum test, Drum 1 contained less than 1% of the starting level of aromatics and Drum 2 was non-detect for all analytical tests. It is apparent that the conditions utilized during the Drum Test are effective at removing the chlorinated benzenes from the soil matrix in the test drums. Figure 4 also shows the levels of dioxins in the soils before and after the pilot test, in addition to the "Pre Drum 2" level of furans for comparison to the dioxin levels. These data indicate that dioxins were not generated during the heating of the soil in Drum 1 or Drum 2. Moreover, the levels of dioxins/furans in the pre-treatment soil samples were below the soil standard of 1 ppb TEQ. As discussed above, the starting material in Drum 1 contained elevated levels of chlorinated benzenes. Figure 5 shows the measured levels of tri- and dichlorobenzenes

after Drum 1 and after Drum 2 in the vapor phase during the pilot test (note that the start of Drum 1 heating is the starting point of the x axis of Figure 5). The vapor phase levels exiting the GAC canister are not shown, since all but one data point was "below reportable limits" of the analytical method and the concentration of the one "hit" represented a 99.8% removal efficiency. Data presented in Figure 5 present a consistent pattern in that Drum 2 did not effectively remove the chlorinated benzenes, once volatized from Drum 1. In contrast, the GAC treatment of the cooled vapor stream was shown to be highly effective.

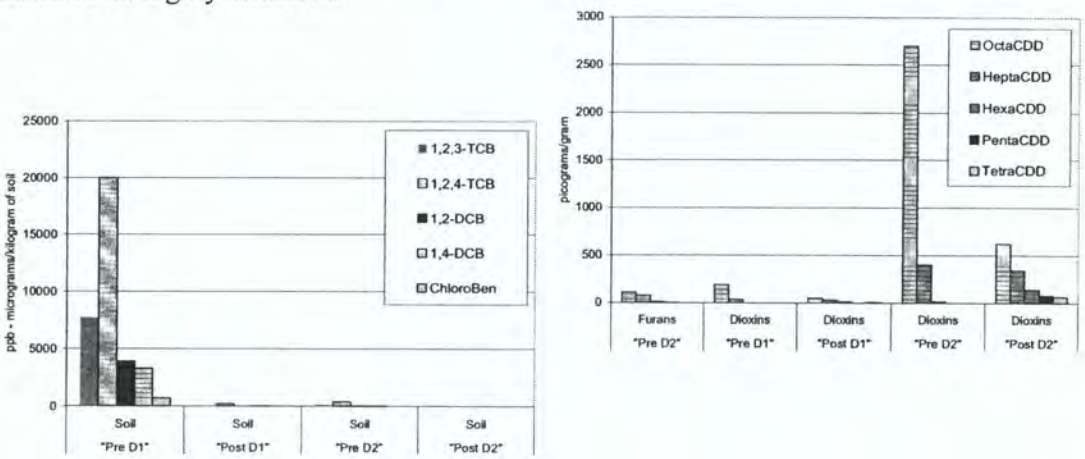

FIGURE 4. Pre- and Post-Treatment Concentrations of Chlorinated Benzenes and PCDD/Fs

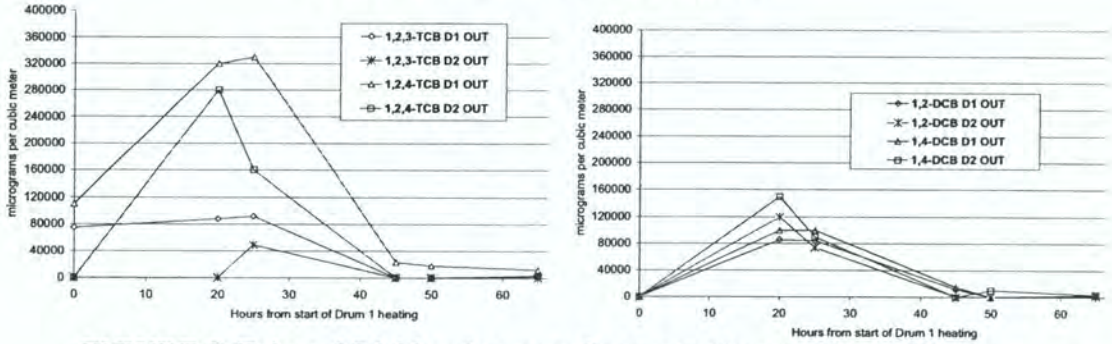

FIGURE 5. Tri- and Dichlorobenzene Concentrations in Vapor Phase

DISCUSSION

A mass balance performed on the data from the pilot test indicates that 60 to 75 percent of the original chlorobenzenes were destroyed by IPTD. The majority of the destruction likely occurred in Drum 1 after the steam drive. The chlorinated benzenes that were steam stripped from Drum 1 during the steam drive were largely transported through Drum 2 and removed effectively by the GAC canister. The 95-99% of the contaminant mass that is typically destroyed within the soil during ISTD and IPTD is attributable to the slow passage of contaminant vapors through superheated soil in the proximity of operating heater-vacuum wells, prior to the collection of the gas from the soil for aboveground treatment (Stegemeier and Vinegar 2001). Soil temperatures in the

proximity of heater-vacuum wells are generally in the 400-500°C range. By contrast, the use of the band heaters around the circumference of Drum 2 and the lack of a heater-vacuum well within Drum 2 limited the maximum soil temperature to ~230°C, thereby also limiting the amount of in-soil destruction that could occur there. Baker and Bierschenk (2001), summarizing the work of Kuhlman (2001), report that for polycyclic aromatic hydrocarbons heated to 230°C, pyrolysis is too slow to result in significant amounts of destruction. Oxidation rates, while higher, are still orders of magnitude slower within soil at 230°C than would occur at 400-500°C. Although we lack similar data for chlorobenzenes, the same trends can be expected.

SUMMARY

The pilot test indicated that TerraTherm's IPTD technology is potentially capable of removing chlorinated benzenes from the soils at the Eastland Woolen Mill site and ultimately meeting the remedial target soil concentrations. In addition, vapor emissions from the GAC drum were below the method detection limits for all but one sample, indicating that TerraTherm's IPTD would be capable of attaining the Maine Ambient Air Guidelines (MAAGs) at the fenceline. Although the overall performance of the pilot test was promising, design and operational limitations prevented a true evaluation of the feasibility and effectiveness of using a heated/treated soil pile for pre-treatment of the vapors. The pilot test did demonstrate that in situ distillation and steam stripping processes can effectively remove chlorinated benzenes at temperatures below their boiling points. It is believed that if the vapors produced during the distillation and steam stripping phase were to have passed through a typical superheated region around a heater/vacuum well (soil temperatures of 400-500°C), very high in-situ destruction efficiencies (e.g., 95-99%) would have occurred. In addition, comparison of the pre- and post-treatment 2,3,7,8-tetrachloro-dibenzodioxin toxicity equivalent (TEQ) data indicated that IPTD did not create dioxins during the course of the pilot test.

ACKNOWLEDGMENTS

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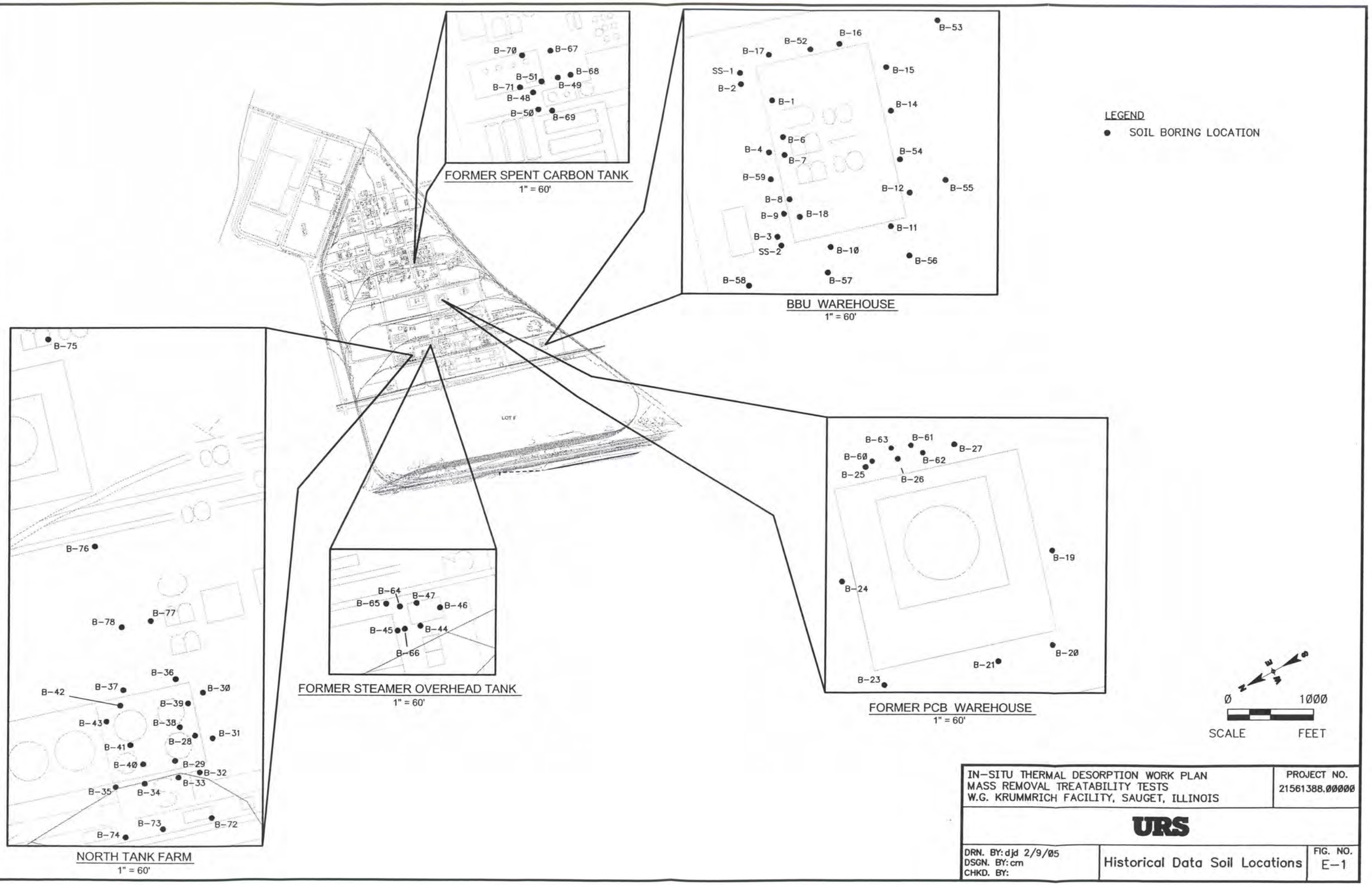
EVS MCB/DCB DATA SET



IN-SITU THERMAL DESORPTION WORK PLAN MASS REMOVAL TREATABILITY TESTS W.G. KRUMMRICH FACILITY, SAUGET, ILLINOIS	PROJECT NO. 21561388.00000
URS	
DRN. BY: djd 2/9/05 DSGN. BY: cm CHKD. BY:	Historical Data Soil Locations — FIG. NO. E-1

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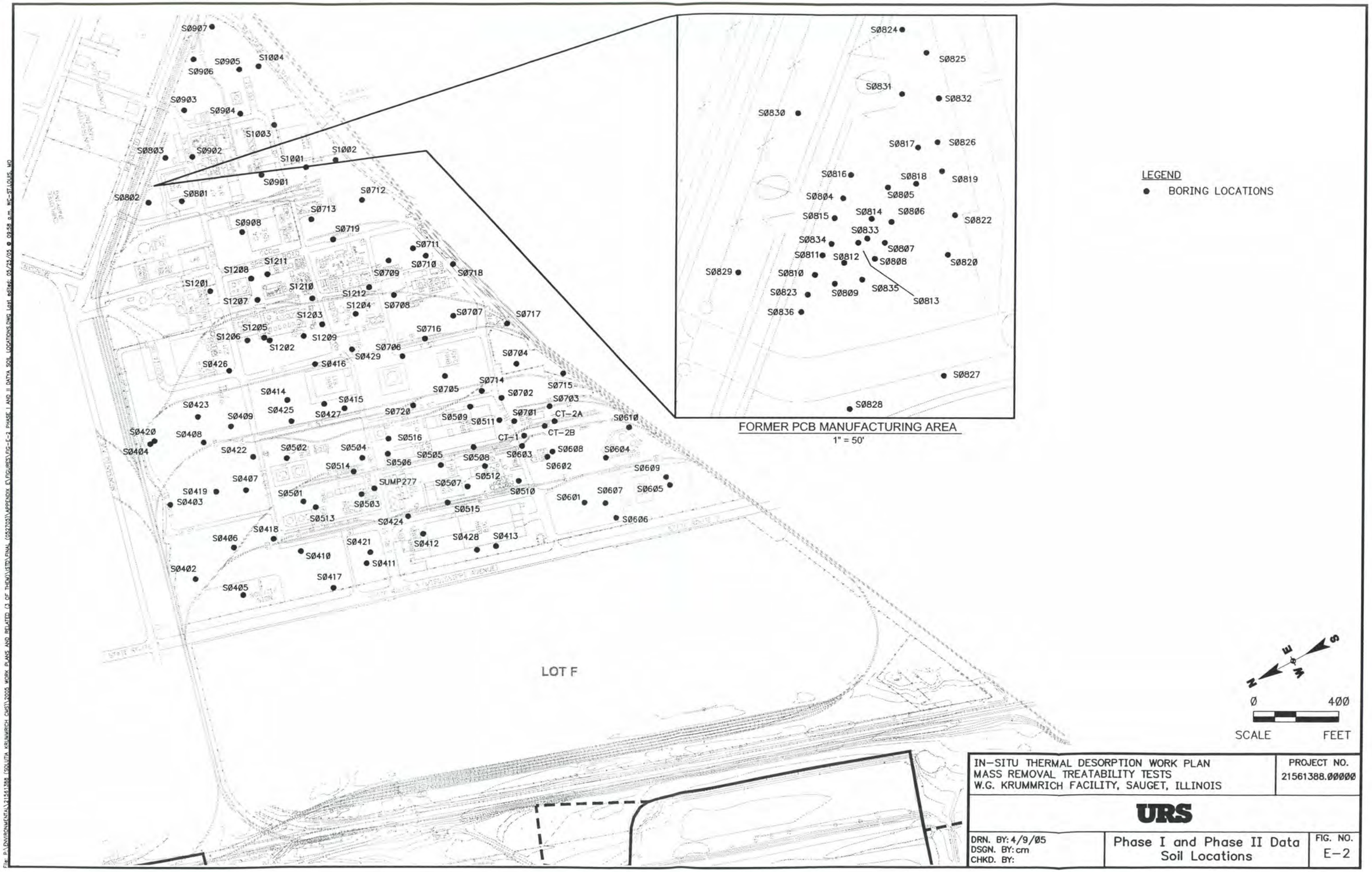

IN-SITU THERMAL DESORPTION WORK PLAN MASS REMOVAL TREATABILITY TESTS W.G. KRUMMRICH FACILITY, SAUGET, ILLINOIS	PROJECT NO. 21561388.00000
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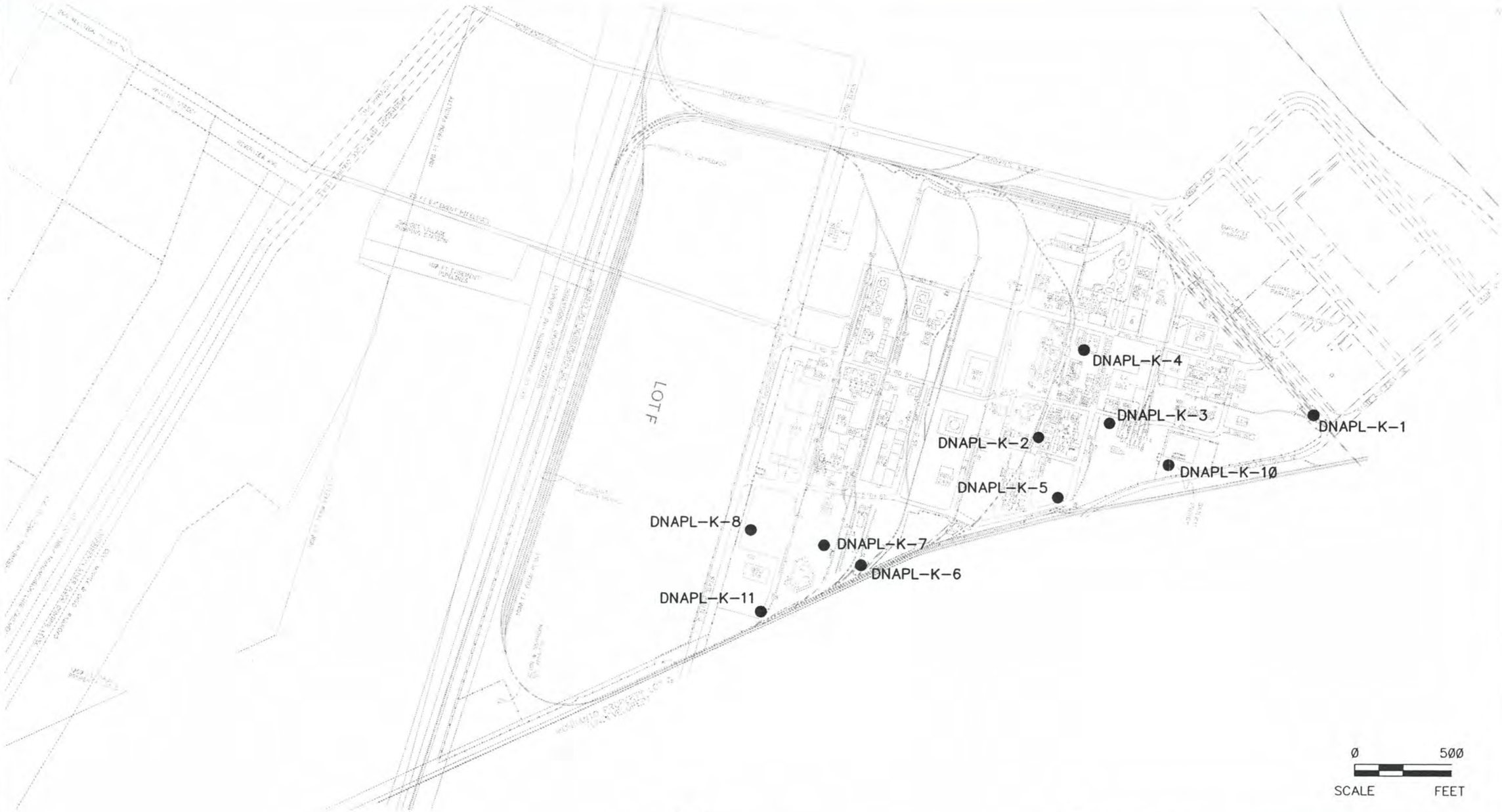
DRN. BY: 4/9/05 DSGN. BY: cm CHKD. BY:	Phase I and Phase II Data Soil Locations
	FIG. NO. E-2



LEGEND

● SOIL BORING LOCATION

IN-SITU THERMAL DESORPTION WORK PLAN MASS REMOVAL TREATABILITY TESTS W.G. KRUMMRICH FACILITY, SAUGET, ILLINOIS	PROJECT NO. 21561388.00000

URS

DRN. BY: 4/9/05 DSGN. BY: cm CHKD. BY:	DNAPL Data Soil Locations	FIG. NO. E-3

APPENDIX E
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 3.1 THROUGH 3.6

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
Historical Boring Data Soil Locations (see Figure E-1)					
BBUB1	2294404	701824	7	0.071	<1
BBUB10	2294295	701836	7	0.094	0.58
BBUB11	2294288	701792	7	<1	<1
BBUB12	2294302	701770	7	<1	<1
BBUB14	2294359	701755	7	0.034	<1
BBUB15	2294388	701743	6	<1	0.9
BBUB16	2294417	701764	5	0.0096	<1
BBUB17	2294433	701811	4	0.0059	<1
BBUB18	2294323	701845	3	0.013	9.8
BBUB18	2294323	701845	6	20	90
BBUB2	2294424	701838	5	0.028	<1
BBUB3	2294318	701865	5	<1	21.8
BBUB3	2294318	701865	7	0.16	0.46
BBUB4	2294373	701843	7	0.05	<1
BBUB52	2294424.6	701782.9	2.25	<1	N.A.
BBUB52	2294424.6	701782.9	3.75	N.A.	<1
BBUB52	2294424.6	701782.9	15	<1	<1
BBUB53	2294400	701696	2.25	<1	N.A.
BBUB53	2294400	701696	3.25	N.A.	15
BBUB53	2294400	701696	12	N.A.	<1
BBUB53	2294400	701696	13.25	0.005	N.A.
BBUB54	2294325.98	701765.11	2.25	<1	N.A.
BBUB54	2294325.98	701765.11	3	N.A.	34.3
BBUB54	2294325.98	701765.11	13	0.19	<1
BBUB55	2294298.53	701743.92	3	<1	57.23
BBUB55	2294298.53	701743.92	7	<1	0.8
BBUB56	2294262.2	701790.5	3	<1	<1
BBUB56	2294262.2	701790.5	5	0.67	0.65
BBUB57	2294278.9	701846.1	3	71	480
BBUB57	2294278.9	701846.1	8.5	0.7	<1
BBUB58	2294296.7	701899.2	3.5	<1	14.3
BBUB58	2294296.7	701899.2	7.5	<1	<1
BBUB59	2294355.6	701850.8	3	0.54	410
BBUB59	2294355.6	701850.8	7	0.64	<1
BBUB6	2294378	701829	7	0.034	<1
BBUB7	2294366	701834	7	0.071	<1
BBUB8	2294337	701845	7	19	<1
BBUB9	2294330	701854	7	0.21	<1
BBUNEEntrance	2294431	701834	6	<1	<1
BBUNWEntrance	2294312	701865	6	0.025	11
KR/BC34	2294937	703206	5	240	73
KR/BCB29	2294941	703180	7	22	5.4

Notes:
1) <1 ppm indicates sample results was below the lowest concentration depicted on the figure. N.A. indicates the sample was not analyzed for that constituent.
2) ft bgs = feet below ground surface

APPENDIX E
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 3.1 THROUGH 3.6

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
Historical Boring Data Soil Locations (see Figure E-1)					
KR/BCB30	2294974	703141	5	56	21
KR/BCB31	2294943	703150	3	0.47	3.1
KR/BCB32	2294926	703169	3	38	3.04
KR/BCB33	2294930	703184	7	30	4.4
KR/BCB35	2294944	703224	3	210	7.5
KR/BCB36	2294991	703153	1	<1	0.95
KR/BCB36	2294991	703153	7	26	9.3
KR/BCB37	2295001	703188	3	200	23
KR/BCB38	2294960	703166	5	500	98
KR/BCB39	2294972	703154	5	240	30.5
KR/BCB40	2294949	703201	1	500	59
KR/BCB40	2294949	703201	7	1000	54.4
KR/BCB41	2294965	703202	5	38	245
KR/BCB42	2294993	703195	3	360	58
KR/BCB43	2294988	703208	5	12	19
KRBCB28	2294950	703160	7	420	3.4
NTFB72	2294892.2	703176.8	5	0.52	<1
NTFB73	2294902.1	703210.2	3	13	<1
NTFB73	2294902.1	703210.2	7	25	<1
NTFB74	2294908.4	703234.8	3	30000	2.97
NTFB74	2294908.4	703234.8	7	210	<1
NTFB75	2295244.3	703115.9	1	410	<1
NTFB76	2295099.4	703159	1	2.4	<1
NTFB77	2295035.5	703149.4	1	150	42.9
NTFB78	2295041.3	703168	2.5	1.4	0.83
PCBB19	2295339	702516	5	<1	<1
PCBB20	2295281	702546	5	0.09	<1
PCBB21	2295289	702585	5	<1	<1
PCBB23	2295311	702662	5	0.02	<1
PCBB24	2295388	702655	7	0.019	<1
PCBB25	2295451	702603	5	0.0094	<1
PCBB26	2295446	702581	3	<1	4000
PCBB27	2295436	702542	5	0.05	<1
PCBB60	2295453	702597	1	N.A.	<1
PCBB60	2295453	702597	5	N.A.	<1
PCBB61	2295450	702568	1	N.A.	<1
PCBB61	2295450	702568	5	N.A.	<1
PCBB62	2295441	702563	3	N.A.	<1
PCBB62	2295441	702563	7	N.A.	<1
PCBB63	2295455	702581	4.5	N.A.	47.98
SCTB48	2295942	702627	3	1500	104
SCTB48	2295942	702627	9	5200	930

Notes:

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APPENDIX E
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 3.1 THROUGH 3.6

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
Historical Boring Data Soil Locations (see Figure E-1)					
SCTB49	2295944	702607	5	1.1	<1
SCTB50	2295930	702629	7	24	3.7
SCTB51	2295947	702618	7	7900	153
SCTB67	2295963.5	702603.2	11	23000	296.1
SCTB68	2295941.8	702598.9	3	0.013	0.24
SCTB68	2295941.8	702598.9	5	790	9.65
SCTB69	2295925.6	702621.5	3	1.9	<1
SCTB69	2295925.6	702621.5	7	110	3.9
SCTB70	2295969.6	702621.4	7	800	54.75
SCTB71	2295949.6	702632.5	7	2000	31.22
SOTB44	2295013	702910	5	0.2	1.27
SOTB45	2295018	702925	5	<1	<1
SOTB46	2295018	702892	5	0.52	<1
SOTB47	2295028	702905	3	0.012	<1
SOTB64	2295029.1	702911.6	7	<1	N.A.
SOTB64	2295029.1	702911.6	13	<1	N.A.
SOTB65	2295034.8	702918.6	3	0.84	N.A.
SOTB65	2295034.8	702918.6	13	0.3	N.A.
SOTB66	2295014.9	702915.6	3	0.23	N.A.
Phase I and Phase II Data Soil Locations (see Figure E-2)					
CT11	2294846	702177.1	14	<1	<1
CT12	2294846	702177.1	1	0.0091	<1
CT2a1	2294840	702068.2	14	1.4	<1
CT2b1	2294838.9	702067.6	14	<1	<1
S0402	2294970.5	703836.7	14	<1	<1
S0403	2295334.7	703775.6	3	<1	<1
S0404	2295630.5	703722.8	14	<1	<1
S0405	2294797.5	703674.6	3	<1	<1
S0406	2295014.9	703608.4	11	<1	<1
S0407	2295225.7	703432	13	0.2	<1
S0408	2295522.8	703501.4	7	90	<1
S0409	2295526.4	703352.8	11	0.46	<1
S0410	2294853.5	703343.8	14	0.062	<1
S0411	2294657.3	703101.7	15	0.025	<1
S0412	2294653.9	702803	14	<1	<1
S0413	2294445.2	702533.3	11	390	<1
S0414	2295513.7	703063.7	5	<1	0.55
S0415	2295353.6	702848.8	13	<1	<1
S0416	2295603.5	702872.8	4	0.013	1.2
S0417	2294630.6	703291.8	1.5	<1	<1
S0417	2294630.6	703291.8	11	<1	<1
S0417	2294630.6	703291.8	15	<1	<1

Notes:

1) <1 ppm indicates sample results was below the lowest concentration depicted on the figure. N.A. indicates the sample was not analyzed for that constituent.

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APPENDIX E
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 3.1 THROUGH 3.6

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
Phase I and Phase II Data Soil Locations (see Figure E-2)					
S0418	2294963.4	703427.5	1.5	<1	<1
S0418	2294963.4	703427.5	10	<1	<1
S0418	2294963.4	703427.5	15	<1	<1
S0419	2295285.7	703558.8	1	<1	<1
S0419	2295285.7	703558.8	11	<1	<1
S0419	2295285.7	703558.8	15	<1	<1
S0420	2295633.6	703700.3	1	<1	<1
S0420	2295633.6	703700.3	7	<1	<1
S0420	2295633.6	703700.3	15	<1	<1
S0421	2294695	703061.6	1.5	<1	<1
S0421	2294695	703061.6	7	<1	<1
S0421	2294695	703061.6	15	<1	<1
S0422	2295350.2	703328.8	1	<1	<1
S0422	2295350.2	703328.8	11	<1	<1
S0422	2295350.2	703328.8	15	<1	<1
S0423	2295640.9	703469.4	1	<1	<1
S0423	2295640.9	703469.4	11	0.092	<1
S0424	2294760.8	702827	1	<1	<1
S0424	2294760.8	702827	7	<1	<1
S0424	2294760.8	702827	15	<1	<1
S0425	2295415.8	703094.1	1	<1	<1
S0425	2295415.8	703094.1	7	<1	<1
S0425	2295415.8	703094.1	15	<1	<1
S0426	2295763.7	703235.9	2	<1	<1
S0426	2295763.7	703235.9	11	8.9	<1
S0426	2295763.7	703235.9	15	0.74	<1
S0427	2295416.8	702923.4	1	<1	<1
S0427	2295416.8	702923.4	5	0.059	<1
S0427	2295416.8	702923.4	15	0.13	<1
S0428	2294470.4	702619	2	0.19	<1
S0428	2294470.4	702619	7	1100	<1
S0428	2294470.4	702619	15	810	<1
S0429	2295583.2	702688.6	2	0.0054	<1
S0429	2295583.2	702688.6	7	0.02	<1
S0429	2295583.2	702688.6	15	0.022	<1
S0501	2295053.5	703224.4	12	0.17	<1
S0502	2295271.7	703195.7	7	560	<1
S0503	2294955.9	702969	9	<1	<1
S0504	2295106.1	702885.6	14	<1	<1
S0505	2294902.3	702579.5	11	<1	<1
S0506	2295066.8	702773.3	14	<1	<1
S0507	2294754.1	702518.1	11	0.012	<1

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APPENDIX E
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 3.1 THROUGH 3.6

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
Phase I and Phase II Data Soil Locations (see Figure E-2)					
S0508	2294906.7	702406.1	14	0.033	<1
S0509	2295081.7	702331.6	4	<1	<1
S0510	2294665.8	702297.4	7	0.007	<1
S0511	2294963.3	702241.7	9	<1	<1
S0512	2294802.6	702402.9	2	0.063	<1
S0512	2294802.6	702402.9	11	32	<1
S0512	2294802.6	702402.9	15	0.89	<1
S0513	2295002.6	703187	2	4.5	10
S0513	2295002.6	703187	9	10	<1
S0513	2295002.6	703187	15	2.4	<1
S0514	2295068	702952.4	2	<1	<1
S0514	2295068	702952.4	6	<1	<1
S0514	2295068	702952.4	15	0.041	<1
S0515	2294730.6	702634.2	2	<1	<1
S0515	2294730.6	702634.2	11	<1	<1
S0515	2294730.6	702634.2	15	<1	<1
S0516	2295128.8	702736.5	2	<1	<1
S0516	2295128.8	702736.5	7.5	<1	<1
S0516	2295128.8	702736.5	15	0.23	<1
S05SMP27701	2294951.5	702905.2	2	<1	<1
S05SMP27701	2294951.5	702905.2	10	0.54	<1
S05SMP27701	2294951.5	702905.2	15	1.9	<1
S0601	2294430.5	702072.6	9	0.68	<1
S0602	2294702.7	702125.2	7	36	1.4
S0603	2294805.5	702205.4	7	0.006	<1
S0604	2294570.2	701885.5	15	5.3	<1
S0605	2294315.4	701683.9	14	<1	<1
S0606	2294296.5	701975.6	2	0.21	<1
S0606	2294296.5	701975.6	7	0.54	<1
S0606	2294296.5	701975.6	15	0.32	<1
S0607	2294381.7	701988	2	<1	3.6
S0607	2294381.7	701988	10	1.4	<1
S0607	2294381.7	701988	15	5.1	<1
S0608	2294713.9	702092.3	2	0.69	0.43
S0608	2294713.9	702092.3	9	0.52	<1
S0608	2294713.9	702092.3	15	0.24	<1
S0609	2294357.7	701681.5	2	0.81	<1
S0609	2294357.7	701681.5	7	18	<1
S0609	2294357.7	701681.5	15	1.2	<1
S0610	2294646.6	701721.8	2	0.32	<1
S0610	2294646.6	701721.8	11	64	<1
S0610	2294646.6	701721.8	15	19000	<1

Notes:

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APPENDIX E
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 3.1 THROUGH 3.6

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
Phase I and Phase II Data Soil Locations (see Figure E-2)					
S0701	2294926.9	702183	7	<1	<1
S0702	2295052.3	702183	4	<1	<1
S0703	2294909.5	702004.1	6	<1	<1
S0704	2295160.1	702043.7	15	29	0.46
S0705	2295267.2	702364.1	3	<1	<1
S0706	2295443.6	702495.9	14	3.9	0.68
S0707	2295496.1	702198.3	3	<1	<1
S0708	2295716.6	702397.1	5	<1	<1
S0709	2295873.5	702341.6	3	<1	0.39
S0710	2295808.3	702178.7	14	<1	58
S0711	2295867.2	702215.2	13	<1	<1
S0712	2296178.5	702321.3	4	0.032	<1
S0713	2296212.4	702569.8	7	3.2	<1
S0714	2295124.6	702249.3	2	<1	<1
S0714	2295124.6	702249.3	11	<1	<1
S0714	2295124.6	702249.3	15	0.039	<1
S0715	2295017.8	701874.6	2	14	0.45
S0715	2295017.8	701874.6	7	58	<1
S0715	2295017.8	701874.6	15	0.0061	<1
S0716	2295465.9	702363.8	2	<1	<1
S0716	2295465.9	702363.8	7	<1	<1
S0716	2295465.9	702363.8	15	0.4	<1
S0717	2295349.5	701996	2	<1	<1
S0717	2295349.5	701996	7	<1	<1
S0717	2295349.5	701996	15	<1	<1
S0718	2295714.1	702086.5	2	<1	<1
S0718	2295714.1	702086.5	11	<1	16.8
S0718	2295714.1	702086.5	15	5.1	0.44
S0719	2296080.7	702524.7	2	2.2	2.6
S0719	2296080.7	702524.7	11	90	4400
S0719	2296080.7	702524.7	15	31	1.99
S0720	2295212.8	702559.7	2	<1	<1
S0720	2295212.8	702559.7	7	<1	<1
S0720	2295212.8	702559.7	15	<1	<1
S0801	2296569.5	703060.9	5	<1	<1
S0801	2296569.5	703060.9	15	0.15	<1
S0802	2296633.5	703196.7	3	1.5	6.6
S0803	2296786.5	703032.1	2	<1	<1
S0901	2296501.6	702674.9	2	<1	<1
S0902	2296730.5	702920.3	10	0.12	<1
S0903	2296742.4	702850.1	11	0.22	<1
S0904	2296801.8	702627.5	7	<1	0.5

Notes:

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APPENDIX E
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 3.1 THROUGH 3.6

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
Phase I and Phase II Data Soil Locations (see Figure E-2)					
S0905	2296990.9	702530.6	2	<1	<1
S0906	2297135.6	702698.3	3	<1	<1
S0907	2297231.5	702548.2	14	0.065	<1
S0908	2296308.9	702878.5	7	<1	<1
S1001	2296439.2	702476.3	3	<1	<1
S1002	2296404	702340.3	4	<1	<1
S1003	2296682.5	702513.8	6	<1	<1
S1003	2296682.5	702513.8	13	<1	<1
S1004	2296961.8	702444.9	7	0.32	<1
S1201	2296136.7	703139.8	5	<1	<1
S1202	2295800.6	703004	8	<1	<1
S1203	2295753.4	702755.4	4	4	<1
S1204	2295722.6	702595.1	7	0.0072	<1
S1205	2295824.5	703019.8	2	0.032	<1
S1205	2295824.5	703019.8	7	0.008	<1
S1205	2295824.5	703019.8	14	<1	<1
S1206	2295849.5	703094	2	<1	<1
S1206	2295849.5	703094	7	<1	<1
S1206	2295849.5	703094	15	0.011	<1
S1207	2295996.3	702693.9	2	0.64	28
S1207	2295996.3	702693.9	9	300	4.3
S1207	2295996.3	702693.9	15	2000	690
S1208	2296097.2	702942.8	2	<1	<1
S1208	2296097.2	702942.8	11	0.15	<1
S1208	2296097.2	702942.8	15	<1	<1
S1210	2295882.7	702738.9	2	0.049	<1
S1210	2295882.7	702738.9	7	0.14	N.A.
S1210	2295882.7	702738.9	15	9.1	1.29
S1211	2296080.3	702867.9	2	<1	<1
S1211	2296080.3	702867.9	9	0.091	<1
S1211	2296080.3	702867.9	15	0.085	<1
S1212	2295803.3	702481.9	1	30	14.38
S1212	2295803.3	702481.9	7	900	227.6
S1212	2295803.3	702481.9	15	540	1.72
S129	2295746	702855.7	2	0.013	<1
S129	2295746	702855.7	9	0.29	<1
S129	2295746	702855.7	15	2.4	<1
DNAPL Data Soil Locations (see Figure E-3)					
K-1	2297228.69	702637.28	9	39	49
K-10	2296495.02	702372.18	9.75	<1	<1
K-11	2294384.23	701602.11	7.25	0.009	<1
K-11	2294384.23	701602.11	14.75	0.014	<1

Notes:

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APPENDIX E
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 3.1 THROUGH 3.6

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
DNAPL Data Soil Locations (see Figure E-3)					
K-2	2295812.71	702516.44	4	<1	<1
K-3	2296185.85	702591.75	9	170	307
K-3	2296185.85	702591.75	14	2300	4330
K-3	2296185.85	702591.75	14	860	6280
K-4	2296048.69	702975.95	9	1600	13850
K-5	2295917.62	702200.89	4	4.9	11.05
K-5	2295917.62	702200.89	14	<1	7.24
K-6	2294900.82	701842.36	9	4.2	0.154
K-6	2294900.82	701842.36	11.5	0.003	0.039
K-7	2294707.90	701947.28	1.5	0.0063	<1
K-7	2294707.90	701947.28	11.5	<1	0.11
K-8	2294328.37	702026.80	6.5	<1	<1

Notes:
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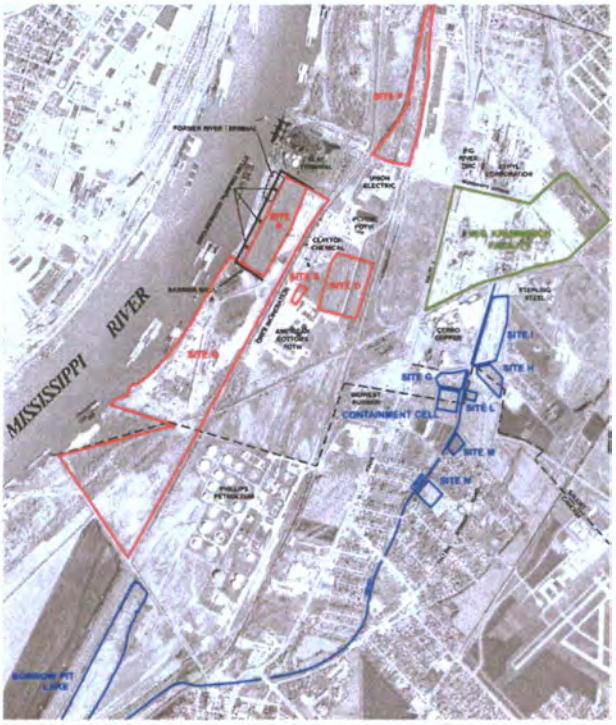
2) ft bgs = feet below ground surface

SOLUTIA - 198-2

ENHANCED AEROBIC BIOREMEDIATION WORK PLAN

MASS REMOVAL TREATABILITY STUDY

SOLUTIA INC. W.G. KRUMMRICH FACILITY



Prepared by:
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St. Louis, Missouri 63141

SOLUTIA

URS

GROUNDWATER SERVICES, INC.

May 2005

ENHANCED AEROBIC BIOREMEDIATION WORK PLAN MASS REMOVAL TREATABILITY TEST

Prepared by:

Solutia Inc.
W.G. Krummrich Facility
Sauget, Illinois

May 27, 2005

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FIGURES

Figure 1.1 Site Location Map
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1.0 INTRODUCTION

On May 3, 2000, USEPA executed a Resource Conservation and Recovery Act (RCRA) 3008(h) Administrative Order on Consent for Solutia Inc.'s W.G. Krummrich facility in Sauget, Illinois (**Figure 1.1**). Solutia Inc. signed the Administrative Order on Consent, Docket No. R8H-5-00-003, on May 26, 2000. Sections VI.1a, 1b, 2, 3 and 5, respectively, required Solutia to submit a Description of Current Conditions Report, investigate the nature and extent of any releases at or from the W.G. Krummrich facility, stabilize groundwater migration and show that any discharge of groundwater to surface water is either insignificant or currently acceptable, control completed pathway human exposures to contamination and propose final corrective measures for the site.

To fulfill the requirements of the AOC Solutia submitted a Description of Current Conditions Report, performed site investigations for air, soil, DNAPL and groundwater, completed Environmental Indicator Determinations for Migration of Contaminated Groundwater under Control (CA750) and Current Human Exposure Under Control (CA725) and submitted a Final Corrective Measures Study as summarized in the following table:

Summary of Work Performed to Fulfill the Requirements of the W.G. Krummrich RCRA AOC (Docket No. R8H-5-00-003)

• Description of Current Conditions Report	August 1, 2000
• Sediment, Surface Water and Fish Tissue Sampling	October and November 2000
• Ecological Risk Assessment	June 1, 2001
• CA750 Migration of Contaminated Groundwater Under Control Environmental Indicator Determination	May 26, 2004
• CA725 Current Human Exposure Under Control Environmental Indicator Determination	May 26, 2004
• Air, Soil, DNAPL and Groundwater Investigation	2003 and 2004
• Corrective Measures Study	August 27, 2004

In addition to these actions, Solutia implemented or planned a number of removal and remedial actions at Sauget Area 1, Sauget Area 2 and the W.G. Krummrich Facility prior to and after the May 26, 2000 RCRA AOC. A time line of the various removal actions and remedial actions and estimated expenditures for each action are given below:

Time Line of Sauget Area 1, Sauget Area 2 and W.G. Krummrich Removal/Remedial Actions and Estimated Expenditures

Sauget Area 1	2001	Dead Creek Culvert Replacement Removal Action	$750,000
	2002	Dead Creek Time Critical Sediment Removal Action	12,300,000
	2004	Dead Creek Segment B, D and F Soil Removal Action Plan	
Sauget Area 2	1979	Site R Capping	
	1985	Site R Riverbank Stabilization	750,000
	2003/4	Groundwater Migration Control System	25,400,000
W.G. Krummrich	1987	Route 3 Drum Site Impermeable Cap	
	2000	Sewer System Improvements	17,100,000
	2001	Chlorobenzene Process Area Spill	
	2003	Plant Process Area Permeable Covers	310,000
		Estimated Total Expenditure	$56,610,000

On November 18, 2004, USEPA issued 51 pages of comments on Volumes I, II and III of the August 27,

2004 W.G. Krummrich RCRA Corrective Measures Study, including 21 general comments and 71 specific comments. In partial response to USEPA's November 18, 2004 comments, Solutia will undertake bench-scale treatability tests to determine whether or not DNAPL mass removal at the Former Chlorobenzene Process Area is technically practicable. These bench-scale treatability tests are designed to provide a yes/no answer as to whether or not it is technically **feasible** to remove contaminant mass in the Former PCB Manufacturing Area and the Former Chlorobenzene Process Area.

In-situ thermal desorption (ISTD) was identified as the best treatment technology for performing bench-scale PCB and Chlorobenzene (MCB) and Dichlorobenzene (DCB) mass removal treatability tests on unsaturated soil samples from the Shallow Hydrogeologic Unit (SHU) at the Former PCB Manufacturing Area and the Former Chlorobenzene Process Area (**Figures 1.1 and 1.2**). Bench-scale EABR treatability tests will be performed on saturated soil from the Middle and Deep Hydrogeologic Units. As directed by USEPA, bench-scale enhanced aerobic biodegradation treatability tests will also be conducted on saturated SHU soils from the Former Chlorobenzene Process Area.

This EABR Work Plan includes the following sections:

- Section 1.0 Introduction
- Section 2.0 MCB DNAPL Mass Removal EABR Treatability Test

2.0 MCB/DCB DNAPL MASS REMOVAL EABR TREATABILITY TEST

2.1 Technology Evaluation and Selection

A literature search was conducted to identify technologies with bench-scale, pilot-scale or full-scale treatability tests of DNAPL-impacted source areas with elevated concentrations of MCB and/or DCB in the saturated zone. The literature search included technical journals, conference proceedings, technical presentations, and Internet databases, such as the EPA Clu-In website. Key findings of the 12 studies identified during this literature search are summarized on **Table 2.1** and the twelve studies are included in **Appendix A**. Surfactant-enhanced solubilization, chemical oxidation, and enhanced aerobic bioremediation were tested in these studies for their potential to treat DNAPL-impacted, saturated-zone source areas with elevated concentrations of MCB and/or DCB. These technologies were evaluated for their potential applicability at the W.G. Krummrich Facility based on performance and implementation.

2.1.1 Surfactant-Enhanced Solubilization

Performance - Surfactant flushing (with or without cosolvent) was developed as an aggressive remediation technology for DNAPL in the saturated zone. The feasibility of this technology is based on the interaction between the surfactant, DNAPL and the media in which they are present, typically water. Surfactants alter the interfacial properties of fluids, with the end result of enhancing the amount of mass that can be present in an aqueous phase at equilibrium. This transfer of DNAPL from the oil phase to the aqueous phase, using surfactants to lower the interfacial tension between the DNAPL and the surrounding aqueous phase, enhances DNAPL solubilization and mobilization, making it more amenable to flushing or other remedial efforts.

Two literature reports describe surfactant enhanced solubilization of chlorobenzenes at the bench-scale. McCray et al. (2000) reported that the apparent water solubility of MCB; 1,2-DCB; and 1,4-DCB increased 900 to 3,200% in a 10% solution of cyclodextrin surfactant (a non-toxic, modified sugar). Based on these results, the authors modeled the removal of 1,2-DCB DNAPL from the subsurface and concluded remediation time frame may be shortened by as much as 97% using surfactant flushing. In another study, Ramsburg and Pennell (2002) investigated surfactant flushing coupled with alcohol flushing (i.e., density modified displacement). In a two-dimensional simulated aquifer, the technology successfully removed 90% of an emplaced DNAPL.

Performance of this technology in promoting source depletion at a variety of chlorinated solvent (primarily perchloroethene and trichloroethene) sites was generally positive. A recent performance survey of source depletion technologies (McGuire, et al., in review, Performance and Rebound of DNAPL Source Depletion Technologies at 59 Field Sites, Ground Water Monitoring and Remediation, submitted October 2004) noted that at four sites where surfactant/cosolvents were used, reduction in parent compound

concentrations ranged from 91 to 99%. However, only limited data for daughter product formation was available for this survey, so it is unknown whether the total concentration of chlorinated organics matched the pattern for the parent compound. All applications of this technology required less than 52 days of surfactant addition, and concentrations continued to decrease over time in the majority of wells. Therefore, it appears that the technology was demonstrated at a number of sites, and continued management following completion is minimal.

Implementation – Field-scale, surfactant-enhanced solubilization was attempted at relatively few sites. This technology requires a significant level of hydraulic control to be effective and necessitates a large network of injection and recovery wells, as well as extensive characterization of the subsurface flow patterns before and after the placement of wells. In addition, most field-scale implementations and demonstrations of this technology were conducted at depth intervals that are shallower than 15 m below ground surface. Constituents at the W.G. Krummrich Facility were detected at intervals deeper than 30 m below ground surface. Overall, surfactant/cosolvent addition is one of the most complex of the three technologies considered, both from a chemical and mechanical perspective.

2.1.2 Chemical Oxidation

Performance - As discussed previously, chemical oxidation acts to deplete source mass via a chemical reaction between a strong oxidant and an organic constituent with the goal of directly converting the compound to CO_2. Common chemicals used for this purpose include, in order of decreasing oxidation potential, Fenton's Reagent, ozone, hydrogen peroxide and potassium permanganate ($KMnO_4$).

The literature search generated seven reports documenting use of chemical oxidation for the treatment of chlorobenzenes in saturated media (**Table 2.1 and Appendix B**). The seven studies represent three bench-scale tests, two pilot tests, and two full-scale remediation projects. In all three bench-scale studies, dissolved phase chlorobenzene concentrations were reduced by more than 98%. Each bench-scale test utilized different oxidants (potassium permanganate, ozone gas, and Fenton's reagent). Reductions in dissolved phase MCB/DCB concentrations were lower in both pilot-scale and full-scale chemical oxidation projects. At one full-scale remediation site (Williamson et al., 2004), the authors reported that MCB concentrations rebounded in source zone wells following three phases of oxidant injection.

While in-situ chemical oxidation was successfully demonstrated at a number of sites, continued treatment may be necessary to prevent rebound. In a recent performance survey of source depletion technologies (McGuire, et al., in review, Performance and Rebound of DNAPL Source Depletion Technologies at 59 Field Sites, Ground Water Monitoring and Remediation, submitted October 2004), the median reduction in parent compound concentrations was 88% at twelve sites studied, and the reduction in total COCs

(parents plus daughter products) was 72%. However, two out of seven sites where a long-term (greater than one year) temporal record was available after treatment showed complete rebound in concentrations, and all seven sites showed some rebound. To minimize the potential for rebound, oxidant addition to the subsurface must be sustained in amounts high enough to meet demand including the demand from natural organic matter.

Implementation - Effective oxidant delivery requires significant hydraulic control in the subsurface. Recirculation can be considered to re-use unreacted oxidant, but this increases costs related to well placement. In addition, the formation of solid precipitates during the oxidation process can necessitate the use of a downstream removal mechanism prior to reinjection. If recirculation is not used, off-site migration of oxidant is possible.

DNAPL within the MCB/DCB DNAPL source area contains a significant fraction of high boiling point organic compounds, not identified by VOC and SVOC analyses that may require higher oxidant loadings. At these higher loadings, well and matrix clogging become more important factors. In addition, soil analysis at Krummrich demonstrated that organic carbon content (as measured by total organic carbon) exceeds 0.1% in many depth intervals in the saturated zone, and oxidant demand will increase accordingly in these regions.

For all applications of this technology, oxidant delivery must be carefully monitored and varied when necessary to ensure adequate performance and reliability. The incidence of rebound at a number of field sites suggests that long-term monitoring following the initial treatment is necessary, and additional oxidant injection events may be required.

2.1.3 Enhanced Aerobic Bioremediation

Performance - Enhanced aerobic bioremediation involves direct injection of oxygen through well points in the DNAPL source area to stimulate aerobic biodegradation. Either pure oxygen or air can be injected in this treatment approach, however, lower injection volumes are needed when oxygen is used. The oxygen is introduced at low flow rates and in pulsed delivery, so there is no need for installation of soil vapor extraction wells and associated equipment.

Chlorobenzenes, including MCB and the DCB isomers, are biodegradable under aerobic conditions. Several studies show that aerobic microorganisms utilize MCB (Reineke and Knackmuss, 1988, Microbial Degradation of Haloaromatics, Annual Review of Microbiology, 42, 263-287; van der Meer et al., 1998, Evolution of a Pathway for Chlorobenzene Metabolism Leads to Natural Attenuation in Contaminated Groundwater, Applied and Environmental Microbiology, 64(11), 4185-4193; Rittman and McCarty, 2001, Environmental Biotechnology: Principles and Practices, McGraw Hill, New York) and the DCB isomers (Reineke and Knackmuss, 1988; van der Meer, 1991, Cloning and Characterization of Plasmid-Encoded

Genes for the Degradation of 1,2-Dichloro-, 1,4-Dichloro-, and 1,2,4-Trichlorobenzene of Pseudomonas sp. Strain P51, Applied and Environmental Microbiology, 173(1), 6-15; Nielsen and Christensen, 1994, Variability of biological degradation of aromatic hydrocarbons in an aerobic aquifer determined by laboratory batch experiments, Journal of Contaminant Hydrology, 15, 305-320; Rittman and McCarty, 2001) as growth-promoting substrates. These and other studies further indicated that the microorganisms capable of carrying out such degradation reactions are commonly encountered at contaminated sites.

The pathway for aerobic biodegradation of MCB is similar to that observed for BTEX degradation (van der Meer et al., 1998), and results in complete mineralization of MCB to chloride, carbon dioxide, and water. Van der Meer et al. (1991) proposed a similar pathway for the aerobic biodegradation of the DCB isomers. Due to complete mineralization, the aerobic biodegradation of chlorobenzenes does not result in the production or accumulation of "daughter" products.

The literature search identified four studies that investigated aerobic bioremediation of MCB/DCB in the saturated zone (**Table 2.1 and Appendix C**). Three bench-scale tests reported reductions of MCB/DCB dissolved phase concentration ranging from 78 to 100%, and one pilot test reported a 63.5% reduction in MCB. In all cases, authors report that MCB and DCB are readily biodegraded in the presence of oxygen.

Implementation - Oxygen is readily available, and delivery of oxygen to the subsurface is relatively straightforward. This is a proven technology with hundreds of applications at petroleum hydrocarbon sites and is relatively easy to design and implement.

2.1.4 Selected Technology

Enhanced aerobic bioremediation was selected for further evaluation and treatability testing for addressing MCB/DCB DNAPL in the Former Chlorobenzene Process Area saturated zone. This selection was based on better performance and implementation reported in the literature for enhanced aerobic bioremediation than for surfactant-enhanced flushing and in-situ chemical oxidation.

2.2 Soil Sample Location

Environmental Visualization System software (EVS, Version 7.92) was used to identify the highest concentrations of monochlorobenzene (MCB) and total dichlorobenzene (DCB) in saturated soils in the plant process area, define the geometry of high mass areas and to quantify the MCB/DCB mass present in saturated soils at the site using existing data (**Appendix D**). The goal of this modeling was to define a high mass area where soil samples should be collected to perform bench-scale treatability studies.

Table 2.2 presents the EVS modeled MCB and DCB mass and volume in the saturated soils over the

plant process area and in the area of highest MCB/DCB mass. **Figures 2.1 and 2.2** are plan view depictions, respectively, of maximum MCB and DCB concentrations in the plant process area. In these depictions, the concentrations of MCB and DCB in saturated soils (395-380 ft MSL) are projected to the surface. **Figures 2.3 and 2.4** are plan view depictions, respectively, of maximum MCB and DCB concentrations in the plant process area. In these depictions, the concentrations of MCB and DCB in saturated soils (380 ft MSL-Bedrock) are projected to the surface. Color-coded zones of increasing MCB and DCB concentration (1 to 10, 10 to 100, 100 to 250, 250 to 500 and greater that 500 ppm) were created to clearly depict areas of increasing mass.

The Former Chlorobenzene Process Area has the highest MCB and DCB concentrations in the plant process area (**Figures 2.5 and 2.6**), for the shallow (395-380 ft MSL) and middle and deep (380 ft MSL-Bedrock) intervals respectively. The saturated soils (395 ft MSL-Bedrock) portion of the plant process area contains roughly 5.7 times more DCB mass per cubic yard of soil than the overall site (0.062 Kg/cy vs. 0.011 Kg/cy).

Area	Volume of DCB-Containing Soil (cubic yards)	Mass of DCB (Kg)	Percent of DCB Volume	Percent of DCB Mass	DCB Density Kg /cy
Chlorobenzene Process Area	1,868,990	116,645	15.6	90.3	0.062
Overall Plant Process Area	12,007,400	129,143	100	100	0.011

NOTE: 1) Modeled soil volume corresponds to DCB concentrations greater than 1 mg/kg
2) MCB mass is contained within DCB mass, so the volume of the former is not included in table. Note that 88.1% of the MCB mass is contained in the Former Chlorobenzene Process Area.
3) The confidence of the model ranges from 45 to 100%, which is the key indicator on the confidence of the volume estimates.

For these reasons, the Former Chlorobenzene Process Area was selected as the location to sample for the MCB/DCB saturated soil thermal treatability tests.

The MCB/DCB EABR bench-scale saturated SHU soil treatability test sample will be collected in the Former Chlorobenzene Process Area from the target depth of 14.5 to 18.5 ft bgs at the location shown on **Figure 2.7** (sample location K-4 at a depth of 16.5 ft bgs) because it is the highest concentration/highest mass location within the plant process area. The saturated MHU/DHU soil treatability test sample will be collected from a target depth of 44.5 to 48.5 ft bgs at the location shown on **Figure 2.8** (sample location K-4 at a depth of 46.5 ft bgs). Sample collection will not be performed until USEPA approves the selected sampling location.

2.3 Soil Sample Collection

Soil samples will be collected as described in the Field Sampling Plan (**Appendix E**). To provide baseline sample characterization information, a soil sample will be collected from the saturated SHU and saturated MHU/DHU soil target depths at the approved sampling locations, placed in appropriate containers, cooled

and shipped at 4°C directly from the site to Severn Trent Laboratories in Savannah, Georgia for chemical and geotechnical analyses.

After collection of the baseline saturated SHU sample, approximately 4 kg (10 lbs) of soil will be collected from the saturated SHU soil target depth at the approved sampling location. The soil sample will be placed in two half-gallon containers, cooled and shipped at 4°C to Groundwater Services in Houston, Texas.

After collection of the baseline saturated MHU/DHU sample, approximately 18 kg (40 lbs) of soil will be collected from the saturated MHU/DHU soil target depth at the approved sampling location. The soil sample will be divided into nine even sections and each section will be split evenly among nine half-gallon containers. After filling the nine half-gallon containers, they will be cooled and shipped at 4°C to Groundwater Services in Houston, Texas for homogenization and separation into bench-test aliquots at the Rice University Civil and Environmental Engineering laboratory.

2.4 Treatability Test

2.4.1 Objective and Approach

The objective of the Enhanced Aerobic Biodegradation treatability study is to demonstrate that MCB and DCB DNAPL mass transferred from the aquifer matrix to groundwater in the aquifer pore spaces can be readily biodegraded by native microorganisms in the presence of oxygen. A series of simulated flow-through aquifer systems will be constructed using large diameter columns and soil from the saturated SHU and MHU/DHU beneath the Former Chlorobenzene Process Area. In order to minimize the volume of soil required for the experiment and the time required to perform the treatability test, each column will be approximately 3-inches diameter and 6-inches long. Larger, tank-based microcosms, such as those used by Greenberg et al., 1998 (In-Situ Fenton-Like Oxidation of Volatile Organics: Laboratory, Pilot, and Full-Scale Demonstrations, Remediation, 8(2), 29-36) and Clement et al., 2004 (Experimental and Numerical Investigation of DNAPL Dissolution Processes, Groundwater Monitoring and Remediation, 24(4), 88-96), were not selected for these bench-scale treatability tests because the larger simulated aquifer volumes increase the amount of time needed to perform the tests. The experimental approach will involve the operation of multiple systems in parallel, with particular columns sacrificed at 2 week intervals to assess temporal compound reduction levels in the soil matrix. The control treatment for the experiment will be a column with an oxygen-free influent.

Water will be introduced to the simulated aquifer microcosms via a peristaltic pump at a rate equivalent to the groundwater velocity in the Shallow Hydrogeologic Unit (10.4 ft/yr) and in the Middle and Deep Hydrogeologic Units (i.e. 104 ft/yr) (Solutia, 2005, Results of DNAPL Characterization and Remediation Study, Saguet Area 1 Sites). After a one week equilibration period, industrial grade oxygen (100% v/v)

will be sparged continuously into the influent reservoir, and the influent will consist of oxygen saturated water for the remainder of the experiment. Because of the low flow rates selected for this test (as described in **Section 2.4.3**), it is potentially feasible to use site groundwater to conduct the EABR treatability tests. However, it is necessary to remove all volatile and semivolatile organic compounds (in particular, MCB and DCBs) initially present in site groundwater prior to its use as influent to avoid confounding the results of the treatability tests. This can be accomplished by air stripping the VOCs and sorbing the SVOCs on granular activated carbon. If VOCs and SVOCs are not removed from the influent, there are two sources of organics in the aquifer microcosms: 1) influent groundwater and 2) DNAPL dissolution from the aquifer matrix soil in the column. A much simpler approach is to use dechlorinated tap water or distilled and deionized water, with minerals and other nutrients added to simulate concentrations measured in site groundwater. To eliminate variability introduced by using site groundwater, distilled and deionized water amended with nutrients (see **Section 2.4.3**) will be used for the EABR treatability tests. Changes in aqueous phase MCB/DCB concentrations in column effluents, as well as the pre-treatment and post-treatment MCB and DCB concentrations in microcosm soils, will be monitored to determine if enhanced aerobic bioremediation is effective in removing DNAPL mass.

2.4.2 Initial Soil Handling and Characterization

The saturated SHU and saturated MHU/DHU treatability test soil samples will be analyzed for of MCB, DCB, VOCs, SVOCs, EOX, Moisture Content, Particle Size and Permeability by Severn Trent Laboratories using the following methods:

MCB/DCB Treatability Test Soil Sample Characterization

Parameter	Analytical Method
MCB/DCB	USEPA Method 5035/8260B
VOCs	USEPA Method 5035/8260B
SVOCs	USEPA Method 8270C
Extractable Organic Halides (EOX)	USEPA Method 9023
Moisture Content	ASTM D 2216
Particle Size	ASTM D 422
Permeability	ASTM D 2434 (Granular Soil) ASTM D 5084 (Fine-Grained Soil)

As directed by USEPA, VOCs, SVOCs and EOX were added to the analytical parameter list. Samples will be analyzed as described in the Field Sampling Plan-Quality Assurance Project Plan (**Appendix E**).

Upon receipt of the saturated SHU and saturated MHU/DHU soil samples, Groundwater Services will log in the eleven half-gallon, untreated soil sample containers and place them in refrigerated storage at a temperature of 4°C. The cooled saturated SHU soil sample will be homogenized by emptying the two containers into a large mixing pan and blending until visually homogeneous using stainless steel utensils. GSI will then split the sample into four equal aliquots.

Bench-Scale MCB/DCB Thermal Treatability Test Homogenized Untreated Saturated SHU Soil Sample Aliquots

Aliquot	Purpose	Description	
• Aliquot 1	Sample Chemical Characterization	MCB/DCB, VOC, SVOC and EOX Analysis	
• Aliquot 2	Verification of Sample Homogenization	MCB/DCB, VOC, SVOC and EOX Analysis	
• Aliquot 3	Sample Geotechnical Characterization	Moisture Content and Particle Size Analysis	
• Aliquot 4	Treatability Test Sample	SHU Microcosm 1	12 Week Duration

The cooled saturated MHU/DHU soil samples will be homogenized by emptying the nine sample containers into a large mixing pan and blending until visually homogeneous using stainless steel utensils. As a part of the homogenization process, any large and/or agglomerated particles will be broken into smaller, more manageable sizes. GSI will then divide the soil sample into ten equal aliquots as shown below:

Bench-Scale MCB/DCB Thermal Treatability Test Homogenized Untreated Saturated MHU/DHU Soil Sample Aliquots

Aliquot	Purpose	Description	
• Aliquot 1	Sample Chemical Characterization	MCB/DCB, VOC, SVOC and EOX Analysis	
• Aliquot 2	Verification of Sample Homogenization	MCB/DCB, VOC, SVOC and EOX Analysis	
• Aliquot 3	Sample Geotechnical Characterization	Moisture Content and Particle Size Analysis	
• Aliquot 4	Treatability Test Sample	MHU/DHU Microcosm 1	2 Week Duration
• Aliquot 5	Treatability Test Sample	MHU/DHU Microcosm 2	4 Week Duration
• Aliquot 6	Treatability Test Sample	MHU/DHU Microcosm 3	6 Week Duration
• Aliquot 7	Treatability Test Sample	MHU/DHU Microcosm 4	8 Week Duration
• Aliquot 8	Treatability Test Sample	MHU/DHU Microcosm 5	10 Week Duration
• Aliquot 9	Treatability Test Sample	MHU/DHU Microcosm 6	12 Week Duration
• Aliquot 10	Treatability Test Control	MHU/DHU Microcosm 7	12 Week Duration

NOTES: 1) Treatability Test Control (Microcosm 7) receives zero oxygen influent with bactericide (10 mg/L of sodium azide) to measure effect of DNAPL dissolution in absence of microbial activity.

SHU and MHU/DHU aliquots 1, 2 and 3 will be placed in appropriate containers, cooled and shipped at 4°C to Severn Trent Laboratories in Savannah, Georgia for chemical and geotechnical analyses as described above. Results of the baseline and homogenized untreated soil sample analyses will be sent to USEPA. Treatability tests will proceed once the Agency confirms that the MCB/DCB concentrations in the treatability study aliquots are representative of site conditions and that the treatability study soil sample is adequately homogenized.

2.4.3 Treatability Test

The treatability test will be conducted in custom-made glass columns (Specialty Glass, Houston, TX). Column dimensions include a diameter of 3 inches and a column flow length of 6 inches, yielding a total volume of 695 mL per column. Fitted caps at both the influent and effluent ends will be constructed to ensure gas-tight conditions. All caps and flow lines will be Teflon, MasterFlex®, or stainless steel to minimize sorption. Peristaltic pumps will be used to deliver a specified flow rate through each column, and sample collection reservoirs will be placed at the effluent end. Components of this design are detailed as follows:

Composition of Simulated Groundwater - The influent will consist of nutrient-amended deionized water that is similar in composition to the groundwater in the SHU and MHU/DHU at the Krummrich site. From the perspective of stimulating biodegradation, it is necessary to determine if microbial growth and catalysis will occur in field-specific nutrient conditions. Additionally, it is important to use groundwater with geochemical characteristics similar to the site groundwater to assess the influence of alternate electron acceptors on the stimulation of aerobic biodegradation of MCB and DCB. In the subsurface at Krummrich, there is no significant amount of nitrate, but sulfate is present at levels generally between 100 and 200 mg/L. In addition, there is significant carbonate alkalinity to support methanogenesis and provide adequate buffer capacity for further microbial activity. The bulk concentration of constituents in the influent water to be used in the treatability test is based on standard formulations for aerobic growth media (specifically *Pseudomonas* sp. capable of catalyzing MCB degradation), with modifications as necessary to 1) simulate site geochemistry, and 2) minimize chloride interference:

MCB/DCB DNAPLTreatability Test: Influent Composition (modified from van der Meer et al., 1998)

Compound	Bulk Concentration in Influent (mg/L)
$MgSO_4 \cdot 7H_2O$	50
$FeSO_4 \cdot 7H_2O$	3.0
$(NH_4)_2SO_4$	500
H_3BO_3	0.1
$CaSO_4 \cdot 5H_2O$	0.05
$ZnSO_4 \cdot 7H_2O$	0.05
$Na_2MoO_4 \cdot 2H_2O$	0.05
K_2HPO_4	1750
KH_2PO_4	1380
$CoCl_2 \cdot 7H_2O$	0.6
$NaHCO_3$	500
$MnSO_4 \cdot H_2O$	2.0

NOTES: 1) Media composed of low chloride concentration to allow for measurement of chloride released during test.

The influent water will be prepared and pumped from vented influent reservoirs (8 L). The influent composition will be the same for both the SHU and the MHU/DHU microcosms, and water will be maintained at a temperature range of 55 to 60°F.

Influent Flow Rate - Simulated groundwater will be flushed through each system at a rate designed to mimic flow conditions in the corresponding hydrologic unit at the Krummrich site. For the MHU/DHU, this is based on a Darcy velocity of approximately 104 ft/yr for the MHU/DHU and 10.4 ft/yr for the SHU. Using the cross-sectional area of the treatability test microcosms yields the following:

$$\textbf{MHU/DHU Flowrate} = \text{velocity} \times \text{area} = \frac{104\ \text{ft}}{\text{yr}}\left(\frac{3}{2}\ \text{in}\right)^2\left(\frac{2.54\text{cm}}{\text{in}}\right)^2 \pi\left(\frac{30.48\ \text{cm}}{\text{ft}}\right)\left(\frac{\text{yr}}{365\ \text{d}}\right)\left(\frac{\text{mL}}{\text{cm}}\right) = \mathbf{396\ \frac{mL}{d}}$$

$$\textbf{SHU Flowrate} = \text{velocity} \times \text{area} = \frac{10.4\ \text{ft}}{\text{yr}}\left(\frac{3}{2}\ \text{in}\right)^2\left(\frac{2.54\text{cm}}{\text{in}}\right)^2 \pi\left(\frac{30.48\ \text{cm}}{\text{ft}}\right)\left(\frac{\text{yr}}{365\ \text{d}}\right)\left(\frac{\text{mL}}{\text{cm}}\right) = \mathbf{39.6\ \frac{mL}{d}}$$

Therefore, a flow of 396 mL/d will be pumped through each MDU/DHU column and a flow of 39.6 mL/d will be pumped through the SHU column using multi-head peristaltic pumps and MasterFlex tubing. This will allow for all systems to be operated in parallel at identical flow rates. The influent will be pumped from a reservoir that will serve all MDU/DHU columns (except the control) and 1 SHU column, meaning that approximately 3.0 L of simulated groundwater will be required per day during the first phase of the experiment. Influent volumes will decrease during the test as microcosms are sacrificed to determine changes in soil concentrations.

Oxygen Sparging - For all systems except the control microcosm, oxygen will be added to the influent to assess the ability to stimulate aerobic biodegradation of MCB/DCB. This requires sparging of the influent prior to introduction into the columns. This will be accomplished in the influent feed reservoir located upstream of the pumps. A gas line will be introduced to the influent reservoir, with a constant inflow of pure O_2 (100% v/v) supplied via a separate O_2 cylinder. A submerged diffusing stone will be placed at the end of the line connecting the O_2 cylinder and the influent reservoir, and atmospheric pressure will be maintained in the reservoir by pressure-release vents and constant upstream pumping of the water through the columns. This process will saturate the influent water will oxygen at levels between 40 and 50 mg/L (based on equilibrium partitioning). Oxygen levels in the reservoir will be tested periodically to check for system integrity. Note that the control microcosm will be sparged with N_2 instead of O_2 to measure dissolution in abiotic systems.

Temperature - To simulate subsurface conditions at Krummrich, influent groundwater will be pumped into the columns at a temperature of 55 to 60°F. This will be accomplished by placing the influent reservoir in a chiller capable of maintaining a temperature range of 55 to 60°F.

Control Microcosm - The control microcosm will receive influent that will be pumped from a separate influent reservoir than the other columns. Because the purpose of the control is to provide baseline dissolution conditions in the absence of microbial activity, this reservoir will be sparged with nitrogen rather than oxygen, and a bulk concentration of 10 mg/L of sodium azide (as a biocide) will be maintained in the reservoir.

Sampling and Operation - An in-line sample collection reservoir will be placed at the effluent end of each aquifer microcosm. These are modified glass collection vials equipped with valves to permit sampling with a syringe and needle. Reservoirs will be approximately 60 mL to provide sufficient sample volume for analysis of VOCs by USEPA Method 8260. Because they are designed as flow-through cells,

there is no headspace in the vials. The vials will contain a removable cap that will allow insertion of probes for the periodic sampling of pH, redox, and dissolved oxygen.

Water from the sample collection reservoir will be sampled twice during the one week equilibrium period to establish dissolution conditions. Once oxygen addition begins, effluent samples will be collected weekly from each microcosm to measure the progress of bioremediation. A total of 82 effluent samples will be collected for analysis on the following schedule:

MCB/DCB DNAPL Treatability Test Effluent Sampling Schedule

	MHU/DHU Microcosms							SHU Microcosm
Week	1	2	3	4	5	6	7	4
-1	●	●	●	●	●	●	●	●
0	●	●	●	●	●	●	●	●
1	●	●	●	●	●	●	●	●
2	●	●	●	●	●	●	●	●
3		●	●	●	●	●	●	●
4		●	●	●	●	●	●	●
5		●	●	●	●	●	●	●
6			●	●	●	●	●	●
7			●	●	●	●	●	●
8				●	●	●	●	●
9					●	●	●	●
10					●	●	●	●
11						●	●	●
12						●	●	●
Total	4	6	8	10	12	14	14	14

Sacrifice of aquifer microcosms will involve sectioning each column into thirds (top, middle, and bottom) and performing VOC, SVOC, EOX and microbial analyses of the soil matrices. For the 8 columns that are part of the EABR treatability test, this will result in a total of 24 treated soil sample analyses.

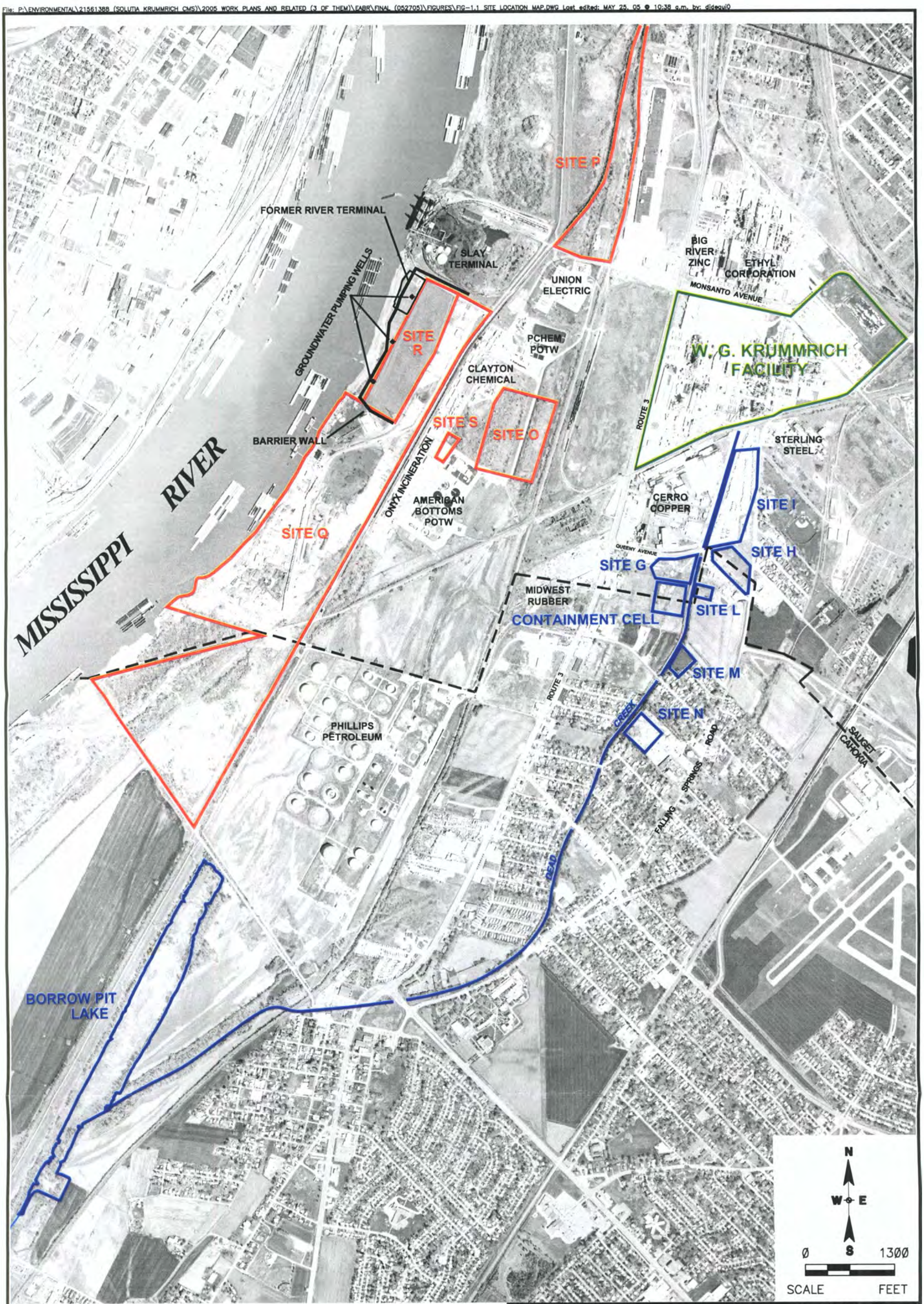
Data Analysis - The efficacy of enhanced aerobic bioremediation will be evaluated by comparison of soil phase MCB/DCB concentrations before and after treatment. Temporal changes in dissolved phase MCB/DCB concentrations will also be evaluated to i) determine correlations in mass removal and concentration reduction, and ii) estimate the mass flux enhancement due to bioremediation by comparison of mass removal rates during the equilibrium period to removal rates after oxygen addition.

Additional design data will be generated with respect to the efficiency of oxygen addition in promoting MCB/DBC destruction (mg degraded per mg of oxygen added). Because aerobic activity may result in the complete utilization of oxygen prior to the column effluent, MCB/DCB-degrading activity in anoxic conditions may occur and be quantifiable. Finally, sacrificing individual columns at specific intervals will yield data related to the time requirements for establishment of microbial activity.

Upon completion of laboratory analyses and data validation, a treatability study report that describes testing protocols, treatability test results, and includes all data collected during the study including laboratory notes and reports, will be prepared and submitted to USEPA. Total project duration is expected to be 180 days.

Figures

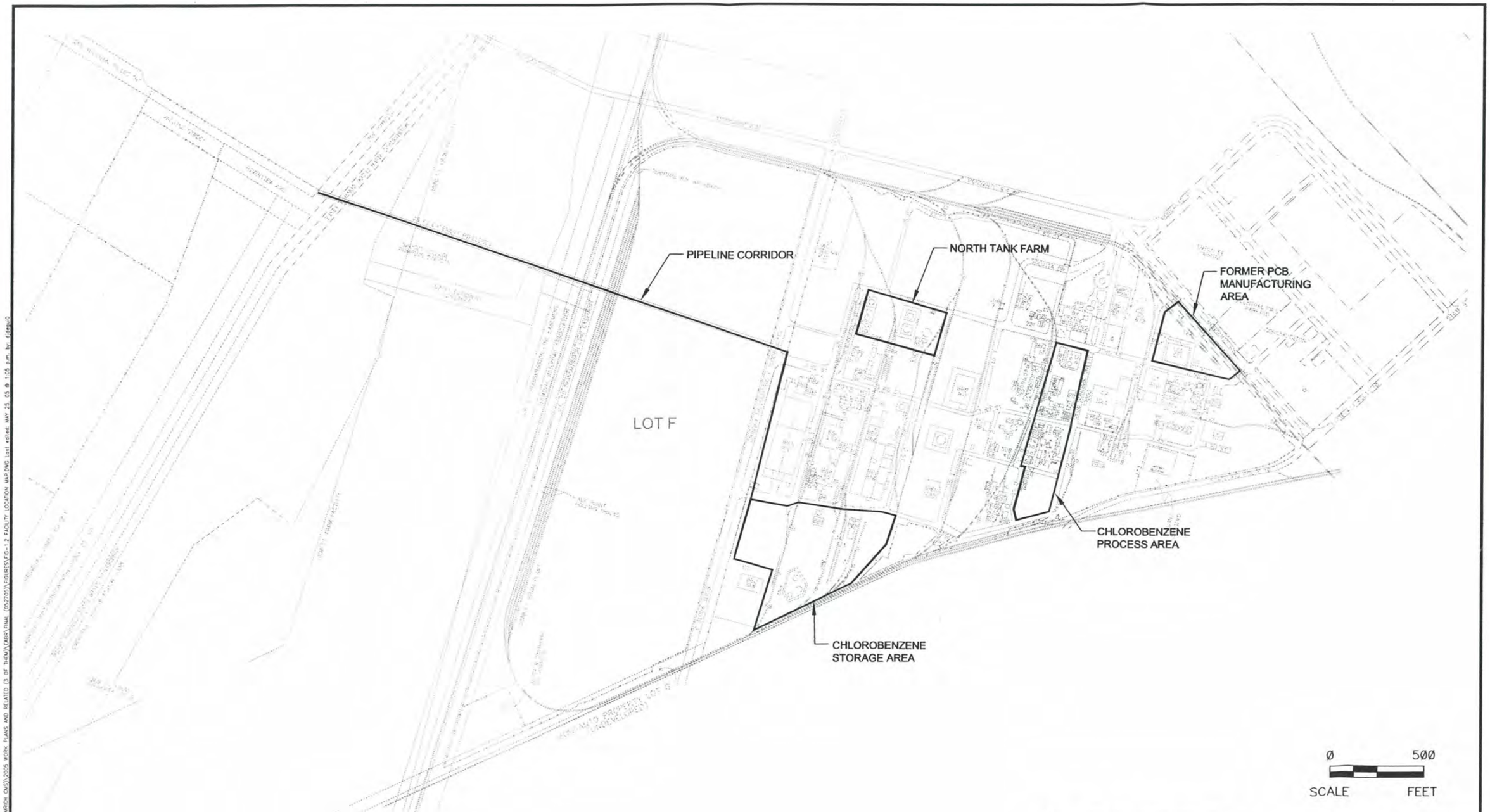
File: P:\ENVIRONMENTAL\21561388 (SOLUTIA KRUMMRICH CMS)\2005 WORK PLANS AND RELATED (3 OF THEM)\FABR\FINAL (052705)\FIGURES\FIG-1.1 SITE LOCATION MAP.DWG Last edited: MAY 25, 05 @ 10:38 a.m. by: didequi0



LEGEND

- W.G. KRUMMRICH FACILITY
- SAUGET AREA #1
- SAUGET AREA #2

IN-SITU BIOREMEDIATION WORK PLAN MASS REMOVAL TREATABILITY TESTS W.G. KRUMMRICH FACILITY, SAUGET, ILLINOIS	PROJECT NO. 21561388.00000
URS	
DRN. BY: 2/9/05 DSGN. BY: tja CHKD. BY:	Site Location Map — FIG. NO. 1.1



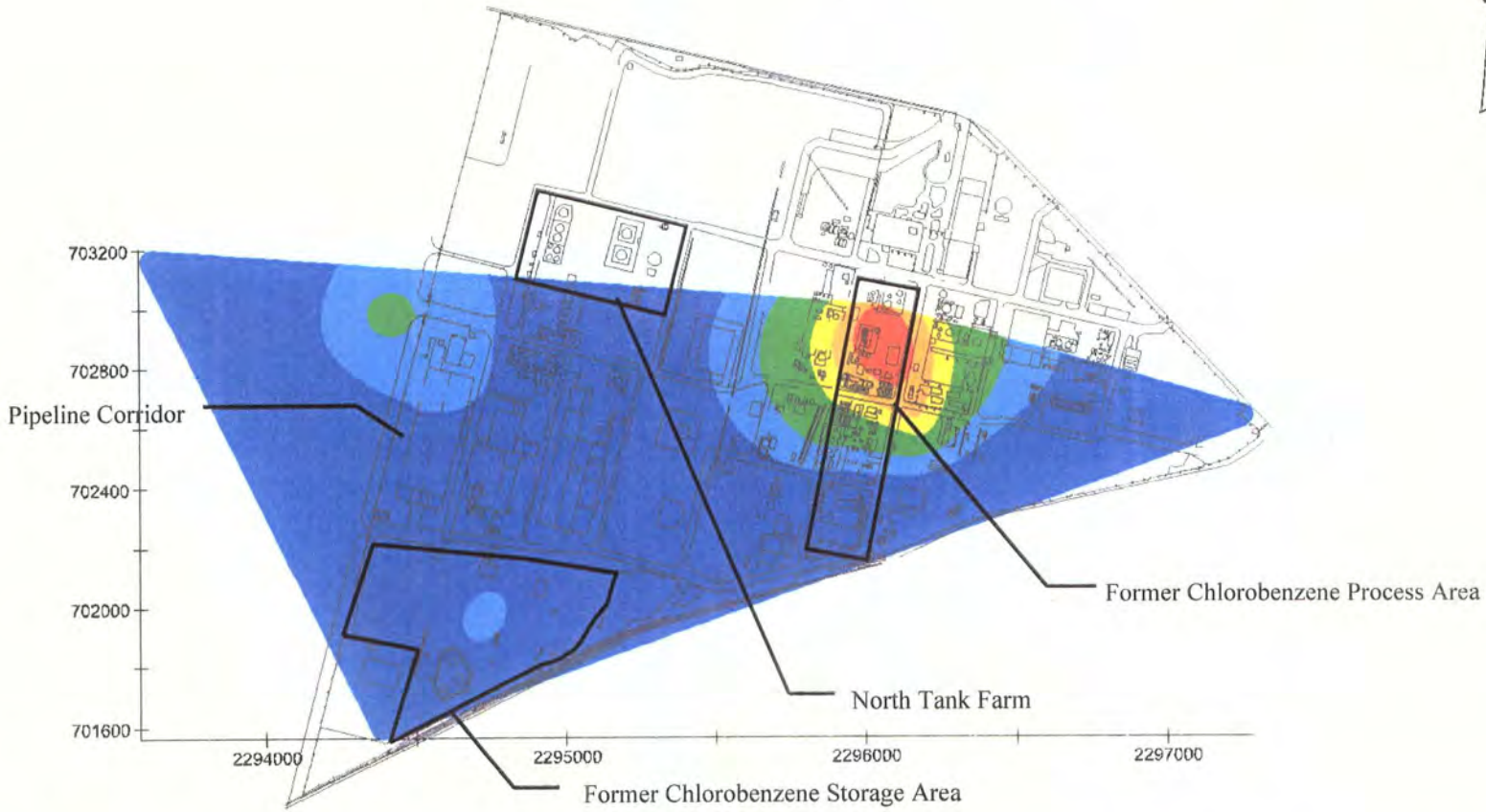
IN-SITU BIOREMEDIATION WORK PLAN MASS REMOVAL TREATABILITY TESTS W.G. KRUMMRICH FACILITY, SAUGET, ILLINOIS	PROJECT NO. 21561388.00000
URS	
DRN. BY: 4/9/05 DSGN. BY: cm CHKD. BY:	Facility Location Map — FIG. NO. 1.2

File: P:\ENVIRONMENTAL\21561388 (SOUTH KRUMMRICH OMS)\2005 WORK PLANS AND RELATED (3 OF THEM)\FABRI FINAL (052705)\FIGURES\FIG-1.2 FACILITY LOCATION MAP.DWG Last edited: MAY 25, 05 @ 1:05 p.m. by: dldeguzi0

Plan View

MCB Distribution in Shallow Saturated Soils (395-380 ft MSL)

URS



- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

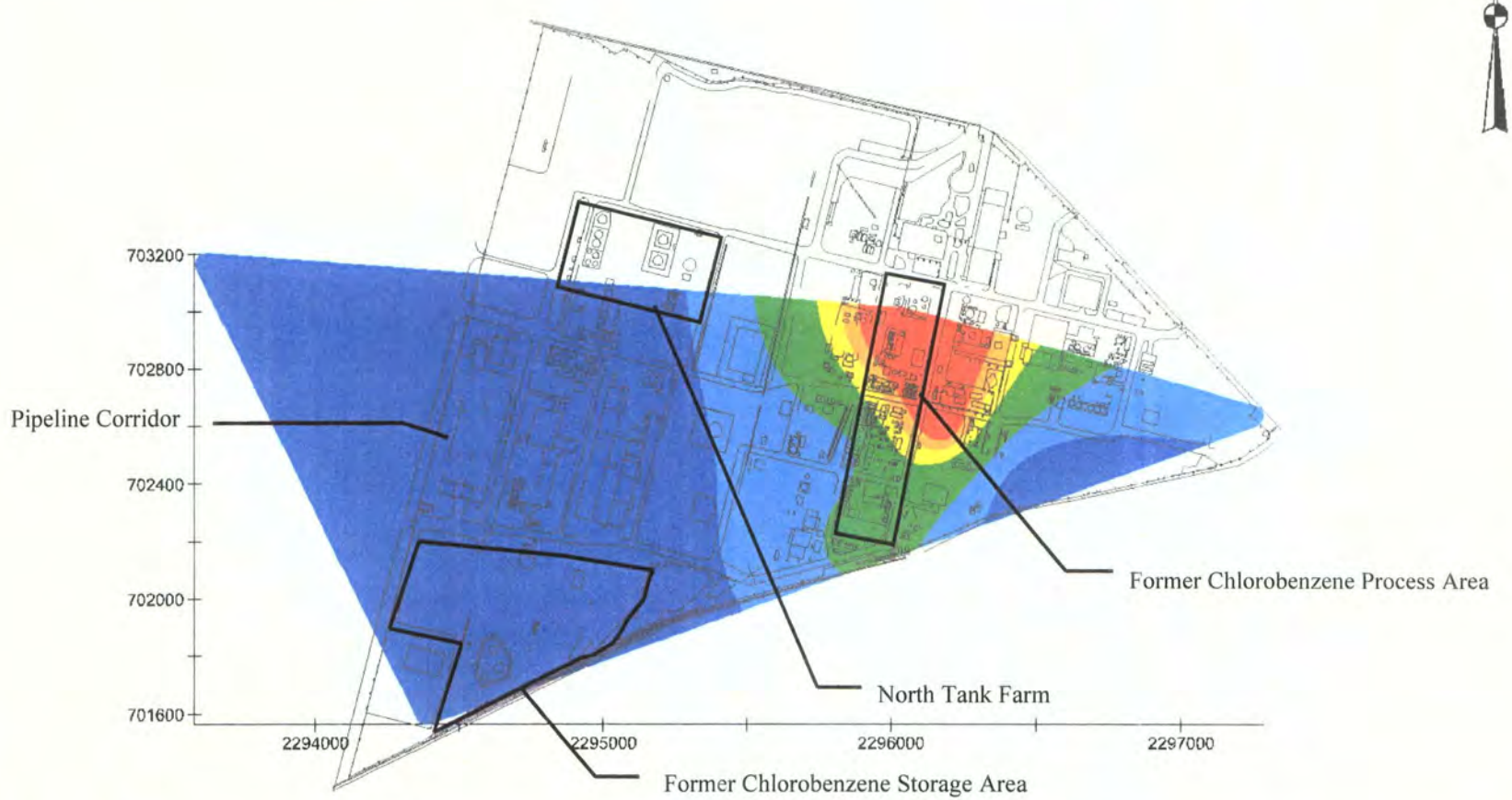
Date:	02/03/05
Figure Number:	2.1
Project Number:	21561573.00000

In-Situ Bioremediation Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

Plan View

URS

DCB Distribution in Shallow Saturated Soils
(395-380 ft MSL)



- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

Date:	02/03/05
Figure Number:	2.2
Project Number:	21561573.00000

In-Situ Bioremediation Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

Plan View

MCB Distribution in Middle and Deep Saturated Soils (380 ft MSL - Bedrock)

URS

- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

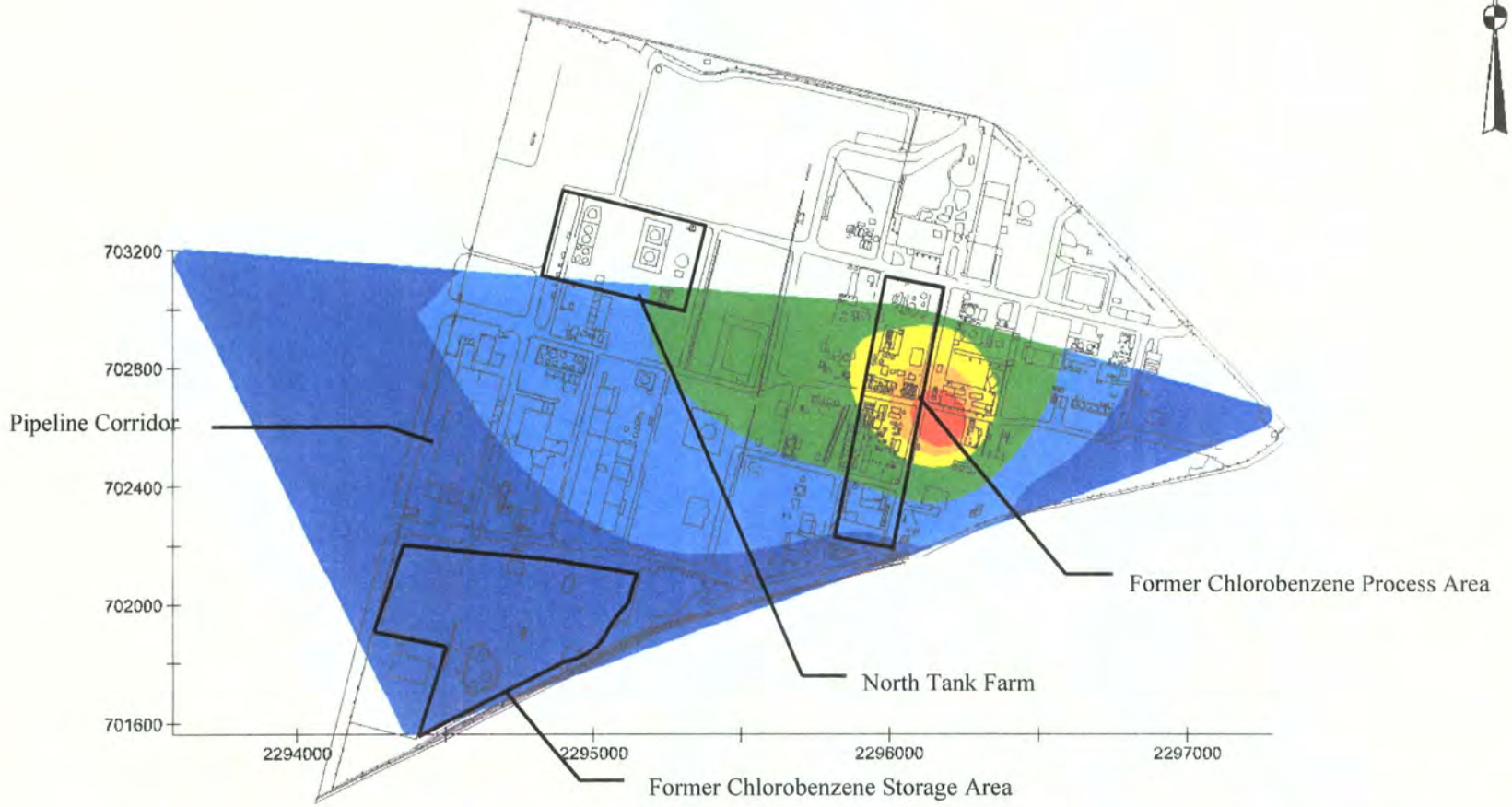
Date:	02/03/05
Figure Number:	2.3
Project Number:	21561573.00000

In-Situ Bioremediation Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

Plan View

DCB Distribution in Middle and Deep Saturated Soils (380 ft MSL - Bedrock)

URS



- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

Date:	02/03/05
Figure Number:	2.4
Project Number:	21561573.00000

In-Situ Bioremediation Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

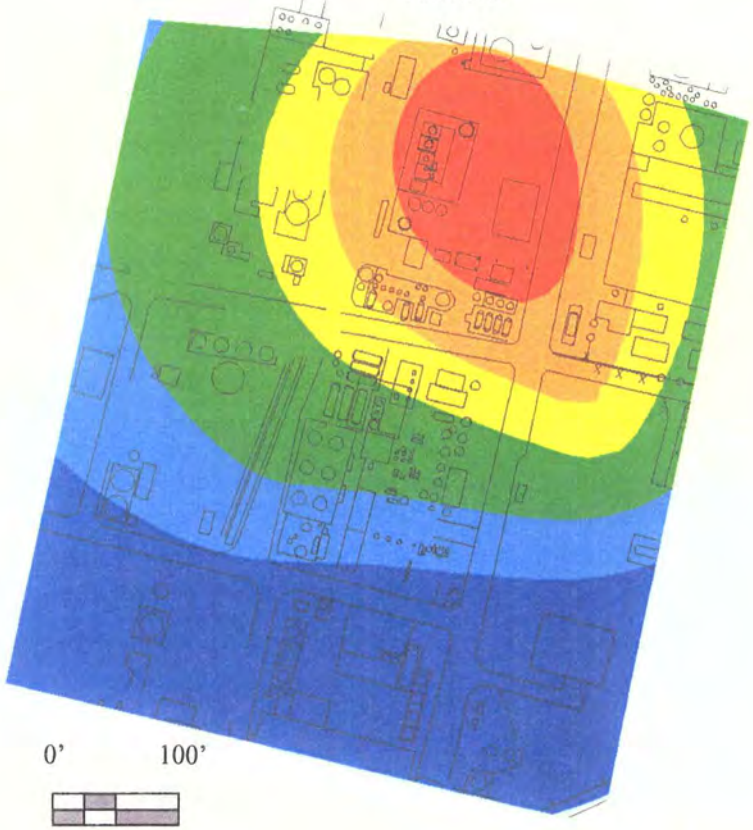
Plan View

MCB/DCB Distribution in Former Chlorobenzene Process Area Shallow Saturated Soils (395-380 ft MSL)

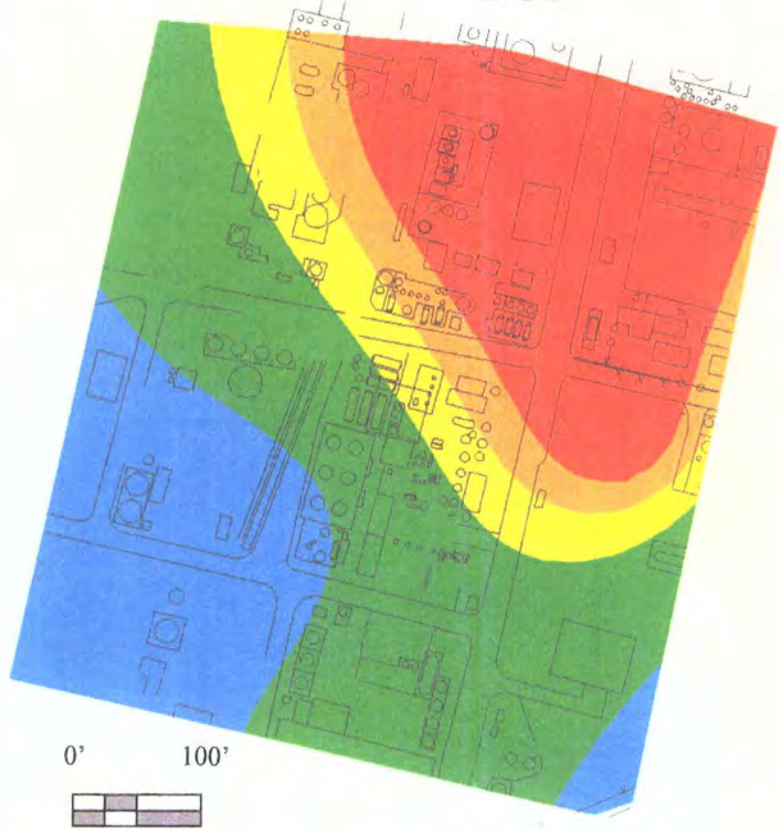
URS

N

MCB



DCB



- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

Date:	02/03/05
Figure Number:	2.5
Project Number:	21561573.00000

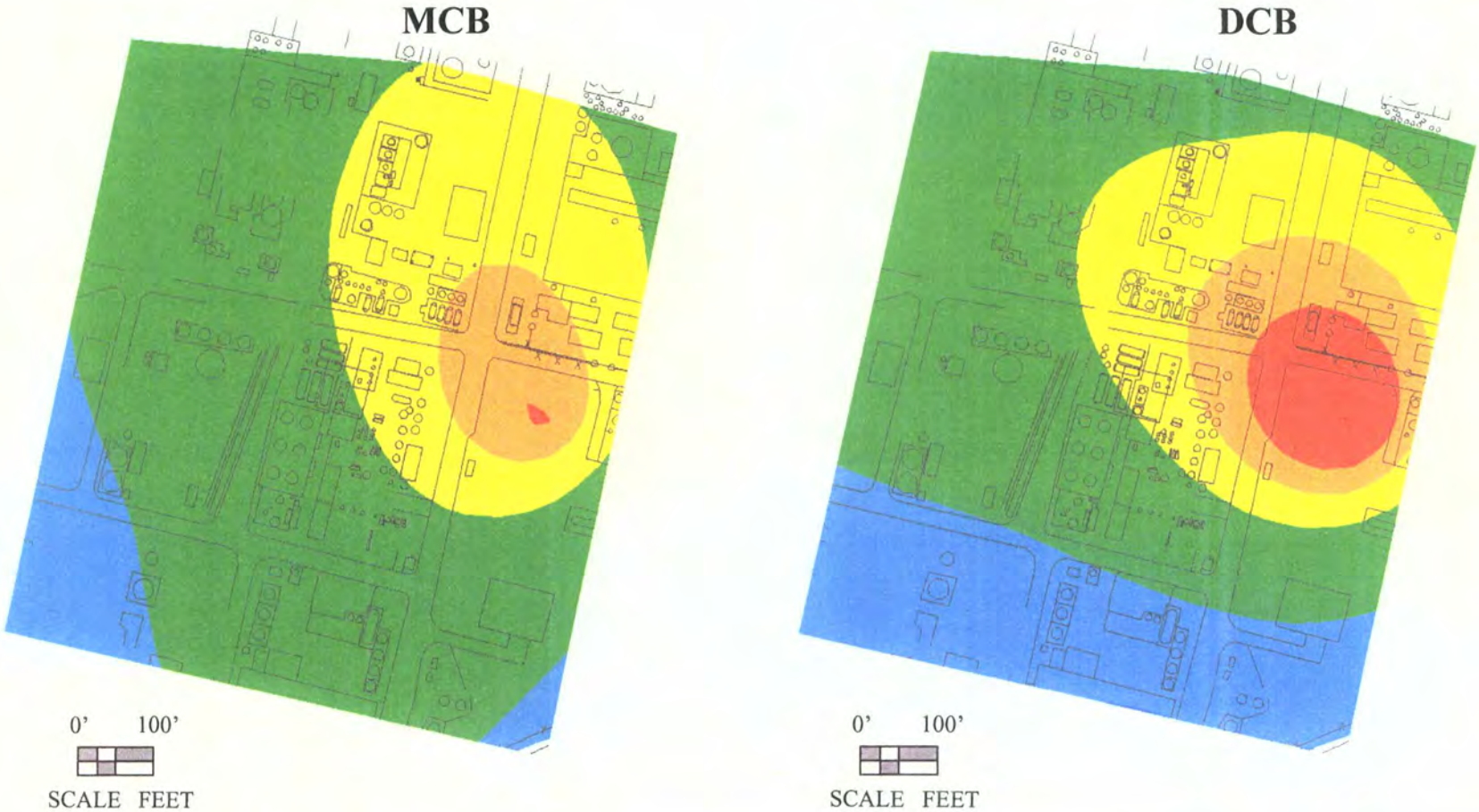
In-Situ Bioremediation Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

Plan View

MCB/DCB Distribution in Former Chlorobenzene Process Area Middle and Deep Saturated Soils (380 ft MSL - Bedrock)

URS

N



- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

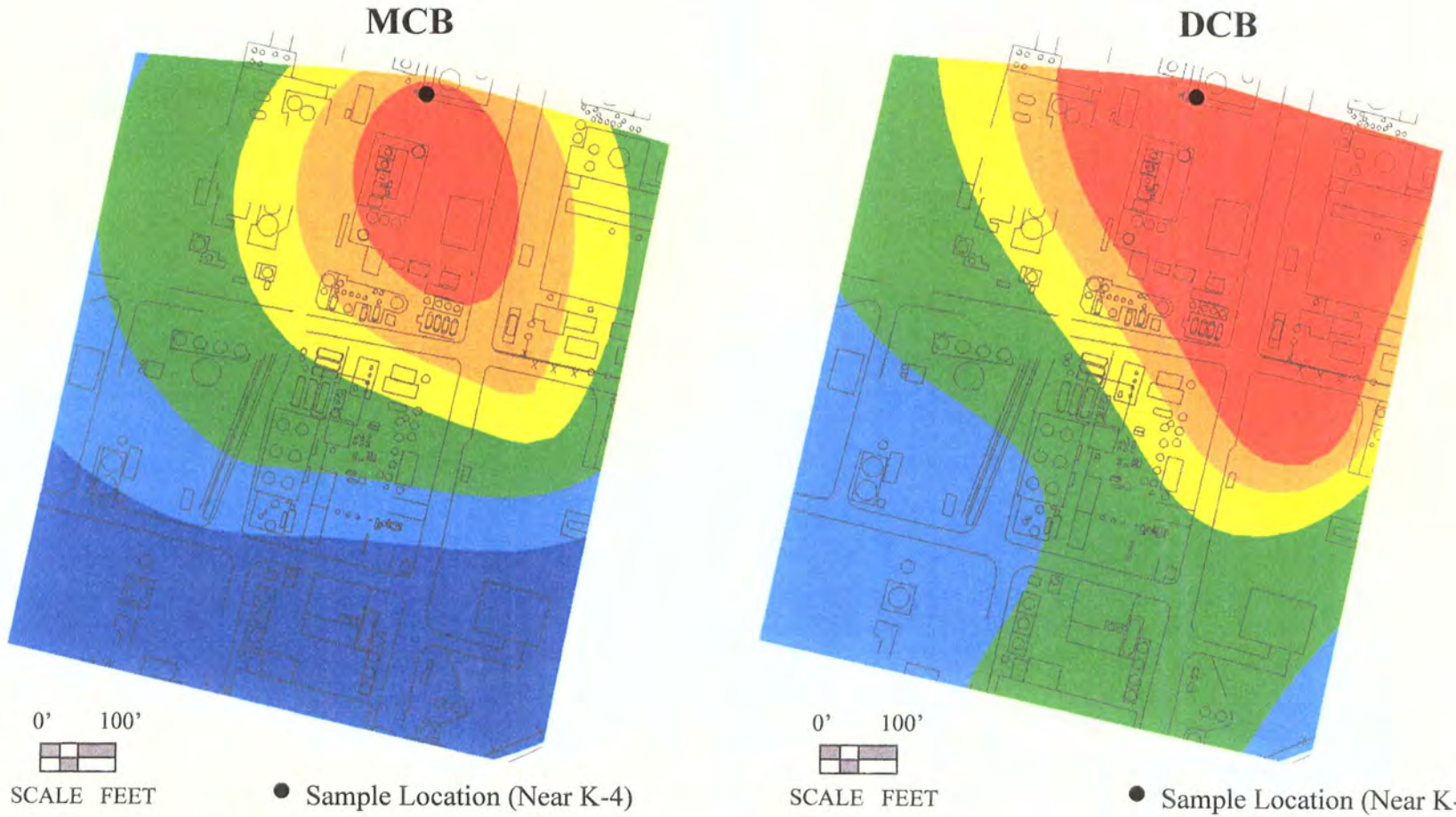
Date:	02/03/05
Figure Number:	2.6
Project Number:	21561573.00000

In-Situ Bioremediation Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

Plan View

URS

Saturated SHU In-Situ EABR Treatability Test Sample Location



<1 ppm	100 to 250 ppm
1 to 10 ppm	250 to 500 ppm
10 to 100 ppm	>500 ppm

SOLUTIA

Date:	02/03/05
Figure Number:	2.7
Project Number:	21561573.00000

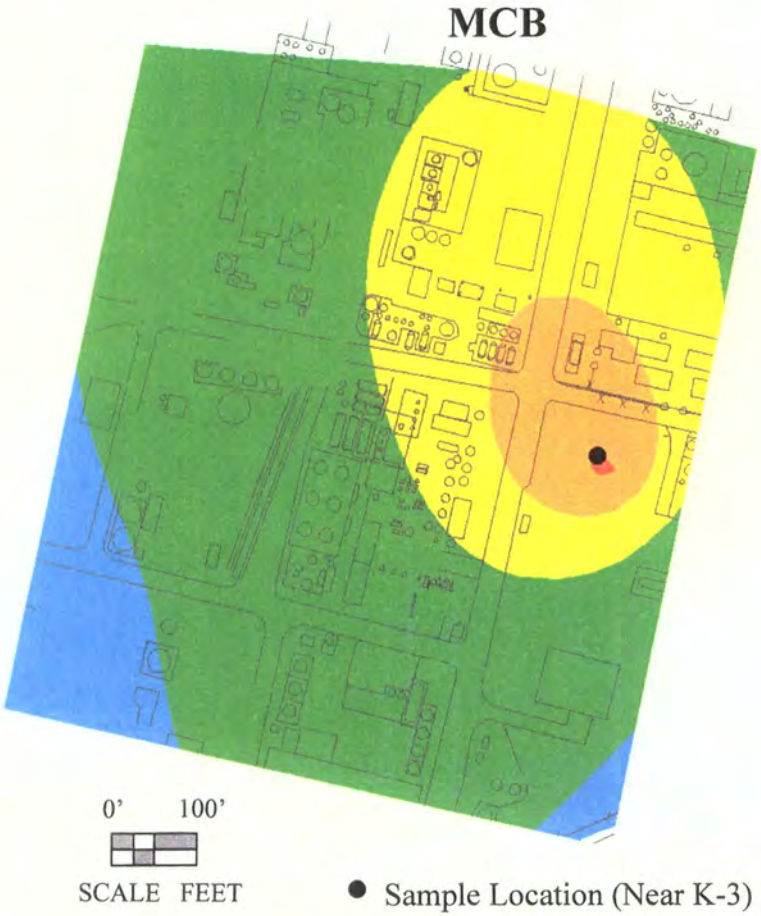
In-Situ Bioremediation Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

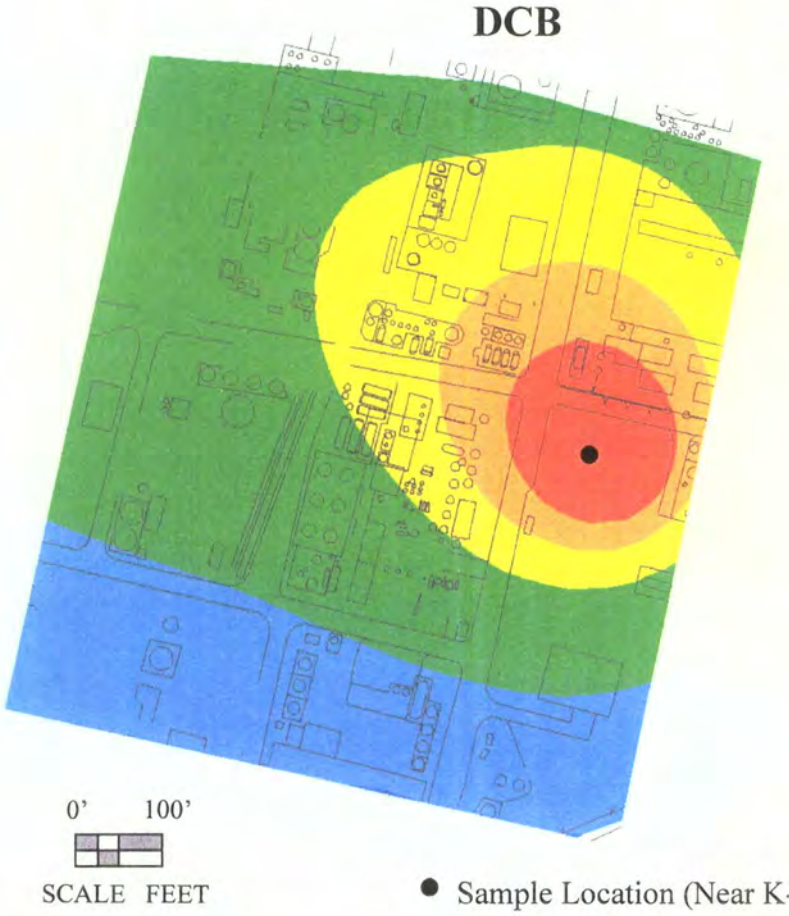
URS

Plan View

Saturated MHU/DHU In-Situ EABR Treatability Test Sample Location

N





- <1 ppm
- 1 to 10 ppm
- 10 to 100 ppm
- 100 to 250 ppm
- 250 to 500 ppm
- >500 ppm

SOLUTIA

Date:	02/03/05
Figure Number:	2.8
Project Number:	21561573.00000

In-Situ Bioremediation Work Plan
Mass Removal Treatability Tests
W.G. Krummrich Facility
Sauget, Illinois

TABLE 2.1
REVIEW OF MCB/DCB DNAPL TREATMENTS IN THE SATURATED ZONE

Solutia Inc., W.G. Krummrich Facility
Sauget, Illinois

Reference	Treatment Scale	Constituent(s)	Initial Conc. (mg/L)	Conc. Reduction	Treatment Duration	Comments
Surfactant Flushing						
McCray et al., 2000	Bench	MCB 1,2-DCB 1,4-DCB	NA	Simulated removal due to surfactant >55% for 1,2-DCB	NA	• 900-3200% increase in solubility observed in presence of 10% surfactant (cyclodextrin, HPCD). • Simulated reduction in remediation timeframe for 1,2-DCB = >97% (from 1409 days during water flushing to 48 days using cyclodextrin enhanced flushing)
Ramsburg and Pennell, 2002	Bench	MCB	NA	90% DNAPL recovery	1.2 pore volumes n-butanol; 1.2 pore volumes surfactant; and 1 pore volume H_2O	• Density Modified Displacement (DMD) technology used in conjunction with surfactant flushing • DMD converts DNAPL to LNAPL via alcohol injection to enhance recovery • 2-D aquifer cells flushed with aqueous solution (containing CB, surfactant Aerosol MA-80I or Aerosol OT and 6% *n*-butanol)
Chemical Oxidation						
Horst et al., 2002	Bench	MCB 1,2-DCB	61.67 32.67	99.4% 99.9%	Not reported	• Column studies containing soil spiked with MCB and DCB • After equilibration, 1.89% KMnO4 solution was re-circulated in column • Oxidant Demand Estimates: (not taking into account matrix demand) → 35lb $KMnO_4$ to oxidize 1 lb MCB → 54 lbs $KMnO_4$ to oxidize 1 lb DCB

Note:
MCB = monochlorobenzene; DCB = dichlorobenzene; NA = not applicable

TABLE 2.1
REVIEW OF MCB/DCB DNAPL TREATMENTS IN THE SATURATED ZONE

Solutia Inc., W.G. Krummrich Facility
Sauget, Illinois

Reference	Treatment Scale	Constituent(s)	Initial Conc. (mg/L)	Conc. Reduction	Treatment Duration	Comments
Horst et al., 2002	Pilot	MCB 1,2-DCB	68 20	75 – 92% ~84%	12 weeks	• 10 injection events over a period of 12 weeks resulting in a total of 1540 lb (6000 gal) permanganate solution (3%). • No apparent effect on permeability of soil due to precipitation of $KMnO_4$ • Target compound concentrations stable in some wells but fluctuated in others suggesting that the ability of permanganate to sufficiently react with target compounds was limited
Schaal, 2002	Bench	1,2-DCB	2.50	97% >98%	20 minutes 60 minutes	• Ozone gas flow rate – 0.12 scfm • Ozone gas flow rate – 0.09 scfm • Ozone concentration = 1.2% (w/w)
Sedlak and Andren, 1991	Bench	MCB	0.16	>99	1 hour	• Evaluated formation of intermediates during the oxidation of chlorobenzene with Fenton's Reagent • In absence of oxygen, intermediate products of chemical oxidation are dichlorobiphenyls, chlorophenols, and phenolic polymers • In aerobic environments, production of hyperoxy radicals lead to further oxidation of intermediates • At pH=3: 5 mol of H_2O_2/mol MCB was required to oxidize all aromatic intermediates

Note:
MCB = monochlorobenzene; DCB = dichlorobenzene; NA = not applicable

TABLE 2.1
REVIEW OF MCB/DCB DNAPL TREATMENTS IN THE SATURATED ZONE

Solutia Inc., W.G. Krummrich Facility
Sauget, Illinois

Reference	Treatment Scale	Constituent(s)	Initial Conc. (mg/L)	Conc. Reduction	Treatment Duration	Comments
Williamson, et al., 2004	Field	CB DCBs	> 10 mg/L	**Phase 1:** →minimal change **Phase 2:** →56% reduction **Phase 3:** → 82% reduction → 54% reduction after 3 months of post-treatment monitoring.		• Groundwater contaminated from 5 to 15 ft below ground surface • Goal = 90% reduction of dissolved phase concentration **Phase 1:** • 11 injectors at 2 elevations with 3 ft screens • 32,600 lbs of 50% H_2O_2 injected **Phase 2:** • 28 additional injectors • 50,000 lbs of 50% H_2O_2 injected **Phase 3:** • 6 additional injectors • 31,000 lbs of H_2O_2 injected • **Rebound** in source area wells • Additional treatment (aerobic biostimulation) in process of being implemented

Note:
MCB = monochlorobenzene; DCB = dichlorobenzene; NA = not applicable

TABLE 2.1
REVIEW OF MCB/DCB DNAPL TREATMENTS IN THE SATURATED ZONE

Solutia Inc., W.G. Krummrich Facility
Sauget, Illinois

Reference	Treatment Scale	Constituent(s)	Initial Conc. (mg/L)	Conc. Reduction	Treatment Duration	Comments
ISOTEC, Former DOD Facility, NY	Field	CB 1,4-DCB 1,2-DCB 1,3-DCB	1.33 0.11 0.094 0.05	80.2% 76.9% 87.6% 74.1%	14 months	• 2 injections of ISOTEC^{SM} modified Fenton Reagent (Day 0 and after 13 months)
ISOTEC, Quarry Facility, NJ	Pilot	1,2-DCB 1,4-DCB	3.847 0.489	98.1% 98.0%	4.5 months	• Fractured bedrock underlying glacial overburden of 9-20 ft thick; water table approx. 20-25 ft bgs within the bedrock. • Cost <$100,000
Thermal Treatment						
• No thermal demonstrations for treatment of MCB/DCB in the saturated zone found in literature						
Enhanced Aerobic Bioremediation						
Nielsen and Christensen, 1994	Bench	1,2-DCB 1,4-DCB	0.119 0.120	81.0% 78.3%	149 days	• Study confirmed aerobic biodegradation of DCBs • Tests performed in 2.5-L bottles with site soil and groundwater • Oxygen added by air sparging • Oxygen concentration maintained at ~9 mg/L by periodic air injection
Herrington et al., 2000	Bench	MCB	5.6	87.5%	7 days	• Column studies using site solids and groundwater • Results demonstrated ability of native bacteria to degrade MCB to concentrations below 0.1 mg/L • Influent reservoir oxygenated via air sparging

Note:
MCB = monochlorobenzene; DCB = dichlorobenzene; NA = not applicable

TABLE 2.1
REVIEW OF MCB/DCB DNAPL TREATMENTS IN THE SATURATED ZONE

Solutia Inc., W.G. Krummrich Facility
Sauget, Illinois

Reference	Treatment Scale	Constituent(s)	Initial Conc. (mg/L)	Conc. Reduction	Treatment Duration	Comments
Hicks et al., 1999	Pilot	MCB (Note: mixed contaminant plume; MCB not primary constituent)	0.76	63.5%	6 months	• In-situ aerobic bioremediation pilot-test • Oxygen Release Compound (ORC) used to generate oxygen • Single injection of ORC was performed and groundwater concentrations were monitored for six months • Full-scale application of enhanced aerobic bioremediation using ORC planned
Vogt et al., 2004	Bench/Pilot	MCB	14.5 to 22.5	100%	2 years	• 12 m long reactor filled with aquifer sediment and fed with site groundwater • Demonstrated oxygen was only limiting factor for in-situ aerobic bioremediation • Oxygen produced by injection of hydrogen peroxide at the bottom of the reactor • No chemical oxidation of MCB from hydrogen peroxide • Oxygen quickly consumed • Samples from bottom of reactor did not contain measurable MCB • MCB concentrations increased along the length of the reactor due to desorption from sediment material

Note:
MCB = monochlorobenzene; DCB = dichlorobenzene; NA = not applicable

TABLE 2.2
MCB/DCB DNAPL MASS AND VOLUME IN SATURATED SOILS
(395 ft MSL - Bedrock)

	Soil		Chemical	
	Volume (Cubic Yards)	Mass (Kilograms)	Volume (Cubic Yards)	Mass (Kilograms)
MCB - Plant Process Area				
>1ppm	12,007,400	16,982,900,000	139.405	117944
>10ppm	3,175,640	4,491,700,000	137.064	115964
>100ppm	872,940	1,234,700,000	123.928	104850
>250ppm	201,111	284,450,000	88.069	74511
>500ppm	86,912	122,930,000	57.436	48594
MCB - Former Chlorobenzene Process Area				
>1ppm	1,868,990	2,643,610,000	122.861	103948
>10ppm	1,413,990	1,999,940,000	122.582	103712
>100ppm	703,090	994,480,000	117.746	99619
>250ppm	200,149	283,100,000	87.966	74425
>500ppm	86,914	122,934,000	57.437	48595
DCB - Plant Process Area				
>1ppm	12,007,400	16,982,900,000	132.107	129143
>10ppm	1,352,690	1,913,220,000	131.594	128641
>100ppm	621,350	878,850,000	127.264	124409
>250ppm	210,650	297,950,000	105.398	103033
>500ppm	102,109	144,424,000	80.08	78283
DCB - Former Chlorobenzene Process Area				
>1ppm	1,868,990	2,643,610,000	119.322	116645
>10ppm	1,008,800	1,426,830,000	119.112	116439
>100ppm	495,060	700,210,000	115.896	113295
>250ppm	188,565	266,710,000	99.272	97044
>500ppm	97,060	137,285,000	77.626	75885

Notes:

1) ft bgs = feet below ground surface.
2) Volume and mass determined with Environmental Visualization Software (Version 7.92)

SURFACTANT-ENHANCED SOLUBILIZATION TREATABILITY STUDIES

Cyclodextrin-Enhanced Solubilization of Organic Contaminants with Implications for Aquifer Remediation

by John E. McCray, Thomas B. Boving, and Mark L. Brusseau

Abstract

Reagents that enhance the aqueous solubility of nonaqueous phase organic liquid (NAPL) contaminants are under investigation for use in enhanced subsurface remediation technologies. Cyclodextrin, a glucose-based molecule, is such a reagent. In this paper, laboratory experiments and numerical model simulations are used to evaluate and understand the potential remediation performance of cyclodextrin. Physical properties of cyclodextrin solutions such as density, viscosity, and NAPL-aqueous interfacial tension are measured. Our analysis indicates that no serious obstacles exist related to fluid properties that would prevent the use of cyclodextrin solutions for subsurface NAPL remediation. Cyclodextrin-enhanced solubilization for a large suite of typical ground water contaminants is measured in the laboratory, and the results are related to the physicochemical properties of the organic compounds. The most-hydrophobic contaminants experience a larger relative solubility enhancement than the less-hydrophobic contaminants but have lower aqueous-phase apparent solubilities. Numerical model simulations of enhanced-solubilization flushing of NAPL-contaminated soil demonstrate that the more-hydrophilic compounds exhibit the greatest mass-removal rates due to their greater apparent solubilities, and thus are initially more effectively removed from soil by enhanced-solubilization-flushing reagents. However, the relatively more hydrophobic contaminants exhibit a greater improvement in contaminant mass-removal (compared with water flushing) than that exhibited for the relatively hydrophilic contaminants.

Introduction

Nonaqueous phase organic liquids (NAPLs) are a common cause of ground water pollution and occur in the environment at numerous contaminated sites (Mercer and Cohen 1990; National Research Council [NRC] 1994). The aqueous solubilities of many organic compounds are often very small (e.g., milligrams per liter). Therefore, large amounts of water must be flushed through the subsurface to remove the contaminant mass, even under conditions of equilibrium mass transfer between the NAPL and aqueous phases. The presence of NAPL is the single most important factor limiting cleanup of sites contaminated by organic compounds (NRC 1994).

Due to the well-documented limitations of pump-and-treat remediation, alternative methods for removal of subsurface NAPL contamination are a focus of current research (NRC 1994; Palmer and Fish 1992). Chemically enhanced in situ flushing is an innovative remediation technique currently attracting attention. With this technique, dissolution of NAPL into the aqueous phase is enhanced by the addition of a solubility-enhancement agent to the flushing fluid. Cosolvents (e.g., Augustijn et al. 1994; Rao et al. 1997; Falta 1998) and surfactants (e.g., Abdul et al. 1990; Sabatini et al. 1996; Fountain 1997; Martel et al. 1998) are examples of reagents that have been proposed for enhanced-solubilization remediation.

The solubility-enhancement additive described in this research is cyclodextrin, a polycyclic oligosaccharide or glucose-based molecule

Pages 94–103

formed from the degradation of starch by bacteria (Bender and Komiyama 1978). Cyclodextrins have long been used for pharmaceutical applications (e.g., drug delivery). Base cyclodextrins are composed of several glucose ($C_6H_{12}O_6$) molecules arranged in a toroid. Specifically, the base units comprise a number of "chair-shaped" D(+)-glucopyranose units. Cyclodextrin molecules are designated by Greek letters to denote the number of glucose units in the toroid ($\alpha = 6$, $\beta = 7$, and $\gamma = 8$). Molecular weights of the base cyclodextrins range from 972 to 1297 grams/mole.

These toroidal-shaped molecules have a hydrophobic, nonpolar interior and a hydrophilic, polar exterior. The average outer cylindrical diameter of the cyclodextrin molecule is about 1.5 nanometers (nm), while the average inner diameter has been reported as 0.346 nm (Wang and Brusseau, 1993). Relatively nonpolar organic contaminants partition to the interior of the molecule (i.e., forming inclusion complexes), while the highly polar exterior provides the molecule with a relatively large aqueous solubility. These properties allow cyclodextrin to greatly enhance the aqueous-phase solubility of organic contaminants.

The aqueous solubilities of the base cyclodextrins range from 18 to 232 g/L (Bender and Komiyama 1978). Their solubilities can be increased by addition of polar functional groups. The cyclodextrin derivative used in this research, for example, is hydroxypropyl-β-cyclodextrin (HPCD), which is modified to include hydroxypropyl groups and has a solubility greater than 500 g/L. Such high solubilities allow relatively high concentrations to be used in field applications. The molecular weight of HPCD ranges from 1326 to 1500 grams/mole, depending in part on the degree of hydroxpropyl substitution.

The pK_a (log of the equilibrium acidity constant) of the hydroxyl groups associated with the external surface of the cyclodextrin is about 12 (Bender and Komiyama 1978), thus they remain polar in essentially all natural aqueous environments. Solubilization by HPCD is insensitive to changes in pH and ionic strength, and HPCD is resistant to precipitation (Wang and Brusseau 1995). In addition, the presence of cyclodextrin in water has negligible effect on pH or ionic strength. Therefore, cyclodextrin is unlikely to induce clogging of well screens and sampling devices during field-scale flushing and is not expected to affect aquifer permeability. HPCD has been shown to be resistant to biodegradation for time periods of at least a few months (Wang et al. 1998). However, given the glucose-based composition of cyclodextrin, it is expected to be biodegradable over the long term, particularly at low concentrations. Thus, traces of cyclodextrin that may remain in the subsurface after remediation are expected to be biodegradable.

As a sugar, cyclodextrin has some inherent advantages as a remediation agent. For example, it is nontoxic to humans, so there are minimal health-related concerns associated with the injection of cyclodextrin into the subsurface. In addition, based on laboratory studies by Wang et al. (1998), cyclodextrin solutions do not harm resident microbial populations. Cyclodextrin experiences little or no sorption to aquifer solids (Brusseau et al. 1994) and does not partition appreciably to the NAPL phase (discussed in a later section), so it is easily removed from the subsurface, which is an issue of regulatory concern.

The ability of cyclodextrin to increase the apparent solubility of organic compounds is the basis for its potential use in subsurface remediation. In addition, laboratory experiments show that cyclodextrin solutions can enhance the desorption of organic contaminants from soil and thereby further enhance their removal from porous media (Brusseau et al. 1994). The efficacy of cyclodextrin flushing was demonstrated during a pilot-scale field test (McCray and Brusseau 1998) wherein soil contaminated with a complex NAPL mixture was flushed with 8 pore volumes of a 10% HPCD solution. Based on contaminant concentrations in soil samples collected before and after remediation and on results of partitioning tracer tests, it was determined that approximately 41% of the NAPL was removed from the subsurface during the 10-day flush.

An indirect benefit of cyclodextrins is that they have the potential to enhance in situ bioremediation. For example, Wang et al. (1998) reported that the presence of HPCD enhanced the rate of phenanthrene biodegradation. Thus, it is possible that HPCD may enhance in situ bioremediation as well as solubilization. Specific cyclodextrins have also been shown to complex metals in the presence of organic contaminants, and thus may be useful in remediation of sites contaminated with mixed wastes, such as organics and metals (Brusseau et al. 1997).

HPCD has been shown to perform similarly to other solubility-enhancing agents. Solutions of several remediation agents (surfactants, alcohol, organic matter, and cyclodextrin) of identical aqueous concentrations were tested in the laboratory for NAPL-mass removal effectiveness (Boving and Brusseau 1999). Solutions of the surfactants DOWFAX and SDS, ethanol, dissolved organic matter, and HPCD exhibited similar efficiencies under certain conditions. The cost of technical-grade HPCD is within the range of common surfactants. However, chemical remediation agents are still being tested for remediation applications and the market is just starting to develop, so costs can change frequently. In addition, HPCD has been shown to be readily recyclable after use for NAPL remediation, a characteristic that would greatly improve the cost benefits of cyclodextrin remediation (Boving et al. 1998).

The unique physicochemical properties of cyclodextrin enable it to enhance the subsurface contaminant mass-removal rate when used as a flushing agent compared with conventional water-flushing (pump and treat) techniques. Therefore, when combined with the previously described other advantages, cyclodextrin shows promise for use in subsurface remediation of NAPL contaminants.

In this paper, we first examine some physical properties of aqueous cyclodextrin solutions important to ground water remediation design. Second, we measure cyclodextrin-enhanced solubilization for a suite of typical ground water contaminants and relate the results to the physicochemical properties of the organic compounds. Finally,

we use numerical modeling simulations to demonstrate how data from bench-scale laboratory studies can be used for estimating potential cyclodextrin-enhanced remediation performance.

Theory

The apparent solubility of an organic compound is defined as the equilibrium concentration of the compound in an aqueous solution containing an enhanced-solubilization agent. The apparent solubility values of organic compounds in aqueous cyclodextrin solutions have been observed to increase linearly with the aqueous cyclodextrin concentration (Wang and Brusseau 1993; Bizzigotti et al. 1997). A simple expression of the relationship between cyclodextrin concentration (C_H) and the apparent solubility (S^A) of a single solute is

$$S^A = S^w (1 + K_{cw} C_H) = S^w E \qquad (1)$$

where S^w is the water solubility, K_{cw} is the partition coefficient of the solute for equilibrium mass transfer between cyclodextrin and water, and E is the solubility-enhancement factor. While the enhancement depends on the cyclodextrin concentration, K_{cw} is concentration independent and is thus unique for a given organic compound. The solubility enhancement results from a decrease in the aqueous-phase activity (and thus activity coefficient) compared with a water-only solution, due to the complexation of the organic solute by cyclodextrin. This effect is analogous to the impact of alcohols and surfactants on the solubilities of low-polarity organic compounds.

Materials and Methods

Analytical-grade HPCD with a purity of at least 98.7% (Cerestar USA Inc.) was purchased from Aldrich Chemical Co. (Milwaukee, Wisconsin); the organic chemicals were also purchased from Aldrich Chemical Co., with purity greater than 99%. Methanol, used for standard preparation and sample dilution, was purchased from Baker as HPLC-grade solvent.

Density measurements of a 10% cyclodextrin solution at 21.5°C were obtained by measuring the mass of a 4 mL sample and dividing by the volume. Five replicates were performed. Viscosity measurements of cyclodextrin solution were conducted using a no. 3 "falling ball" viscometer (VWR Scientific, Phoenix, Arizona). Ten replicate measurements were performed. Laboratory measurements of interfacial tension between three NAPLs and aqueous solutions of HPCD were conducted using the du Nuoy tensiometer technique (Fisher Scientific, Surface Tensiomat Model 21) (e.g., Bai et al. 1997).

Batch solubility measurements were performed as follows: 25 mL of water or 10 wt% HPCD was added to 50 mL Corex centrifuge tubes. Then 2 mL of the NAPL was added to each tube, which is in excess of the solubility limits. Tubes containing water and immiscible organic liquid were prepared in an identical manner and in triplicate. All samples were equilibrated by placing them on a vortex shaker for one minute before and after equilibration on a reciprocating shaker for at least 48 hours. The equilibration was performed at 23±1°C. After equilibration, samples were centrifuged at 75 g for 20 minutes to separate the aqueous and organic-liquid phases. Aliquots (0.5 mL) of the aqueous-phase supernatant were withdrawn and diluted with a 50:50 (by volume) methanol/water solution in 10 mL volumetric flasks for subsequent chemical analysis.

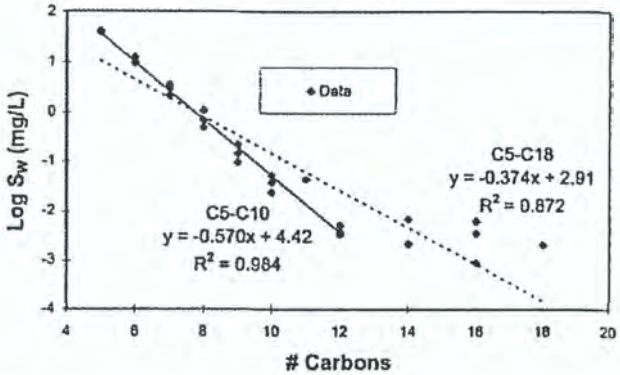


Figure 1. Correlation of literature values for Log Apparent Solubility (Log S^W) vs. carbon number for alkanes (data from McAuliffe 1966; Franks 1966; Baker 1967; Sutton and Calder 1974; Tewari et al. 1982; Schwarzenbach et al. 1993)

The following compounds were analyzed by UV-VIS (the wavelengths used for UV detection are listed in parenthesis): trichloroethene (210 nm), o-dichlorobenzene (230 nm), p- dichlorobenzene (223 nm), o-xylene (230 nm), naphthalene (270 nm). Pyrene was analyzed using fluorescence spectroscopy (394 nm excitation wavelength/ 391 nm emission wavelength). The effect of methanol on the ultraviolet and fluorescence spectrums was negligible (less than 1% effect) for the HPCD and methanol concentrations used here.

The concentrations of p-xylene, toluene, ethylbenzene, trimethylbenzene, decane, and undecane were analyzed by gas chromatography (GC) with a flame-ionization detector (FID). Five mL portions of the aqueous phase of the centrifuged samples were transferred to glass 20 mL head-space vials (Teflon®-lined septum and crimp cap), allowed to equilibrate to room temperature, and analyzed by GC-FID (Shimadzu, GC-17A with capillary column) with a head-space autosampler (Tekmar, 7000).

For the compounds that exist as solids at room temperature, equilibrium was not readily obtained using the above equilibration methods. Thus, a generator column approach (e.g., Wang and Brusseau 1993) was used. The generator column was a 30 cm long, 2 cm inner diameter glass distillation column (Aldrich Chemical Co.) packed with prewashed glass beads (212 to 300 μm, purchased from Sigma Co.) coated with excess chemical. The column was plugged with glass wool at both ends to retain the glass beads in the column and to minimize displacement of solid-phase chemical particles into the aqueous samples.

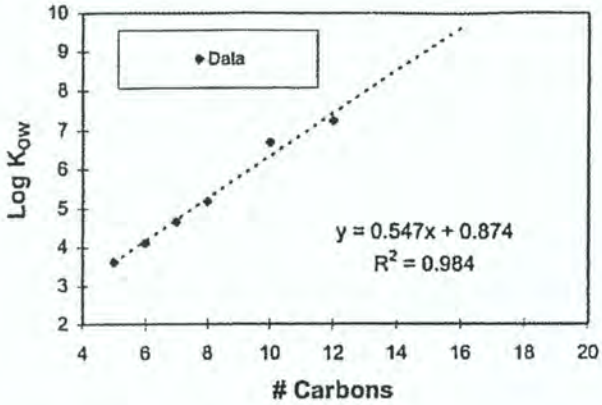


Figure 2. Correlation of literature values for Log K_{OW} vs. carbon number for alkanes (data from Tewari et al. 1982; Burkhard et al. 1985). K_{OW} is the octanol-water partition coefficient.

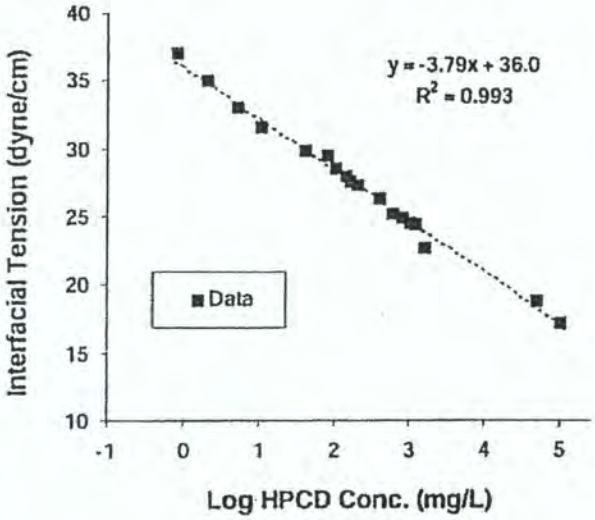


Figure 3. Influence of HPCD on interfacial tension between TCE and aqueous solutions (lower-value interfacial-tension data from Nelson 1999).

The HPCD solutions were passed through the column, and the effluent was analyzed continuously for solute concentrations using UV-VIS or fluorescent spectroscopy until a relatively constant effluent concentration was obtained. Analytical detection limits for these methods are given in McCray (1998).

For the ultra-low-solubility compounds (DDT, decane, undecane, octadecane), water solubilities (S^W) were not measured. The S^W values for these compounds were obtained from the literature. For decane, undecane, and octadecane, measured literature values varied considerably. To obtain S^W for these compounds, a correlation was developed between carbon number (C) and measured water solubility for the general class of alkanes with carbon numbers from C5-C18 (Figure 1). Note that the measured values for alkanes with greater than 12 carbons do not adhere to the highly correlated relationship exhibited by the C5-C12 compounds, probably owing to the difficulty in obtaining accurate measurements for compounds of such low solubility. Thus, the solubilities for DEC and UND were obtained from the C5-C12 correlation, while the solubility for OCT was obtained from the C5-C18 correlation.

Octanol-water partition coefficients (K_{OW}) were taken from the literature for all compounds. For most compounds, a large number of measured Log K_{OW} values were available. Thus, the most common values that were central within the reported range in values were used. Tabulated log K_{OW} values for alkanes were sparse. Thus, to prevent using a spurious measurement, a correlation between carbon number and Log K_{OW} was developed from measured values in the literature (Figure 2).

Results and Discussion

Fluid Properties of Cyclodextrin Solutions

The density and viscosity measurements for a 10 wt% cyclodextrin solution are given in Table 1. These fluid properties of the cyclodextrin solution are favorable for use in the remediation of NAPL-contaminated aquifers. Because the density of a 10 wt% solution is nearly equal to that of water (specifically, 2.6% greater than water), and the solution is completely miscible with water, major density-control problems are not expected. Consideration of density-driven transport may be important for field-implementation of many cosolvents (Roeder and Falta 1998; Martel et al. 1998). The viscosity of a 10 wt% cyclodextrin solution is about 19% greater than that of water, which should be considered when designing flow-

Table 1
Hydrodynamic Parameters for a 10 wt% Aqueous Cyclodextrin Solution (all values measured at 21.5°C).

	Density (kg/L)	Viscosity (cP)	Interfacial Tension (dyne/cm) TCE-Aqueous	PCE-Aqueous	[b]Organic Mixture-Aqueous
10 wt% HPCD	1.024 ± .003	1.153 ± .011	17.2	20.6	15
Water	0.998 ± .004	0.971[a]	34.5[c]	44.4[c]	37

[a]Lide (1992).
[b]For NAPL collected from a Superfund hazardous-waste site (McCray and Brusseau 1998).
[c]Mercer and Cohen (1990).

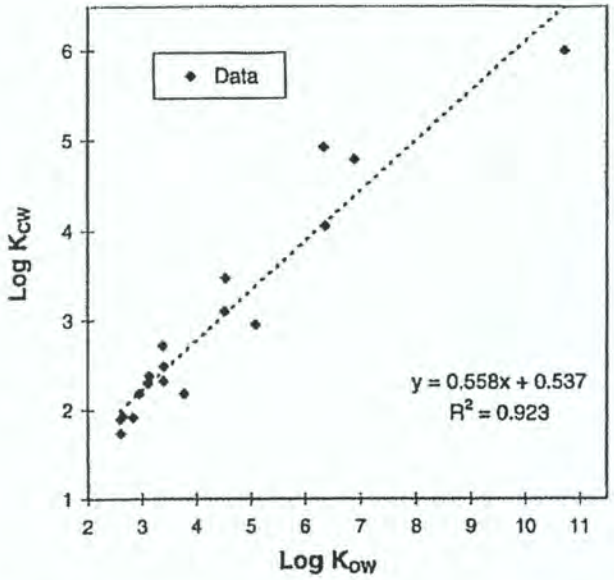


Figure 4. Relationship between Log K_{CW} and. Log K_{OW} for compounds in Table 2. K_{OW} is the octanol-water partition coefficient, K_{CW} is the cyclodextrin-water partition coefficient.

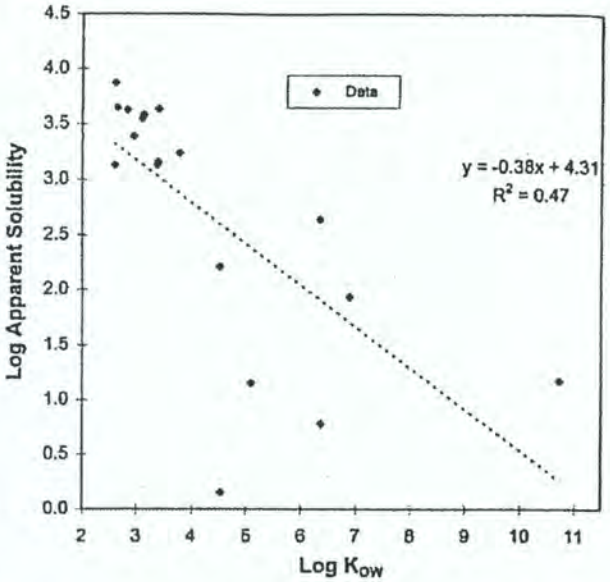


Figure 5. Relationship between log apparent solubility (in 10% HPCD solution) (Log S^A) vs. Log K_{OW} for compounds in Table 2.

delivery systems but should pose no serious obstacle. In addition, a water-miscible remediation fluid with a viscosity greater than water typically results in a more stable front as it displaces the resident water (i.e., viscous fingering is less likely to occur), which provides a more efficient sweep of the contaminated zone (e.g., Lake 1989).

Previous measurements of HPCD-water systems have indicated that surface tension decreased with increasing HPCD concentration from 72 dyne/cm to an apparent asymptote of between 60 and 65 dyne/cm (Wang and Brusseau 1993). Measurements obtained for this research (Table 1, Figure 3) indicate that a 10 wt% HPCD solution reduced the NAPL-water interfacial tension by as much as 60% for TCE and PCE NAPL, and similarly decreased the interfacial tension of the multicomponent NAPL. Figure 3 shows that the relation between the log of HPCD concentration and the aqueous-TCE interfacial tension is linearly correlated for a wide range of HPCD concentrations.

Bizzigotti et al. (1997) determined that β-cyclodextrin aqueous solutions up to 1% concentrations caused slight decreases in the interfacial tension of a PCE system at lower concentrations and slight increases (less than 5%) at concentrations nearer to 1%. The same researchers determined that aqueous solutions of α-cyclodextrin and γ-cyclodextrin (up to 5% concentrations) caused increases in interfacial tension of up to 25% for a PCE system. In our experiments, HPCD lowered the interfacial tension. Thus, the degree of NAPL-water interfacial partitioning for HPCD appears to be more significant than for that of the unaltered cyclodextrin molecules. This increased interfacial partitioning of HPCD may be related to the presence of the hydroxypropyl groups on the exterior of the molecule, which are added to the base molecule to increase its polarity and thus solubility (e.g., Wang and Brusseau 1993). Because this substitution makes the molecule more hydrophilic, it would seem unlikely that it would cause increased partitioning to the organic liquid surface. However, it is possible that the hydroxypropyl groups may impart an "amphiphilic" nature to the molecule that does not exist for the base cyclodextrin. That is, even though the addition of an external group may cause the molecule to be more polar with respect to aqueous-phase partitioning, it may also cause a polar-nonpolar dipole effect that results in added surface reactivity.

Significant reductions in interfacial tension can result in the mobilization of NAPL globules, which can result in effective removal of organic liquid from the subsurface. However, it can be difficult to capture all mobilized globules during remediation (Sabatini et al. 1996; Fountain 1997). Remediation techniques based on mobilization, therefore, may not be appropriate under many circumstances (Fountain 1997). Interfacial tension reductions of the magnitudes indicated in Figure 3 are unlikely to cause significant mobilization of residual NAPL saturations (e.g., McCray and Brusseau 1998). This hypothesis is supported by the results reported by Boving et al. (1999), who examined the use of HPCD solutions for flushing columns containing residual saturations of PCE and TCE (at saturations between 10% and 20%). No NAPL mobilization was observed for HPCD concentrations of 5 wt% and 10 wt%. However, due to the large variations in pore sizes in an aquifer, even a slight reduction in interfacial tension may cause local mobilization of NAPL.

As illustrated in Figure 3, the interfacial tension-reduction effect is relatively easy to characterize for HPCD solutions. The interfacial tension reductions indicated in Figure 3 can, under certain conditions, cause

Table 2
Physicochemical and HPCD-Enhanced Solubility Parameters of Organic Compounds

		Molar Mass (g/mol)	Log K_{ow}	Log K_{cw}	E	S^W (mg/L)	$^aS^A$ (mg/L) (10% HPCD)
trichloroethene	TCE[a]	131.39	2.53[d]	1.71	6.5	1150	7502
tetrachloroethene	PCE[c]	165.83	2.60[d]	1.90	8.9	150	1341
toluene	TOL[a]	92.17	2.65[d]	1.93	9.6	464	4454
chlorobenzene	CB[b]	112.60	2.84[d]	1.92	9.3	456	4249
o-xylene	o-XYL[a]	106.17	2.95[d]	2.18	16.1	152	2453
p-xylene	p-XYL[a]	106.17	3.10[d]	2.30	20.8	170	3536
ethylbenzene	EB[a]	106.17	3.13[d]	2.38	24.9	153	3810
naphthalene	NAP[a,g]	121.18	3.37[d]	2.72	53.5	31	1659
1,4-dichlorobenzene	p-DCB[a]	147.00	3.39[d]	2.32	21.8	65	1419
1,2-dichlorobenzene	o-DCB[a]	147.00	3.40[d]	2.48	31.5	137	4316
1,2,4-trimethylbenzene	TMB[a]	120.19	3.78[d]	2.20	17.0	106	1802
anthracene	ANTH[b,g]	178.24	4.45[d]	3.47	296	0.048	14
phenanthrene	PHEN[a,g]	178.24	4.52[d]	3.10	126	1.30	163
pyrene	PYR[a,g]	202.30	5.09[d]	2.95	90.3	0.157	14
1,1,1-trichloro-2,2-dichloropheynl-ethane	DDT[a,b]	354.49	6.36[d]	4.05	1123	0.0054[d]	6.1
decane	DEC[a]	142.28	6.34[e]	4.92	8345	0.0525[f]	167
undecane	UND[a]	156.30	6.89[e]	4.79	6100	0.0141[f]	98
octadecane	OCT[a,g]	252.40	10.72[e]	4.79	6224	1.5E-04[f]	13

[a]All parameters are measured except where otherwise noted.
[b]Wang and Brusseau (1993)
[c]Bizzigotti et al. (1997)
[d]Montgomery and Welkom (1989)
[e]From correlation shown on Figure 2
[f]From correlations shown on Figure 1
[g]Exists in a solid state under environmental conditions

formation of "macroemulsions" (droplets larger than about 1 μm), which are thermodynamically unstable, opaque, and can usually be detected visually in the aqueous phase (Fortin et al. 1997). No macroemulsions were observed in the laboratory samples. In addition, any macroemulsions that may have formed in the batch-solubility samples were separated from the aqueous-phase by centrifugation prior to solubility analysis, and therefore should not have contributed to the measured solubility enhancements. An interfacial tension of less than about 0.1 dyne/cm is generally considered to be necessary for formation of microemulsions, which cannot generally be detected visually (Bourrel and Schecter 1988; Fortin et al. 1997). However, interfacial tension reductions to this level were not observed in these laboratory experiments.

Solubility Enhancement

The solubility enhancements obtained with a 10% HPCD solution are reported in Table 2. Cyclodextrin causes the largest relative solubility enhancement for the more-hydrophobic compounds. As will be discussed later, this has important implications for ground water remediation. The relationship between Log K_{cw} and Log K_{ow} for the 18 compounds (Figure 4) exhibits a good linear correlation ($R^2 = 0.92$). The linear relationship is not surprising given that the more-hydrophobic compounds (with larger K_{OW} values) are more strongly attracted to the apolar cyclodextrin cavity. Overall, this results in a more favorable entropy change for these compounds, providing for a relatively larger solubility enhancement.

Figure 5 illustrates that the apparent solubility (S^A) is generally greatest for the more-hydrophilic (less-hydrophobic) compounds in the data set. As is apparent from Figure 5, however, this relationship does not exhibit a strong correlation, and may not hold for a particular subset of hydrophobic compounds. Theoretically, the relationship should be linear. That is, as is depicted in Figure 1, many researchers have determined, log S^W vs. log K_{OW} relationships are linear for most classes of compounds (e.g., Tewari et al. 1982; Schwarzenbach et al. 1993). Because the relationship between log K_{CW} and log K_{OW} is linear (Figure 4), the relation between log E and log K_{OW} should be linear. Apparent solubility is defined as the product ES^W, and Log (ES^W) = Log E + Log S^W, thus the relation between log S^A and log K_{OW} should also be linear.

Similar relations may exist for other enhanced-solubility agents (e.g., surfactants and cosolvents). This is true because most traditional surfactants and cosolvents also induce larger aqueous-solubility enhancements for less polar compounds, while the water solubilities of organic compounds generally decrease with decreasing polarity.

Implications for Remediation: Modeling Cyclodextrin-Enhanced Contaminant Mass Removal

In this section, we present model simulations to demonstrate how information gained from experimental

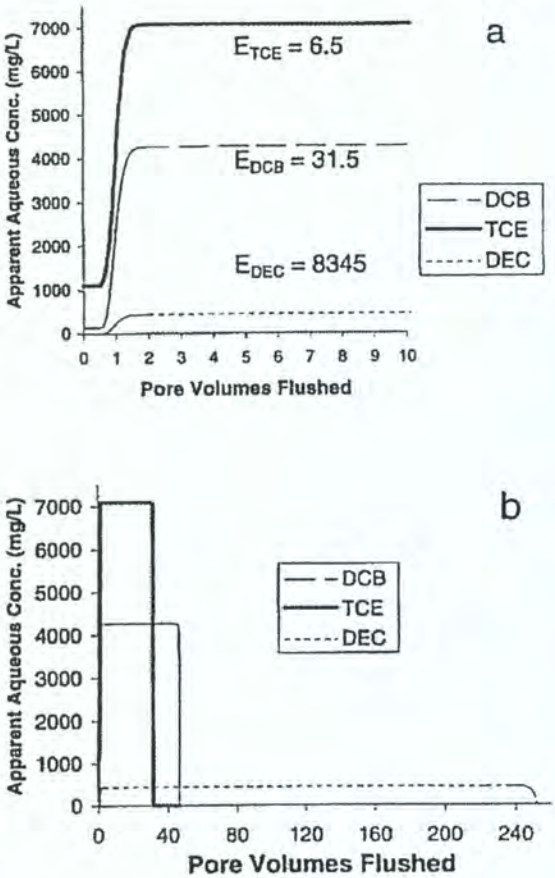


Figure 6. Simulated TCE, 1,2-DCB, and DEC concentrations during flushing of NAPL-contaminated soil with a 10 wt% HPCD solution for (a) the first 10 pore volumes, and (b) for the entire flushing period.

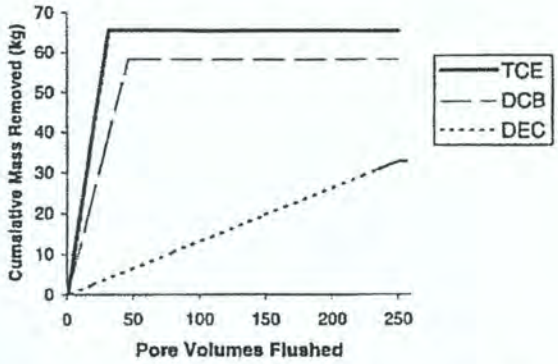


Figure 7. Simulated cumulative mass removal of TCE, 1,2-DCB and DEC from soil during flushing with a 10 wt% HPCD solution.

Table 3
Comparison of Times Required for Complete NAPL Removal Using Cyclodextrin (10 wt%) Flushing and Traditional Pump-and-Treat Remediation (Water Flushing) Based on Numerical Model Simulations

Contaminant	Cyclodextrin-Enhanced Flushing Remediation Time (days)	Water Flushing Remediation Time (days)
TCE	32	197
1,2-DCB	48	1409
DEC	252	2.1×10^6

data is useful for understanding the dissolution and mass-removal behavior of NAPL contaminants during remediation with enhanced-solubility agents. The model used for this purpose, developed by Ji and Brusseau (1998), can simulate enhanced dissolution of single-component NAPLs with subsequent advective-dispersive transport of the dissolved-phase contaminant. Other processes can also be modeled using the model (e.g., sorption of contaminant and flushing agent) but are not included here. The reader is referred to Ji and Brusseau (1997) for details of the model.

Under conditions of equilibrium dissolution, the absolute amount of contaminant mass removed during a flushing event increases as the absolute apparent solubility of the contaminant increases. The apparent solubility is, in turn, a function of the water solubility and the enhancement factor (recall Equation 1). As discussed previously, the water solubility generally decreases with increasing contaminant hydrophobicity, while the enhancement factor generally increases with increasing contaminant hydrophobicity. Therefore, the relationship between the mass-removal efficiency of a certain contaminant and its hydrophobicity is not straightforward. For the contaminants studied in this research, the apparent solubility (and thus the expected mass-removal efficiency) generally decreases with increasing hydrophobicity (Figure 5). These principles will be illustrated with a series of numerical-model simulations.

Enhanced flushing of NAPL-contaminated soil using 10 wt% HPCD solution is simulated for three contaminant scenarios. In all cases, the soil is contaminated with a single-component NAPL. Each simulation assumes equilibrium dissolution of a NAPL during enhanced flushing of a one-dimensional "column" of sandy porous media that is 100 cm long with a volume of 1 m^3. The soil is assigned a porosity of 30% and a bulk density of 1.7 kg/L. The NAPL saturation is designated as 15%, which is common for NAPLs in saturated porous media (Mercer and Cohen 1990). The contaminants used for each scenario are TCE, 1,2-DCB, and DEC, respectively. These chemicals are common ground water contaminants (Mercer and Cohen 1990). The simulations represent enhanced flushing of a 1 m^3-volume of contaminated soil at a hazardous-waste site.

A uniform flushing-solution velocity of 4 cm/hour is used, which is similar to that used during HPCD-flushing operations in the field (McCray and Brusseau 1998) and equivalent to flushing about one pore volume per day. A dispersivity of 10 cm was assumed, which is consistent with a flow-length scale of 100 cm (e.g., Gelhar 1986). For each simulation, 260 pore volumes of cyclodextrin solution were flushed through the soil column.

Figures 6a and 6b depict the effluent concentrations during the early stages of cyclodextrin flushing, and for the entire flushing period, respectively, for the three contaminants. The aqueous solution in the soil is assumed to be in equilibrium with the NAPL at the start of flushing. Thus, the effluent concentration is initially equal to the aqueous solubility for each contaminant. During the first pore volume of flushing, the water within the soil is replaced by the HPCD flushing fluid. After about 1.5 pore volumes, the cyclodextrin solution has achieved maximum concentration (10 wt%) for each flushing scenario. The maximum effluent contaminant concentrations indicated on the figure, as well as the concentration enhancements (E), are equal to those values shown in Table 2.

As expected, the simulations indicate that solubility enhancement is greater for the more-hydrophobic compounds (Figure 6). For example, the solubility enhancement of DEC is more than 1200 times greater than the solubility enhancement for TCE. However, the actual effluent concentration of TCE (7300 mg/L) is considerably greater than that of DEC (167 mg/L). Because of the greater concentration, the TCE NAPL is removed at a faster rate than the other contaminants. The TCE NAPL is completely removed after about 32 pore volumes of flushing. Conversely, 46 pore volumes of flushing are required for complete removal of DCB, while DEC requires 252 pore volumes of flushing for complete removal. Figure 7 illustrates that the mass removal rate is greatest for TCE, even though TCE exhibits the lowest solubility enhancement, while the lowest mass-removal rate occurs for DEC, which is the most hydrophobic and has the largest solubility enhancement. A similar trend would occur for most enhanced-solubilization flushing reagents.

The above simulations illustrate that, when evaluated based on mass-removal rates, enhanced-solubilization flushing techniques are expected to be initially most effective for contaminants that are relatively less hydrophobic. However, compared with water flushing (i.e., traditional pump and treat), enhanced-solubilization flushing may result in a much greater reduction in NAPL removal times for the more-hydrophobic contaminants than for the relatively hydrophilic contaminants. To demonstrate this principle, simulations were conducted to estimate the time required to remove all the NAPL from the soil column using water flushing. As shown in Table 3, the improvement gained by flushing with a cyclodextrin solution is much greater for DEC than for DCB or TCE. This is a direct consequence of the greater solubility enhancement for DEC. Thus, if traditional pump-and-treat remediation is used as a baseline to judge remediation effectiveness (e.g., Rao et al. 1997; McCray et al. 1999), enhanced-solubilization techniques would appear to be more effective for the more-hydrophobic compounds.

The simulated contaminant mass-removal relationships demonstrated here were generally observed in the field during a pilot-scale technology demonstration of cyclodextrin flushing for remediation of a complex organic mixture (McCray and Brusseau 1998). During the 10-day (8 pore-volume) field experiment, the less-hydrophobic target contaminants (such as TCE and DCB) exhibited a greater reduction in contaminant mass than did the more-hydrophobic contaminants (such as TMB, DEC, and UND), even though the more-hydrophobic contaminants generally exhibited higher relative solubility enhancements.

When NAPL mixtures exist, the mass-removal relationships described above are still valid, but are complicated by the impact of a contaminant's NAPL-phase mole fraction on dissolution (e.g., McCray and Brusseau 1999). That is, equilibrium aqueous concentrations (C_i^w) for contaminants in a NAPL mixture are directly proportional to the product of the contaminant's NAPL-phase mole fraction (X_i^N) and aqueous solubility according to Raoult's law (i.e., $C_i^w = X_i^N S_i^w$. This can result in complex dissolution behavior because the mole fraction for each contaminant varies as the NAPL dissolves. It is also possible that rate-limited dissolution will occur to some extent during enhanced flushing, which would reduce the mass-removal rates for all contaminants. Rate-limited dissolution for NAPL mixtures is not well understood, particularly in the presence of remediation agents. However, based on the work of Garg and Rixey (1999), rate limitations are not expected to vary greatly between contaminants, and thus the mass removal processes described here should generally apply under conditions of rate-limited NAPL dissolution.

Summary

Cyclodextrin has advantageous properties that may make it an attractive agent for enhanced-solubility subsurface remediation. The fluid properties of a 10 wt% HPCD solution are similar to water, and thus should pose no serious constraints to its use in subsurface-remediation systems. However, the fluid properties and the effect of cyclodextrin solution on NAPL properties such as interfacial tension should be considered in a potential remediation design.

Chemical agents may greatly enhance the apparent solubilities of contaminants with very low water solubilities, and thus provide a great enhancement over traditional pump-and-treat. However, the overall mass removal during a fixed period may not be large, and remediation of the contaminant may require a considerable period of time. Conversely, while chemical agents may induce a modest solubility enhancement for relatively hydrophilic contaminants (such as for TCE), the net mass removal over a specified time may be much greater than for the more-hydrophobic contaminants. Thus, contaminants that exhibit the greatest solubility enhancement may not be as efficiently removed from the soil as those that exhibit a smaller solubility enhancement. Therefore, if chemical agents are to be used to enhance contaminant solubility, they should be chosen carefully to be most effective for the contaminant of interest. These issues are particularly important to consider when dealing with a multicomponent NAPL, or a site with several separate single-component NAPLs, where a select few cont-

aminants may serve as the regulatory driving force for remediation.

Finally, this research indicates that simple bench-scale solubilization experiments using single-component NAPLs may be useful for understanding the contaminant transport and mass-removal behavior of NAPL contaminants during flushing scenarios, and thus for remediation design. This is true even in cases where multicomponent NAPLs are the source of contamination. The results of this research should also be applicable for other solubility-enhancing agents (e.g., cosolvents and surfactants). Ultimately, however, the performance of enhanced-flushing techniques is influenced by a number of factors, and successful application in the field will depend on resolution of these factors for each specific site.

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Density-Modified Displacement for DNAPL Source Zone Remediation: Density Conversion and Recovery in Heterogeneous Aquifer Cells

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Low interfacial tension (IFT) displacement (mobilization) of nonaqueous phase liquids (NAPLs) offers potential as an efficient remediation technology for contaminated aquifer source zones. However, displacement of dense NAPLs (DNAPLs) is problematic due to the tendency for downward migration and redistribution of the mobilized DNAPL. To overcome this limitation, a density-modified displacement method (DMD) was developed, which couples in situ density conversion of DNAPLs via alcohol partitioning with low IFT NAPL displacement and recovery. The objective of this work was to evaluate the DMD method for two representative DNAPLs, chlorobenzene (CB) and trichloroethene (TCE). Laboratory-scale experiments were conducted in a two-dimensional (2-D) cell, configured to represent a heterogeneous unconfined aquifer system containing low permeability lenses. After release and redistribution of either CB- or TCE-NAPL, the 2-D aquifer cells were flushed with a 6% (wt) *n*-butanol aqueous solution to achieve DNAPL to light NAPL conversion, followed by a low IFT surfactant solution consisting of 4% (4:1) Aerosol MA/Aerosol OT + 20% *n*-butanol + 500 mg/L $CaCl_2$. Visual observations and experimental measurements demonstrated that in situ density conversion and immiscible displacement of both CB and TCE were successful. Effluent NAPL densities ranged from 0.96 to 0.90 g/mL for CB and from 0.95 to 0.92 g/mL for TCE, while aqueous phase densities remained above 0.96 g/L. Density conversion of CB and TCE was achieved after flushing with 1.2 and 4.9 pore vol of 6% *n*-butanol solution, respectively. Recoveries of 90% CB and 85% TCE were realized after flushing with 1.2 pore vol of the low IFT surfactant solution, which was followed by a 1 pore vol posttreatment water flood. Surfactant and *n*-butanol recoveries ranged from 75 to 96% based on effluent concentration data. The observed minimal mobilization during the *n*-butanol density conversion preflood and near complete mobilization during the low IFT displacement flood were consistent with total trapping number calculations. The results reported herein demonstrate the potential efficiency of the DMD technology as a means of DNAPL source zone restoration.

Introduction

Many advances in the immiscible displacement of nonaqueous phase liquids (NAPLs) from unconsolidated aquifer materials are attributable to research in the field of enhanced oil recovery. One of the first applications of surfactant flooding techniques for NAPL recovery was designed to displace free phase gasoline in a laboratory soil column (*1*). Early surfactant enhanced aquifer remediation (SEAR) studies were cognizant of the potential for low interfacial tension (IFT) surfactant solutions to initiate downward migration of dense NAPLs (DNAPLs) (*2*, *3*). Furthermore, experiments conducted by Pennell et al. (*3*) indicate that ultralow IFTs (<0.001 dyn/cm), typically used in enhanced oil recovery, may not be necessary to mobilize entrapped DNAPLs from medium to fine sands.

The immiscible displacement, or mobilization, of entrapped organic liquids is governed by the relative influence of capillary, viscous, and buoyancy forces on NAPL ganglia. The ratio of the viscous to the capillary forces can be described by the capillary number, N_{Ca} (equation 1) (*4*):

$$N_{Ca} = \frac{q_w \mu_w}{\gamma_{ow} \cos \theta} \tag{1}$$

where the upward direction is taken as positive, q_w is the Darcy velocity, μ_w is the aqueous phase dynamic viscosity, γ_{ow} is the IFT between the organic and the aqueous phases, and θ is the contact angle. Traditionally, subsurface systems are often considered to be completely water wetting ($\theta = 0°$), and thus $\cos \theta$ is taken as unity. The relationship between the capillary number and residual saturation has been used to predict the onset and extent of oil displacement (e.g., refs *5* and *6*). A critical N_{Ca} region ($1 \times 10^{-4} < N_{Ca} < 1 \times 10^{-3}$) corresponding to NAPL displacement and sharp reductions in NAPL saturation was identified by several researchers (e.g., refs *6*–*8*). Much of the development of surfactant-based, tertiary oil recovery treatment was based on the concept of reducing the interfacial tension, thereby raising the capillary number beyond the critical value required for oil displacement (*5*). However, the capillary number does not account for the influence of buoyancy (gravitational) forces on the displacement process, which may be particularly important for DNAPLs. To address this issue, the bond number, N_B, may be used to incorporate the effects of buoyancy forces on the mobilization of fluids of different densities (*4*):

$$N_B = \frac{\Delta \rho g k_i k_{rw}}{\gamma_{ow} \cos \theta} \tag{2}$$

where $\Delta\rho$ is the density difference between the aqueous and the organic phases ($\rho_w - \rho_o$), g is the gravitational constant, k is the intrinsic permeability of the medium, and k_{rw} is the relative permeability of the aqueous phase. Pennell et al. (*4*) combined the bond number with the capillary number to yield the total trapping number, N_T:

$$N_T = \sqrt{N_{Ca}^2 + 2N_{Ca}N_B \sin \alpha + N_B^2} \tag{3}$$

where α is the inclination or angle of flow relative to the horizontal axis. Experimental results suggest a critical region for the onset of immiscible displacement between trapping numbers 1×10^{-5} and 1×10^{-4}, with complete displacement observed for trapping numbers greater than 1×10^{-4} (*4*).

Several approaches have been developed to control or contain DNAPL migration during immiscible displacement. The use of vertical flushing to prevent downward DNAPL migration has been examined in column studies (*9*, *10*). Vertical flushing allows mobile DNAPL to be suspended by

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opposing the downward gravitational force acting upon the DNAPL with an applied upward hydrodynamic force. Additionally, brine solutions have been suggested as a means to increase the aqueous phase density (e.g., $\rho = 1.8$ g/mL at 20 °C) to the point that a DNAPL becomes a light NAPL (LNAPL) relative to the displacing solution (*11, 12*). While these systems have been shown to be effective for DNAPL recovery in laboratory experiments, both rely upon upward flow and full (vertical and horizontal) confinement.

Several studies have investigated the use of partitioning alcohols for density reduction in up-flow (vertical flushing) column studies with extensions drawn to horizontal flushing schemes (*13–16*). Martel et al. (*17*) investigated density reduction and mobility control for a complex DNAPL mixture using down-flow column experiments. While significant density reduction and adequate mobility control were achieved using a multi-solution flushing scheme, high influent viscosities (up to ~25 cP) would likely result in hydraulic head losses far too great for application in unconfined aquifer systems. The use of partitioning alcohols to achieve DNAPL density reduction has also been investigated, using both one-dimensional experimental column studies and two-dimensional (2-D) computer simulations (UTCHEM) based on cosolvent flushing techniques (*18, 19*). Comparatively little work has been reported on in situ density reduction employing horizontal flushing schemes in unconfined aquifer systems.

The density-modified displacement (DMD) method couples in situ DNAPL density conversion with immiscible NAPL displacement and recovery (*20, 21*). The DMD process relies on a partitioning alcohol to convert a DNAPL to an LNAPL relative to the resident aqueous solution. The partitioning alcohol can be delivered as a pre-displacement flood (preflood), using horizontal flushing schemes. Following density conversion, NAPL displacement and recovery are achieved by flushing with a low IFT surfactant solution. The DMD method allows for efficient recovery of displaced DNAPLs, while mitigating the risks associated with downward DNAPL migration. The overall objective of this work was to assess the feasibility of the DMD method for recovery of two representative DNAPLs, chlorobenzene (CB) and trichloroethene (TCE). Specifically 2-D aquifer cell experiments were designed to evaluate in situ density conversion of DNAPL to LNAPL using an aqueous *n*-butanol solution, upward displacement of the resulting LNAPL, and effective delivery and recovery of the preflood and displacing solutions.

The selection of a partitioning alcohol for in situ density conversion represents a compromise between the solubility of the alcohol in a delivery solvent (i.e., water) and the tendency of the alcohol to partition into a DNAPL. Such a balance is realized with *n*-butanol, which also satisfies other important considerations such as the absence of detrimental phase behavior (i.e., gel formation) in the presence of the low IFT surfactant solution and the potential for posttreatment biodegradation. Aqueous *n*-butanol concentrations above approximately 6% (wt) have been shown to provide only minimal improvement of equilibrium NAPL compositions and corresponding DNAPL density reduction (*21*). Thus, the partitioning alcohol preflood solution consisted of 6% *n*-butanol, while the low IFT surfactant solution consisted of 4% (4:1) Aerosol MA/Aerosol OT + 20% *n*-butanol + 500 mg/L $CaCl_2$. The experimental results are presented visually to illustrate density conversion and effective NAPL displacement, in combination with measured effluent sample densities and constituent concentrations (surfactant, *n*-butanol, and CB or TCE). In addition, the displacement process was analyzed in terms of end point mobility ratios and the total trapping number concept.

TABLE 1. Properties of the Major Chemicals Used in This Study[a]

compound	*n*-butanol (BuOH)	chlorobenzene (CB)	trichloroethene (TCE)
molecular weight (g/mol)	74.12	112.56	131.39
solubility in water (g/L)	74.5	0.488[b]	1.100
water solubility in organic (wt %)	20.5	0.033	0.320
liquid density (g/mL)	0.806	1.10	1.47
dynamic viscosity (cP)	2.27[b]	0.715[b]	0.532

[a] All data from ref *23*. [b] At 30 °C.

Materials and Methods

Materials. HPLC-grade CB and TCE were obtained from Aldrich Chemical and dyed with Oil-Red-O (Fisher Scientific), an organic soluble dye, at a concentration of 4×10^{-4} M for visualization purposes. Previous work has shown no substantial effects of the Oil-Red-O on the physical properties (e.g., IFT, density, viscosity) of these organic liquids when dyed at low concentration (*22*). HPLC grade *n*-butanol (BuOH) and calcium chloride dihydrate were obtained from Fisher Scientific. All aqueous solutions were prepared with deionized water that was purified using a Nanopure Analytical Deionization (Barnstead/Thermolyne Corporation) system. Relevant properties of the chemicals used in this study are given in Table 1.

Two anionic, sulfosuccinate surfactants (Aerosol series) were obtained from Cytec Industries and used without further purification. Aerosol series surfactants are relatively nontoxic surfactants, widely used in the pharmaceutical industry. Aerosol MA-80I (sodium dihexyl sulfosuccinate) contains 80% active ingredient, with 20% inactive ingredients comprised primarily of water and 2-propanol. Aerosol OT (sodium dioctyl sulfosuccinate) was obtained as a 100% active ingredient solid.

In addition, a water-soluble dye, Ergioglaucin A (Fluka Chemicals), was used to color the aqueous solutions blue to blue-green for visualization purposes. Ottawa Federal Fine (30–140 mesh) and F-70 (40–270 mesh) sands were obtained from U.S. Silica Co. Ottawa Federal Fine sand was selected because the particle size distribution is similar to that of aquifer material obtained from the Bachman Road pilot-scale SEAR test site in Oscoda, MI (*24*). The white color of the Federal Fine sand allowed for easy visualization of dyed organic liquids, while closely approximating the permeability and particle size distribution of the Bachman Road site material. The F-70 Ottawa sand medium offers an order of magnitude reduction in intrinsic permeability from Federal Fine and was used to simulate a confining layer and low permeability lenses within the 2-D aquifer cell.

Aquifer Cell Studies. The 2-D aquifer cell used in this work had dimensions of 63.5 cm (length) × 38 cm (width) × 1.4 cm (thickness) (Figure 1). The end chambers (1.27 cm × 1.27 cm) were fully screened over the entire height of the aquifer cell. The cell was packed under water-saturated conditions with Federal Fine and F-70 Ottawa sands. Two regions of low permeability lenses (F-70 Ottawa sand) were emplaced within the Federal Fine sand to simulate possible heterogeneous field conditions. The first layer of lenses was located up to 3 cm above the confining layer (2 cm of F-70) and covered the entire length of the cell. The second layer of lenses was located 19–21.5 cm above the confining layer and 19 cm from either end chamber. An influent well, constructed from 0.32 cm o.d. 316 stainless steel tubing and

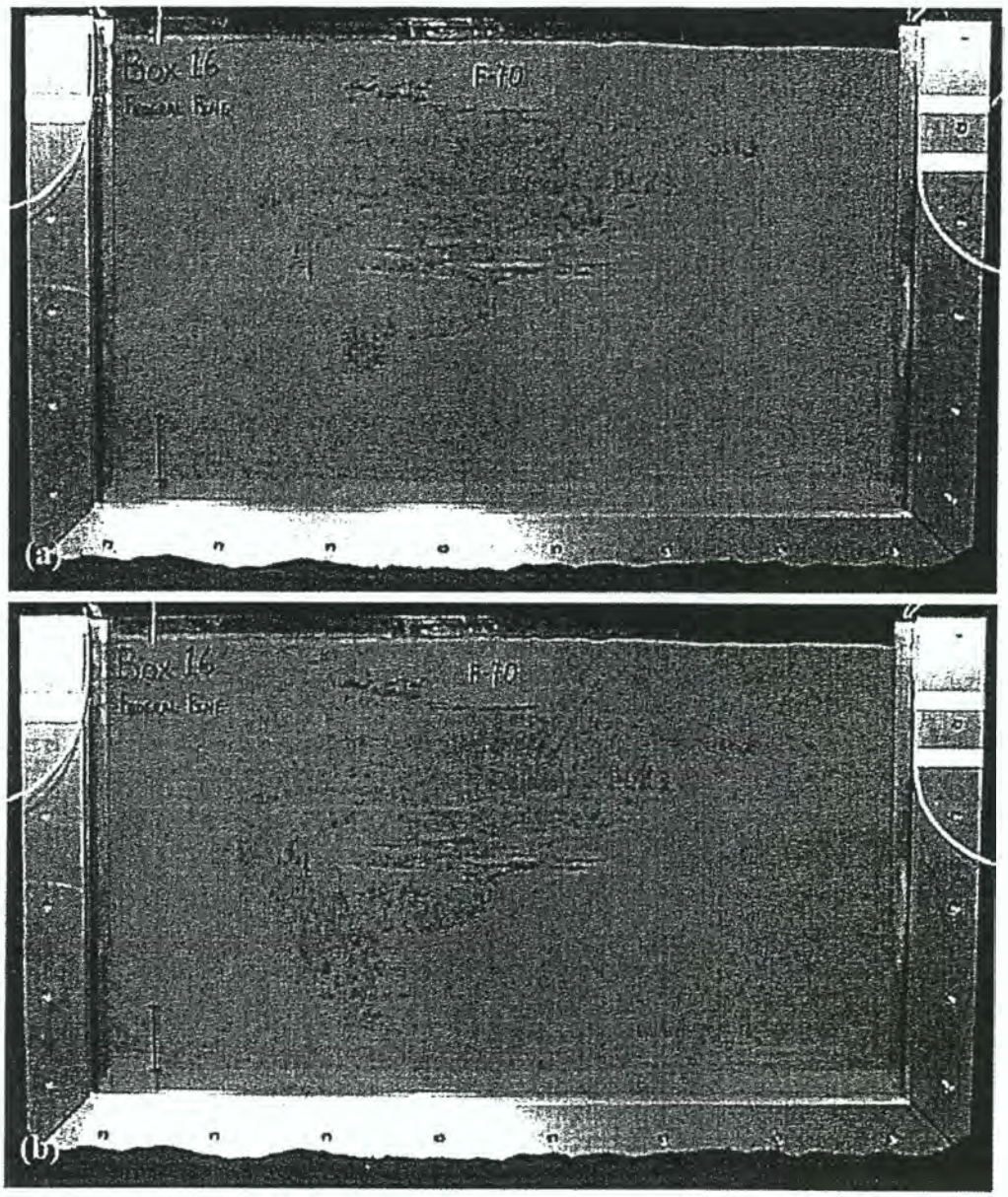

FIGURE 1. Representative early (~350 mL) (a) and late (~1560 mL) (b) time photographs of the preflood in the DMD-CB experiment.

screened over the bottom 5.2 cm was packed in the cell matrix to provide a partially screened injection well. This injection well was used to increase contact between the flushing solutions and the entrapped or pooled DNAPL. Similar injection schemes have been used in field trials of cosolvent flushing to minimize the potential effects of density override of the resident solution by lower density preflood and displacing solutions (e.g., ref *25*). The overall hydraulic conductivity of the cell was determined using Darcy's law based on the reduction in hydraulic head across each cell for several flow rates.

Dyed (Oil-Red-O) organic liquid (CB or TCE) was introduced through a 15.2-cm, 18-gauge needle packed within the box (approximately 5 cm below the surface) at a constant flow rate of 1 mL/min using a Harvard Apparatus (model 22) syringe pump. A region (8 cm × 5 cm) of F-70 Ottawa sand was placed above the injection point to minimize backflow of organic liquid along the needle. Upon completion of the injection process, DNAPL was allowed to redistribute within the domain for a period of 24 h. Subsequently, preflood and surfactant solutions were introduced through the partially screened injection well. Aqueous and NAPL effluent samples were collected from the end chamber using an Isco Retriever II fraction collector.

Analytical Methods. Organic liquid present in the effluent samples was immediately separated from the aqueous phase to prevent further alcohol partitioning. Aqueous and organic liquid densities were measured in triplicate using 2-mL pycnometers that were calibrated before each use with Nanopure water. Viscosities of the flushing solutions and

TABLE 2. Flushing Solution Properties

solution	water	6% (wt) BuOH aq solution	4% (4:1 wt) MA/OT + 20% (wt) BuOH
liquid density (g/mL)	0.997	0.988 ± 0.001	0.966 ± 0.001
dynamic viscosity (cP)	1.00	1.40 ± 0.01	3.30 ± 0.01
IFT with CB (dyn/cm)	42.1 ± 1.3	12.3 ± 0.5	0.125 ± 0.006
IFT with TCE (dyn/cm)	35.2 ± 0.3	13.2 ± 0.7	<0.05

recovered effluent nonaqueous phases were measured in triplicate at 20 °C using a Haake Rheostress 75 rheometer equipped with a double-gap sensor using shear rates ranging from 20 to 1000 s^{-1}. Interfacial tension between aqueous and organic phases was measured in quintuplet using the drop volume method of Hool and Schuchardt (*26*). All replicate analyses were averaged and reported with one standard deviation.

Contaminant and *n*-butanol effluent concentrations were measured using a Hewlett-Packard model 6890 gas chromatograph (GC) equipped with a flame ionization detector (FID). Separation of *n*-butanol and chlorinated organics was accomplished isothermally (45 °C) on a DB-5 column (J&W Scientific, 0.32 mm i.d., 30 m length). Both aqueous and organic samples were prepared for analysis by dilution with 2-propanol (~5× aqueous phase and ~40× organic phase). Additionally, Aerosol MA and Aerosol OT concentrations were quantified via high-performance liquid chromatography (HPLC) using a diode array detector with a method adapted from Field and Sawyer (*27*). Both GC and HPLC analyses used six-point calibration curves generated prior to each sequence run, with calibration check samples run every 10 samples.

Results and Discussion

Selection of Flushing Solutions. Frequently, salts are added to anionic surfactant solutions to produce low NAPL–aqueous IFTs and increased solubilization capacity. Interfacial tension reduction is achieved as the salt effectively renders the surfactant more hydrophobic, thereby moving the system toward the Winsor Type I–Type III transition or into the Winsor Type III system where interfacial tensions can be ultralow (*28–30*). While these solutions are quite effective in the absence of alcohol, the addition of *n*-butanol may facilitate the transition of a Winsor Type I system to a Type III or possibly Type II (*29*). However, the effect of the addition of *n*-butanol on the surfactant phase behavior in the complex system containing two ionic surfactants (Aerosol MA and Aerosol OT), calcium chloride and *n*-butanol, is less definitive. Alcohol is required in the DMD displacement solution to reduce the possibility of reverse alcohol partitioning. Without the presence of alcohol in the surfactant solution, the displacement solution may effectively remove *n*-butanol from the density-converted NAPL, thereby increasing NAPL density. Results presented by Kibbey et al. (*31*) indicate aqueous phase *n*-butanol concentrations may need to be significantly higher in the presence of surfactants to achieve the same equilibrium NAPL *n*-butanol mole fraction. On the basis of a series of salt and *n*-butanol phase behavior scans and previous experiences (*4, 20, 32*), a 4% (4:1) (wt) Aerosol MA/Aerosol OT + 20% (wt) *n*-butanol + 500 mg/L $CaCl_2$ solution was selected to achieve low interfacial tensions necessary for NAPL displacement, while maintaining relatively low viscosity. The properties of the displacing surfactant solutions are given in Table 2. The viscosity of the surfactant solution (3.30 ± 0.01 cP) was due, in large part, to the addition of 20% (wt) *n*-butanol. The same surfactant solution containing no *n*-butanol had a viscosity of 1.34 ± 0.01 cP. Aqueous phase viscosities are critical in subsurface flushing of unconfined aquifers, as the introduction of viscous solutions may result in substantial flow reductions under constant head conditions. The surfactant solution used in this study was moderately more viscous as compared to groundwater and resulted in a maximum gradient in head of 0.1. While the increased viscosity and resulting head loss were acceptable in this scenario, further optimization of the *n*-butanol and salt content may be warranted.

TABLE 3. Overview of Two-Dimensional Aquifer Cell Experimental Conditions

parameter	CB box	TCE box
total pore volume (mL)	1300	1274
permeability (cm^2)	$4.69 \pm 0.36 \times 10^{-7}$	$5.31 \pm 0.15 \times 10^{-7}$
initial NAPL release (mL)	43.4	30.6
overall saturation (%)	3.3	2.4
vol preflood (mL)	1575	6253
preflood flow rate (mL/min)	5.45 ± 0.09	4.74 ± 0.09
vol displacement flood (mL)	1524	1506
displacement flood flow rate (mL/min)	4.21 ± 0.41	4.39 ± 0.50

Chlorobenzene Aquifer Cell Experiment. The 2-D aquifer cell used in the CB experiment had a pore volume of 1300 mL and an overall permeability of $4.69 \pm 0.36 \times 10^{-7}$ cm^2 (Table 3). Injection of dyed CB was conducted as described in the Methods section, and a time-lapse sequence of this process is available in the Supporting Information section (Time Lapse 1). After injection and redistribution, 43.4 mL of CB was entrapped, pooled, or dissolved within the 2-D cell, yielding an overall NAPL saturation of 3.3%. Following redistribution of CB within the cell, a 6% *n*-butanol preflood solution (1575 mL, dyed blue-green) was introduced through the screened well at an average flow rate of 4.45 ± 0.09 mL/min (Supporting Information, Time Lapse 2). A representative photograph at early time (~350 mL) is shown in Figure 1a. Here the preflood solution (dyed blue-green) has contacted the CB-NAPL (dyed red) without any apparent mobilization at the solution front. The lower density preflood solution, 0.988 g/mL versus 0.997 g/mL for the resident aqueous solution, flowed slightly upward from the partially screened well through the zone of CB contamination. Preflood and displacement solutions were introduced only through the partially screened well but were observed to be present in the upper left-hand portion of the cell. This behavior was attributed to flow of the injected solution into the fully screened end chamber and subsequent mixing and flow back into the aquifer cell. At later time (~1560 mL), the resident pore water was completely displaced by the preflood solution as seen in Figure 1b. As a result of alcohol and water partitioning, the CB-NAPL volume increased, which resulted in both upward and downward migration of CB-NAPL. Migration of CB-NAPL was slow, occurring over a period of approximately 4 h, and ceased by the end of the preflood when sufficient *n*-butanol had been introduced for complete density conversion.

Following a flow interruption period of 17 h, 1524 mL of the low IFT surfactant solution was introduced through the partially screened well at an average flow rate of 4.21 ± 0.41 mL/min (Supporting Information, Time Lapse 3). Repre-

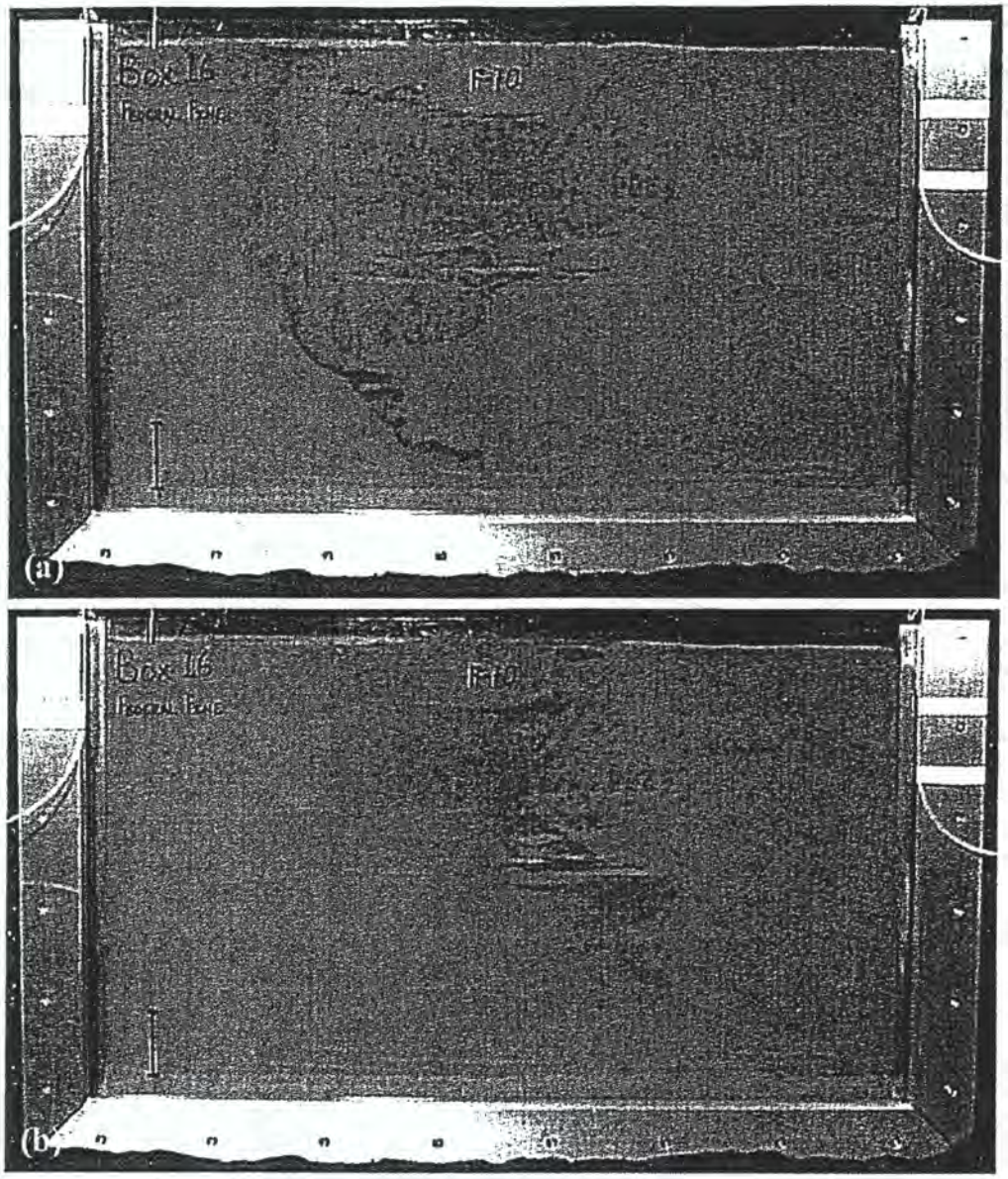

FIGURE 2. Representative early (~330 mL) (a) and late (~840 mL) (b) time photographs of the displacement flood in the DMD-CB experiment.

sentative images of the displacement process at ~330 and ~840 mL are shown in Figure 2, panels a and b, respectively. After approximately 330 mL of the low IFT solution (not dyed) was introduced, CB-NAPL displacement was evident and appeared as a bank of free product that formed along the flow front (Figure 2a). At later time (~840 mL), the NAPL migrated upward through the region of low permeability lenses and moved toward the upper right-hand portion of the cell (Figure 2b). Aqueous phase effluent concentration data for the CB box experiment are shown in Figure 3. Concentration (Figures 3 and 7) and density (Figures 4 and 8) data were plotted relative to the effluent volume collected since the actual aqueous phase pore volume fluctuated as a result of NAPL swelling (decrease) and displacement (increase), as well as potential nonideal mixing. Additionally, vertical lines, shown in Figures 3 and 7, represent the introduction of flushing solutions into the influent well. During the preflood, the effluent concentration of *n*-butanol increased to approximately 45 g/L, which was substantially lower than the injected concentration of 60 g/L. Additionally, the absence of a decrease in BuOH concentration, prior to the appearance of surfactant (i.e., the mobilizing flood), indicates that the BuOH partitioning into CB-NAPL was rapid and that a flow interruption period was not necessary to achieve density conversion. These data indicate that *n*-butanol partitioned readily into the CB-NAPL, yielding an *n*-butanol mole fraction in the NAPL (X_{BuOH}) of approximately 0.50. This value is greater than the X_{BuOH} of 0.41 necessary for density conversion of the CB-NAPL relative to the density of the displacing solution (*21*).

Effluent concentrations of *n*-butanol and CB increased rapidly with the appearance of the low IFT surfactant pulse

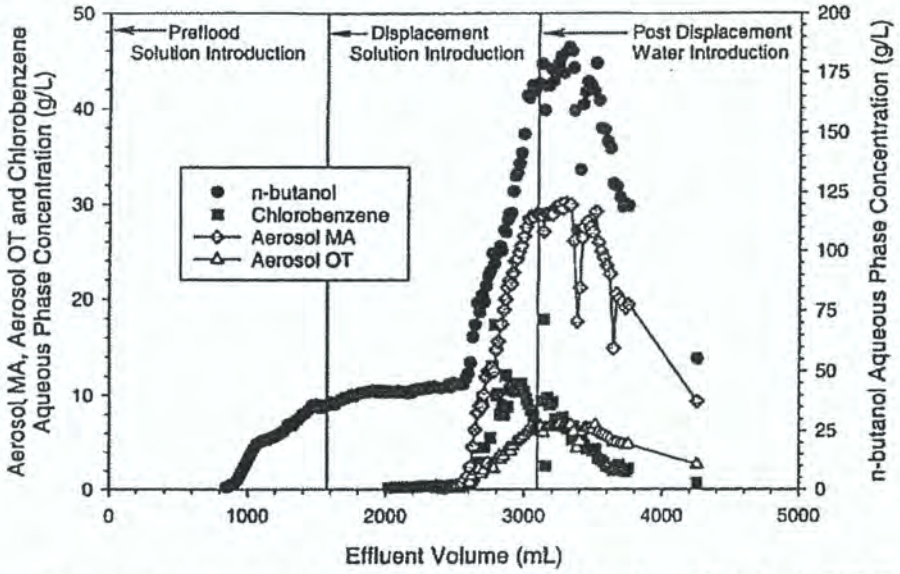

FIGURE 3. Aqueous phase concentrations of *n*-butanol, chlorobenzene Aerosol MA, and Aerosol OT during the DMD-CB experiment.

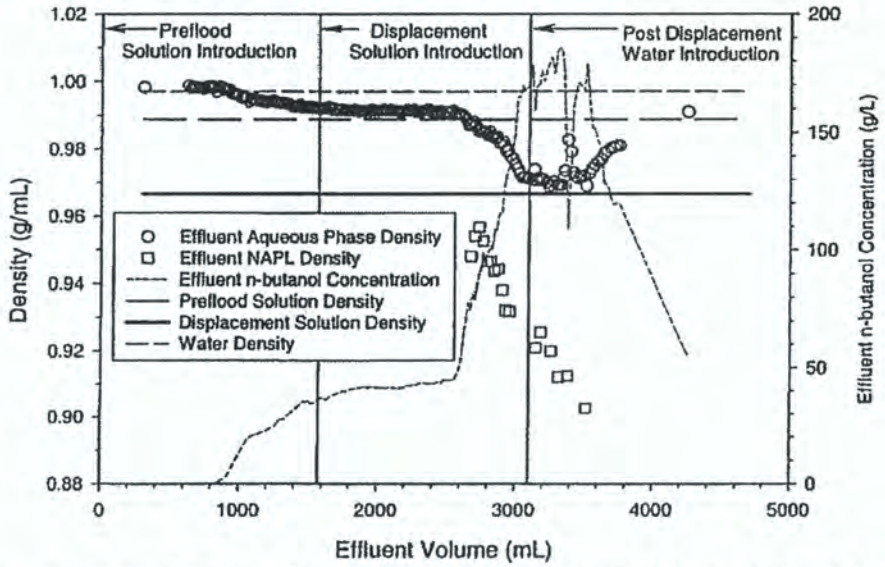

FIGURE 4. Aqueous phase and NAPL effluent densities and corresponding aqueous phase concentration of *n*-butanol during the DMD-CB experiment. Horizontal lines represent influent solution densities, and vertical lines represent the introduction of flushing solutions into the influent.

(1524 mL) in the effluent (Figure 3). During this time, *n*-butanol concentrations approached the influent value of 193 g/L. The effluent concentration of CB increased from approximately 0.275 to 12 g/L, a 25-fold increase over the initial concentration, demonstrating that mobilization and solubilization occurred simultaneously. The change in effluent NAPL and aqueous phase densities over the course of the experiment are shown in Figure 4. Influent flushing solution densities were also measured and appear as horizontal lines in Figure 4. Effluent aqueous phase densities were observed to decrease from the density of water (0.997 g/mL) to slightly greater than the preflood solution density (0.988 g/mL). Effluent densities greater than the preflood solution corresponded with a loss of *n*-butanol, which provides further evidence of alcohol partitioning. At an effluent volume of ~2600 mL, breakthrough of the displacing surfactant solution was observed with a corresponding decrease in aqueous phase density. The aqueous phase density was again shown to be slightly greater than that of the influent solution (0.966 g/mL), indicating *n*-butanol partitioning into the NAPL. After ~3500 mL was recovered, the aqueous phase density approached that of the postflood water, which was introduced to recover surfactant solution. The observed spikes in the aqueous phase density were attributed to corresponding reductions in the *n*-butanol concentration (hairline trace in Figure 4). Effluent NAPL densities ranged from 0.96 to 0.90 g/mL, and all were less than that of the corresponding aqueous phase sample. These densities correspond to CB-NAPL *n*-butanol mole fractions ranging from 0.40 to 0.50 (*21*).

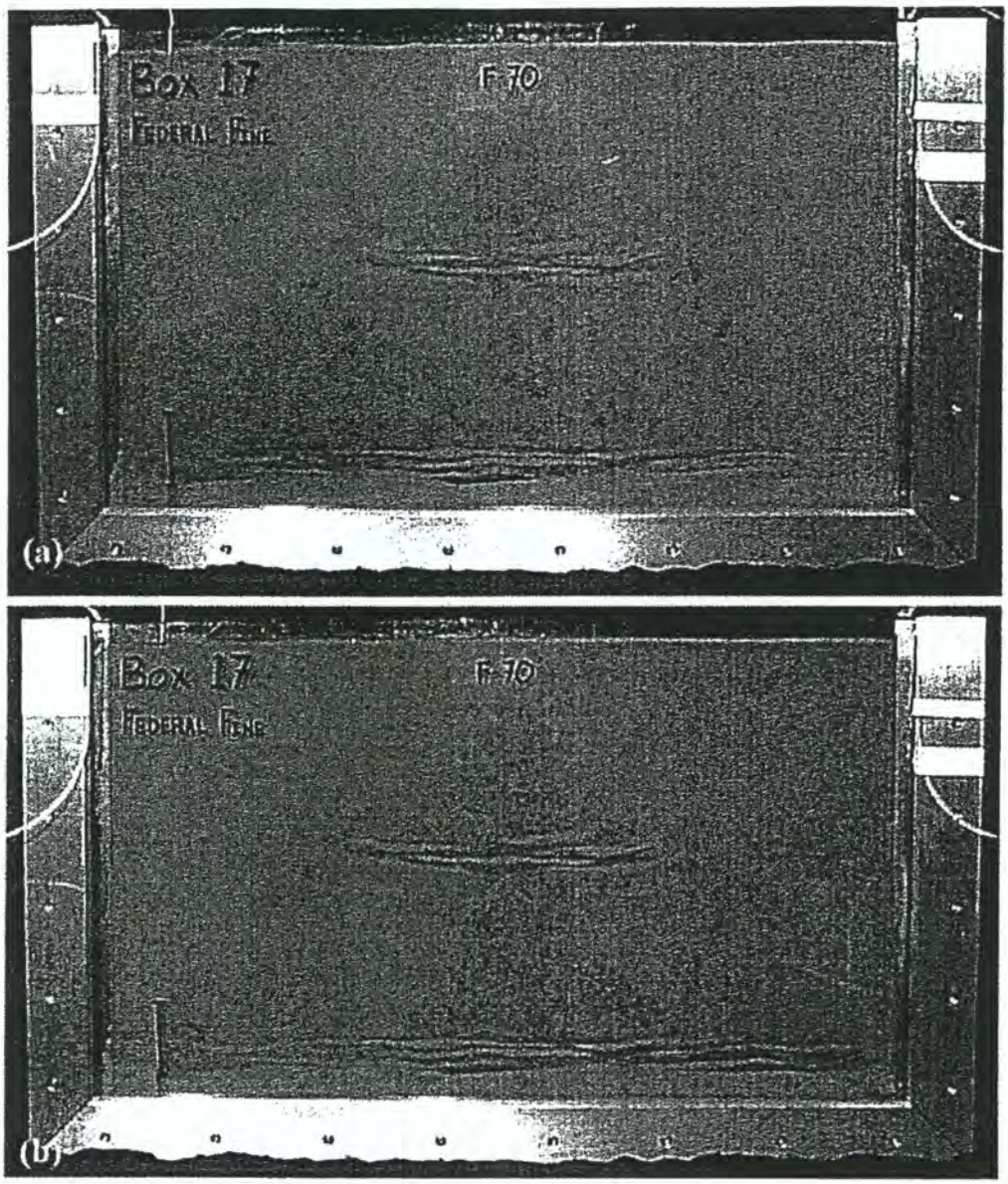

FIGURE 5. Representative early (~330 mL) (a) and late (~5990 mL) (b) time photographs of the preflood in the DMD-TCE experiment.

Trichloroethene Aquifer Cell Experiment. The 2-D aquifer cell used in the TCE experiment had a pore volume of 1274 mL with an overall permeability of $5.31 \pm 0.15 \times 10^{-7}$ cm^2 (Table 3). Following the injection and redistribution of 30.6 mL (2.4% overall NAPL saturation) of TCE (Supporting Information, Time Lapse 4), an extended *n*-butanol preflood (6253 mL) was conducted at an average flow rate of 4.74 ± 0.09 mL/min (Supporting Information, Time Lapse 5). At early time (~330 mL), the 6% *n*-butanol preflood solution (dyed blue-green) flow front contacted TCE-NAPL near the lower confining layer and did not induce free product mobilization (Figure 5a). At later time (~5990 mL) significant increase in NAPL volume (swelling) was observed (Figure 5, panel b contrasted against panel a), accompanied by some upward and horizontal migration of TCE-NAPL. After a flow interruption period of 17.5 h, 1506 mL of low IFT surfactant solution (not dyed) was introduced into the cell through the partially screened well at an average flow rate of 4.39 ± 0.50 mL/min (Supporting Information, Time Lapse 6). Representative early (~270 mL) and late (~1000 mL) time images of this surfactant flood are shown in Figure 6, panels a and b, respectively. Upward displacement of TCE-NAPL is shown in Figure 6a after approximately 270 mL of displacing surfactant solution was introduced. At later time (~1000 mL), horizontal displacement of TCE-NAPL was observed, although the TCE-NAPL did not migrate downward.

Aqueous phase effluent concentration data for the TCE aquifer cell experiment are shown in Figure 7. Here again the vertical lines shown in Figure 7 refer to the introduction of the flushing solutions into the influent well. The *x*-axis scale changes at 6000 mL to clarify the low IFT displacement flood data. The preflood effluent concentration of *n*-butanol increased to approximately 55 g/L as compared to the influent preflood concentration of 60 g/L, indicative of alcohol

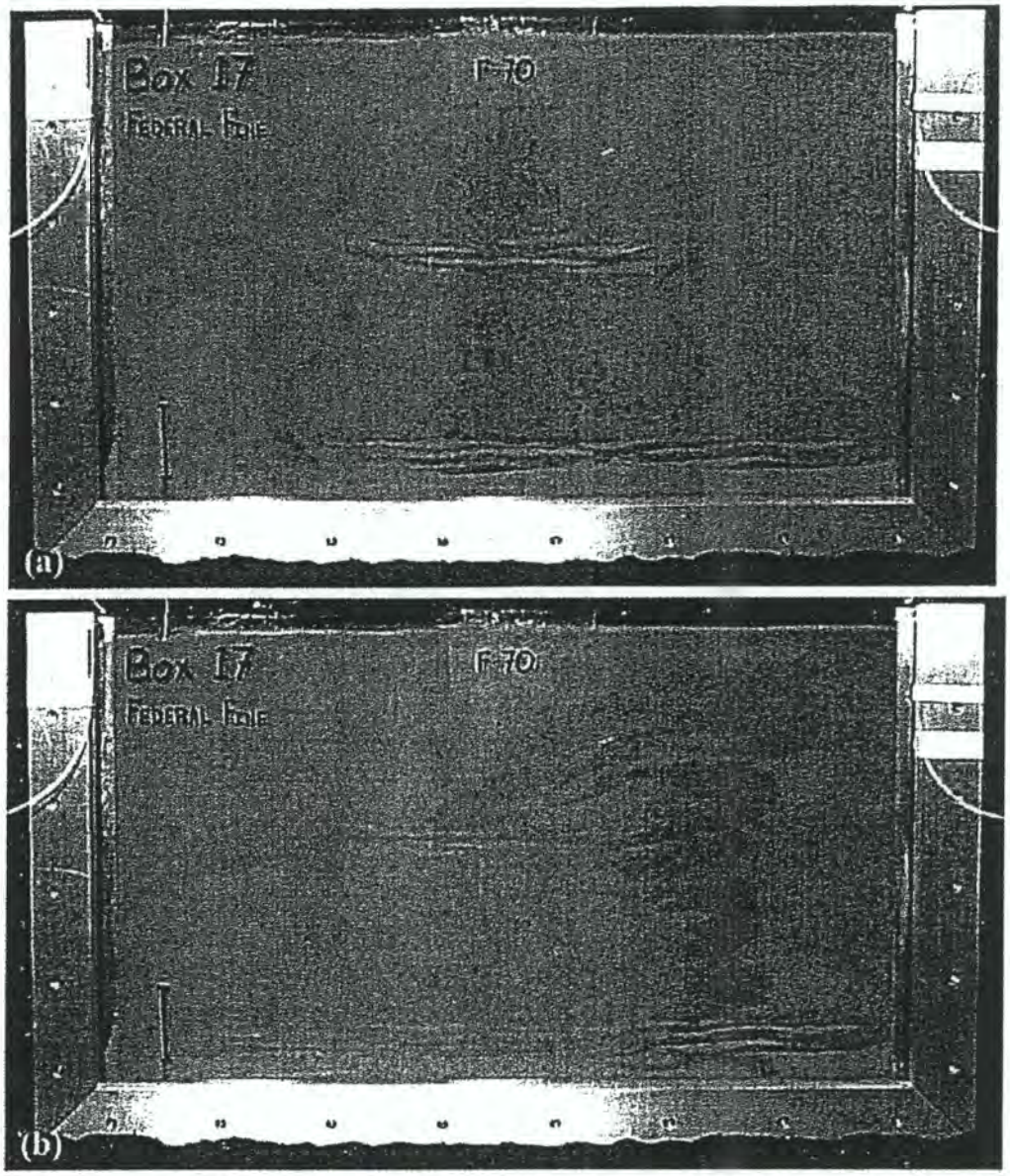

FIGURE 6. Representative early (~270 mL) (a) and late (~1000 mL) (b) time photographs of the displacement flood in the DMD-TCE experiment.

partitioning. It is important to note again that the absence of a decrease in BuOH concentration, prior to the appearance of surfactant (i.e., the mobilizing flood), indicates that BuOH partitioning into TCE-NAPL was rapid and that a flow interruption period was not necessary to achieve density conversion. An aqueous phase *n*-butanol concentration of 55 g/L corresponded with an equilibrium NAPL mole fraction (X_{BuOH}) of approximately 0.5, which is similar to the X_{BuOH} observed for TCE density conversion in batch systems (*21*). The aqueous phase concentrations of TCE during the preflood fluctuated around 300 mg/L and increased substantially to 14 g/L during the displacement flood. Effluent concentrations of *n*-butanol also increased from 55 to 206 g/L during the displacement flood. This concentration of *n*-butanol was greater than the influent value of 193 g/L and was likely a result of NAPL (containing *n*-butanol) solubilization in the low IFT surfactant solution. Increases in aqueous phase concentration of both Aerosol MA and Aerosol OT corresponded to the observed increase in TCE concentrations, which was attributed to micellar solubilization by the low IFT surfactant solution (Figure 7).

Measured densities of the effluent aqueous and organic phases for the TCE aquifer cell experiment are shown in Figure 8. Horizontal lines appearing in Figure 8 represent influent solution densities and provide a basis for which density conversion may be illustrated. Similar to data obtained for the CB aquifer cell experiment (Figure 4), aqueous phase densities decreased over the course of the preflood but remained slightly greater than the influent density of the 6% *n*-butanol solution. Aqueous phase densities decreased with increasing *n*-butanol content of the displacing surfactant flood and rebounded during the final water flood.

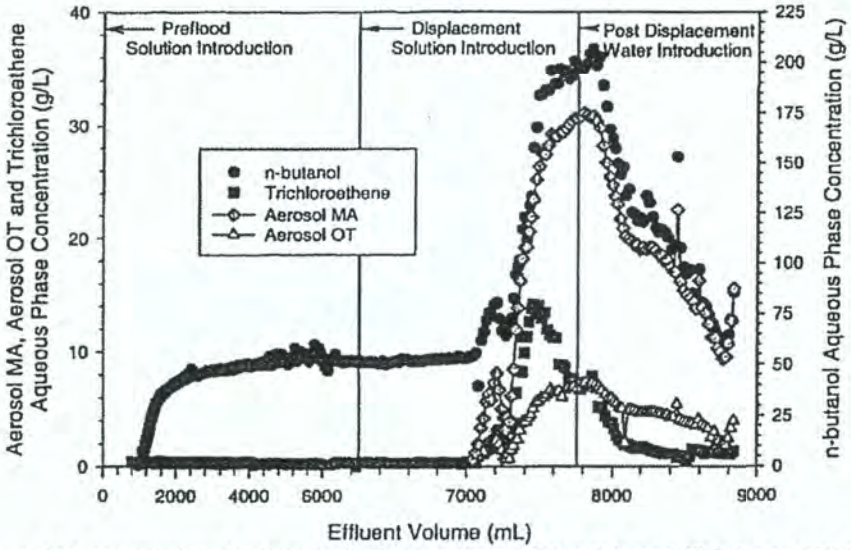

FIGURE 7. Aqueous phase concentrations of *n*-butanol, chlorobenzene Aerosol MA, and Aerosol OT during the DMD-TCE experiment.

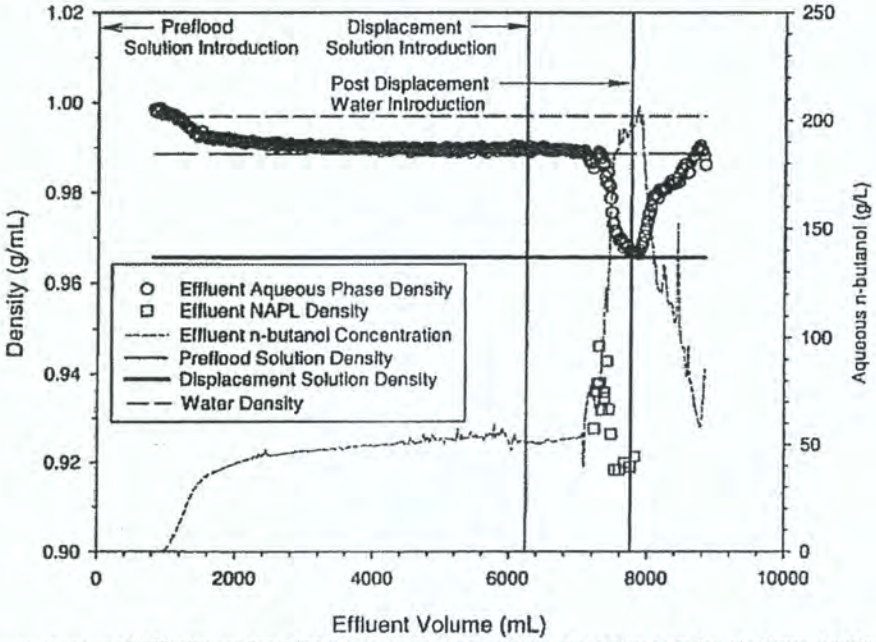

FIGURE 8. Aqueous phase and NAPL effluent densities and corresponding aqueous phase concentration of *n*-butanol during the DMD-TCE experiment. Horizontal lines represent influent solution densities, and vertical lines represent the introduction of flushing solutions into the influent.

Effluent TCE-NAPL densities ranged from 0.95 to 0.92 g/mL, and all were less than the corresponding aqueous phase sample. The relatively low NAPL densities indicated successful in situ density conversion and correspond to equilibrium NAPL *n*-butanol mole fractions of approximately 0.51−0.53 (*21*).

Recoveries of all major components in both the CB and TCE aquifer cell experiments are shown in Table 4. It is important to note TCE and CB recoveries were almost entirely a result flushing approximately 1.2 pore vol of surfactant solution, indicating the efficiency of the low IFT surfactant flood. Comparable SEAR solubilization recoveries are typically achieved after numerous pore volumes of surfactant flushing (e.g., ref *22*). The recoveries of Aerosol MA (75% for the CB experiment and 81% for the TCE experiment) and Aerosol OT (80% for the CB experiment and 88% for TCE experiment) were based solely on aqueous phase measurements. The lower recoveries of surfactant in the CB experiment are likely due to insufficient post-displacement water flooding, which did not allow for complete recovery of surfactants.

Total Trapping Number Calculations. Total trapping numbers were calculated using eq 4 and corresponding batch data (*21*) (Supporting Information, Figure A). On the basis of the reported critical trapping number region of 1×10^{-5} to 1×10^{-4} for PCE (*4*), the CB-NAPL should not have been mobilized until sufficient *n*-butanol had partitioned to allow

TABLE 4. Major Component Effluent Recoveries

parameter	CB box	TCE box
contaminant available to flooding (g)	47.8	45.0
contaminant recovered as NAPL (g)	34.7	28.3
contaminant solubilized (g)	8.26	10.1
total contaminant recovered (g)	43.0	38.4
contaminant recovery (%)	89.9	85.4
BuOH introduced (g)	374	656
BuOH recovered as NAPL (g)	53.9	97.0
aqueous phase BuOH recovered (g)	276	529
total BuOH recovered (g)	330	626
% BuOH recovery	88.1	95.5
Aerosol MA introduced (g)	48.2	46.7
aqueous phase Aerosol MA recovered (g)	35.9	37.8
Aerosol MA recovered (%)	74.5	80.8
Aerosol OT introduced (g)	11.1	11.0
aqueous phase Aerosol OT recovered (g)	8.87	9.65
Aerosol OT recovered (%)	80.0	87.6

the NAPL *n*-butanol mole fraction to reach approximately 0.5. Although some movement of the CB-NAPL was observed early in the *n*-butanol preflood, mobilization as a result of capillary force reduction was not believed to have occurred. Rather, the downward migration of CB-NAPL observed early in the preflood was attributed to swelling and redistribution. If the capillary forces had been reduced sufficiently to allow for CB-NAPL mobilization, the total trapping number would have increased upon density conversion, and thus mobilization would have continued throughout the preflood period (Supporting Information, Figure A). While total trapping number for the TCE preflood approached the lower limit ($N_T = 2 \times 10^{-5}$) of the critical region, no mobilization of the entrapped TCE-NAPL was observed during the *n*-butanol preflood.

The total trapping number curves may also be used to predict density conversion. At the point of neutral buoyancy the bond number is zero, since no density difference exists between organic and aqueous phases. For the case of horizontal flow, the total trapping number is therefore equal to the capillary number and corresponds to a relative minimum in the total trapping number (Supporting Information, Figure A). Interfacial tensions measured for the low IFT displacement solution and CB- and TCE-NAPLs containing various mole fractions of *n*-butanol are shown in Figure B of the Supporting Information section as a function of increasing NAPL *n*-butanol mole fraction. These IFTs were very low (0.02−0.42 dyn/cm) and demonstrate that substantial IFT reductions are possible with these surfactants. Total trapping numbers are shown for both CB-NAPL and TCE-NAPL with the low IFT surfactant solution (Supporting Information, Figure C). The mobilization potential of the displacing surfactant solution (20% *n*-butanol) for both CB-NAPL and TCE-NAPL was evident, as the total trapping number did not decrease below 10^{-4} for either system. This analysis indicated that both CB- and TCE-NAPLs should be nearly completely displaced. No residual saturation of CB or TCE was observed visually, which was consistent with total trapping number calculations.

Flow Instabilities. Control of subsurface flow is of paramount importance for NAPL displacement technologies. However, instabilities, such as gravity tongues or viscous fingering frequently occur when two fluids (miscible or immiscible) are flowing. Several researchers have examined liquid−liquid flow instabilities in porous media (e.g., refs *33*−*40*), and a thorough review of fingering is presented by Homsy (*41*). From visual observations, the relatively minor density differences between flushing and resident solutions (<0.022 g/mL for all floods) did not appear to influence the

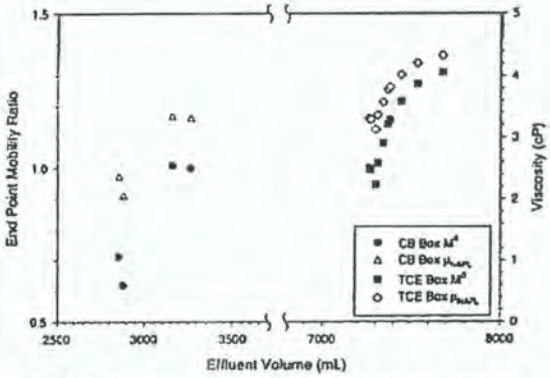

FIGURE 9. NAPL viscosities and end point mobility ratios for the DMD-CB and DMD-TCE experiments.

delivery of flushing solutions significantly. Analysis of the Grashof number (*Gr*) to Reynolds number (*Re*) ratio (as described in ref *38*) and gravity parameter (*G*) (following the scaling argument of ref *39*) indicated that the driving force of the flow in the horizontal direction dominated the buoyancy-induced force in the vertical direction. As such, the influence of the density differences between flushing solutions was determined to be minimal.

Mobility ratios (*M*) have been used extensively to predict viscous instabilities in both miscible and immiscible displacement (e.g., refs *15*, *17*, *42*, and *43*). The mobility ratio is the ratio of the mobility of the displacing fluid (1) to that of the displaced fluid (2), where the mobility of a fluid (λ_i) is the ratio of relative permeability (k_{ri}) to viscosity (μ_i):

$$M = \frac{\lambda_1}{\lambda_2} = \frac{k_{r1}\mu_2}{\mu_1 k_{r2}} \tag{5}$$

Flows with mobility ratios greater than unity are unstable, and viscous fingering typically results (*44*). Because of the complex dependence of multiphase flow relative permeabilities on the capillary number, the use of end point relative permeabilities has been proposed (*45*, *46*). The end point mobility ratio (M^0) is defined as

$$M^0 = \frac{k_{r1}^0\mu_2}{\mu_1 k_{r2}^0} \tag{6}$$

where k_{ri}^0 is the end point relative permeability. End point relative permeabilities are, in effect, the relative permeability at high capillary numbers (i.e., low saturations) and therefore approach unity (*46*).

In both the CB and TCE aquifer cell studies, flow front instabilities were apparent during the displacement of the density-modified NAPL. Instabilities have been shown to be exacerbated by media heterogeneity and density fluctuations (*45*, *46*). Typically capillary forces limit the growth of small instabilities or fingers; however, at low interfacial tension, capillary forces are substantially reduced (*46*). The reduction in capillary forces may result in the growth of otherwise small instabilities, creating greater fingering at low IFT.

End point mobility ratios (eq 6) were calculated assuming the end point relative permeabilities to be unity (*46*) since the low IFT produced relatively large (on the order of 10^{-4}) capillary numbers (eq 1). The calculated mobility ratios suggest unstable flow ($M^0 > 1$) at late times during the CB experiment displacement flood and at nearly all times during the TCE experiment displacement flood (Figure 9). These instabilities resulted in breakthrough of the displacing solution along the NAPL bank. Although the flow front of the

more mobile surfactant solution slowed and smeared the displaced NAPL, no re-entrapment was observed. While the flow instabilities observed in the 2-D aquifer studies were unexpected based on the observed NAPL viscosities (*21*), their effects may be mitigated with further optimization of the displacing surfactant solution to reduce viscosity contrasts.

Effluent NAPL viscosities varied significantly between the CB-NAPL and the TCE-NAPL and were greater than observed batch system viscosities for a given *n*-butanol mole fraction. In the absence of surfactant, however, equilibrated samples for both the CB-NAPL and the TCE-NAPL incorporated the same concentration of water as a function of *n*-butanol concentration, and both exhibited similar increases in viscosity with increasing NAPL *n*-butanol mole fraction (*21*). These observations suggest that increased NAPL viscosities arose from the incorporation of a species not present in the batch investigations. Two possible explanations for the relatively greater effluent viscosities are the incorporation of displaced fine particles and surfactant partitioning into the displaced NAPL.

In closing, experimental results presented herein demonstrate the ability of the DMD method to effectively convert representative DNAPLs to LNAPLs in situ and to recover the resulting LNAPL with a low IFT surfactant solution. Notably, the process was implemented in an unconfined aquifer cell using horizontal flow regimes, without the need for vertical confinement and upward (vertical) flow. For CB-NAPL, a total flushing volume of 3.4 pore vol was required for solution delivery and recovery, whereas a flushing volume of 7.1 pore vol was necessary in the case of TCE-NAPL. This difference resulted directly from the greater volume of aqueous preflood solution (6% *n*-butanol) that was required to achieve in situ density conversion of TCE-NAPL and highlights the need to develop more efficient alcohol delivery systems for relatively dense DNAPLs, such as TCE and PCE (*31*). Although subsurface remediation cost analyses are inherently site-specific, it is important to note that as with most chemical flushing technologies, initial capital costs for active ingredients used in the DMD flushing solutions may be substantial but are likely to be offset by significant cost savings associated with reduced treatment times.

Acknowledgments

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Supporting Information Available

Time-lapse images of injection, preflood, and displacement for both CB- and TCE-NAPL; total trapping number analysis for the CB- and TCE-NAPL prefloods and displacement floods (Figures A and C, respectively); interfacial tension data for CB- and TCE-NAPLs with the low IFT surfactant solution (Figure B). This material is available free of charge via the Internet at http://pubs.acs.org.

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CHLOROBENZENE NAPL OXIDATION USING POTASSIUM PERMANGANATE: BENCH- AND FIELD-SCALE DEMONSTRATION

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ABSTRACT: Potassium permanganate ($KMnO_4$) was selected for use in a short-term field demonstration of chemical oxidation at an active industrial site in the eastern United States. The demonstration was designed to evaluate the feasibility of using permanganate (MnO_4^-) to destroy separate-phase, adsorbed-phase, and dissolved-phase monochlorobenzene (MCB) and 1,2-dichlorobenzene (DCB) present in the saturated soils and groundwater beneath the Site. A bench-scale treatability study confirmed the suitability of the technology for application at the Site. During the field demonstration, approximately 1,540 pounds of $KMnO_4$ were delivered to the subsurface in the form of a three-percent solution (by weight) through a series of ten injection events completed over a period of 12 weeks. The results of groundwater monitoring conducted during the field demonstration indicate that 1) the selected delivery method is effective and 2) the $KMnO_4$ was able to overcome the natural reductive poise throughout the pilot test area. However, it appears that the ability of the permanganate to sustain reaction with the target compounds was limited by an insufficient concentration of permanganate in the subsurface. An attempt to overcome this limitation through the use of an alternate source of permanganate with a higher solubility, such as sodium permanganate ($NaMnO_4$), has been proposed.

INTRODUCTION:

The subject Site is an active industrial facility located in the eastern United States. Overburden at the Site is comprised of unconsolidated deposits of silty sands and gravels ranging in thickness from approximately 30 to 65 feet. Specifically, surficial soils are comprised of an approximately 5 foot thick layer of fill material. Beneath the fill material, a layer of ablation till (poorly sorted sand, silt, and gravel) extends to between 25 and 45 feet below land surface (bls) to a layer of dense basal till ranging from 5 to 20 feet in thickness. The basal till lies directly over the regional bedrock. Groundwater at the site occurs in both the unconsolidated deposits and the fractured bedrock, and is encountered at an average depth of approximately 4.5 feet bls.

Elevated concentrations of MCB and DCB in groundwater indicate the presence of non-aqueous phase liquid (NAPL) in localized areas throughout the Site. The elimination of NAPL in such areas would remove the continuing source of groundwater impacts, thus reducing the total duration and cost to achieve Site-wide remediation goals. In support of this objective, in-situ chemical oxidation was selected for application in the form of a pilot-scale demonstration. Following an evaluation of available oxidation techniques, permanganate (MnO_4^-) in the form of potassium permanganate ($KMnO_4$) was selected for use in the pilot demonstration. This oxidant was selected for several reasons, as follows: 1) commercial availability; 2) high comparative oxidation potential; 2) ability to oxidize compounds with carbon-carbon double bonds, such as those found in MCB and

DCB (LaChance, 1998; Meyers, 1998; Oberle, 2000); 3) ability to react under a wide range of pH conditions and at normal groundwater temperatures (Meyers, 1998; Oberle, 2000); 4) ability to diffuse into lower permeability zones in heterogeneous geologic environments, such as those encountered at the Site (LaChance, 1998); and, 5) the low-energy of the resulting chemical reactions as compared to other oxidation technologies, such as Fenton's reagent. The final pilot demonstration work plan provided for the following:

- A bench-scale treatability study to confirm the suitability of the selected oxidation technology for application at the Site.
- A well network including two injection wells, six monitoring wells, and two sets of three piezometers.
- Delivery of permanganate to the subsurface through a series of ten injections involving a dilute $KMnO_4$ solution.
- Groundwater monitoring, including a baseline-sampling event prior to the injections, five sampling events during the injections, and one sampling event one to two months following completion of the injections.

Evaluation of the treatability study results, the success of the selected delivery method, and the data from the groundwater monitoring activities would be evaluated to determine whether the pilot demonstration was successful and the technology should be retained for use at the Site.

TREATABILITY STUDY

Prior to initiating the field demonstration, a bench-scale treatability study was completed in a laboratory. The objective of the study was to estimate oxidant demand in the Site subsurface. In order to complete the test, a bulk saturated soil sample and a bulk groundwater sample were collected in the area selected for the pilot demonstration and submitted to the ARCADIS laboratory in Durham, North Carolina. Upon receipt of the soil, the bench-scale treatability study was initiated. The key elements of the study were as follows:

- At the laboratory, the Site soil was homogenized and analyzed for total organic carbon (TOC) content. A total of five samples were analyzed for TOC: four were analyzed using the Walkley-Black method, which does not detect elemental carbon (charcoal/coal); and one was analyzed using the Lloyd Kahn method, which does detect elemental carbon.
- The homogenized soil was spiked with 1,000 microliters of MCB and 500 microliters of DCB (this equates to approximately 1,210 milligrams of MCB and 655 milligrams of DCB). The spiked homogenate was left undisturbed for ten days to allow time for the MCB and DCB to achieve partitioning equilibrium. The homogenate was then used to fill three equal-volume glass test columns.

- Each test column was saturated with clean water. In a closed-loop, the water in each test column was circulated several times to assure that equilibrium conditions had been achieved. Pre-treatment desorption samples of the water were then collected and submitted for VOC analysis.
- 500 milliliters (ml) of a 3% $KMnO_4$ solution was then introduced into each test column. In each column, the initial dilution resulted in a 1.89% solution that was recirculated until the concentration of $KMnO_4$ stabilized.
- The $KMnO_4$ solution was then drained, and each column was flushed once with clean water. Post-treatment desorption samples were collected from this water and were submitted for VOC analysis.

Based on numerous published studies and the results of similar testing previously completed in the ARCADIS laboratories, it was assumed that the permanganate molecule could effectively oxidize dissolved-phase constituents with carbon-carbon double bonds (such as MCB and 1,2-DCB). In an effort to make the treatability study more cost-effective, concentrations of the constituents of concern (COCs) in the permanganate effluent were not measured. The treatability study focused on the total oxidant demand assuming that reductions in COC concentrations were the result of successful oxidation.

The overall oxidant demand is generally comprised of two elements: contaminant demand and matrix demand. The matrix demand is principally comprised of naturally occurring organic material in the soil that will consume the oxidant. Matrix demand is generally larger than contaminant demand, such that it controls the magnitude of the overall oxidant demand at a Site. Consequently, soils with high organic content can result in a matrix demand that is hundreds to thousands of times greater than the contaminant demand, making oxidation technology impractical due to cost. Conversely, soils with minimal organic content can result in a very low overall oxidant demand. Based on the results of the TOC analyses, the natural organic carbon content in the Site soil is minimal, less than 500 milligrams per kilogram (mg/Kg), confirming the Site as an ideal candidate for oxidation technology.

The VOC analytical results of the pre- and post-treatment samples collected during the study are summarized below:

Measurement	MCB		1,2-DCB	
	Dissolved (ug/L)	In Soil (mg/Kg)	Dissolved (ug/L)	In Soil (mg/Kg)
Pre-treatment concentration	61,667	34,333	32,667	30,333
Post treatment concentration	346	<38	650	140
Apparent reduction:	99.4%	99.9%	98.0%	99.5%

Notes:
ug/L Micrograms per liter
mg/Kg Milligrams per kilogram

Using the average concentrations of MCB and DCB detected in the desorption samples, a conservative estimate of the sorbed-phase concentration of MCB and DCB was developed using published organic carbon/water partitioning coefficients (USEPA 1996b; Montgomery and Welkom, 1990) and equilibrium relationship equations (USEPA, 1996a). Knowing the average mass of the soil matrix in each test column, the total sorbed-phase mass of MCB and DCB oxidized in each column could be then determined. By comparing these results to the average total $KMnO_4$ consumed by each column, Site-specific oxidant utilization ratios were determined for MCB and DCB, as follows:

- 35 pounds of KMnO4 required to oxidize 1 pound of MCB (35:1)
- 54 pounds of KMnO4 required to oxidize 1 pound of DCB (54:1)

The above utilization ratios take into consideration the matrix demand created by the naturally occurring organic material in the Site soil. Due to the lack of matrix demand, the utilization ratios determined through the treatability study are less than ten times the stoichiometric utilization ratio of approximately 6:1 for both MCB and DCB. As previously mentioned, matrix demand can range from hundreds to thousands of times greater than the contaminant demand. Consequently, the results of the treatability study confirm the suitability of the technology for application at the Site.

PILOT DEMONSTRATION WELL NETWORK

The well network associated with the pilot demonstration was installed in an area of the Site where sufficient impacts were known to be present. The well network was configured such that both the performance of the oxidation process and the extent of the resulting in situ reactive zone could be evaluated. The injection wells were configured to target two discrete lithologic zones in the Site subsurface, one shallow and one deep (just above bedrock). The monitoring wells were arranged radially around the injection points, and were configured to monitor the entire saturated interval across which the chemical oxidant would be injected. The layout and profile of the pilot demonstration well network are depicted on Figures 1 and 2, respectively.

FIELD ACTIVITIES

A total of 10 injection events were completed over a period of 12 weeks. Over the course of the injection events, a total of 1,540 pounds of $KMnO_4$ was delivered to the subsurface in approximately 6,000 gallons of solution (approximately 3 percent by weight). In conjunction with the injection events, a total of seven groundwater sampling events were completed (one baseline, five during the treatment period, and one post-treatment). Based on the data collected, the following observations can be made:

- Injection pressures were negligible through all ten events, indicating that precipitation of manganese dioxide (MnO_2, a by product of $KMnO_4$ oxidation reactions) had a minimal effect on the soil permeability in the pilot area. This validates the effectiveness of the delivery method selected for the pilot demonstration.

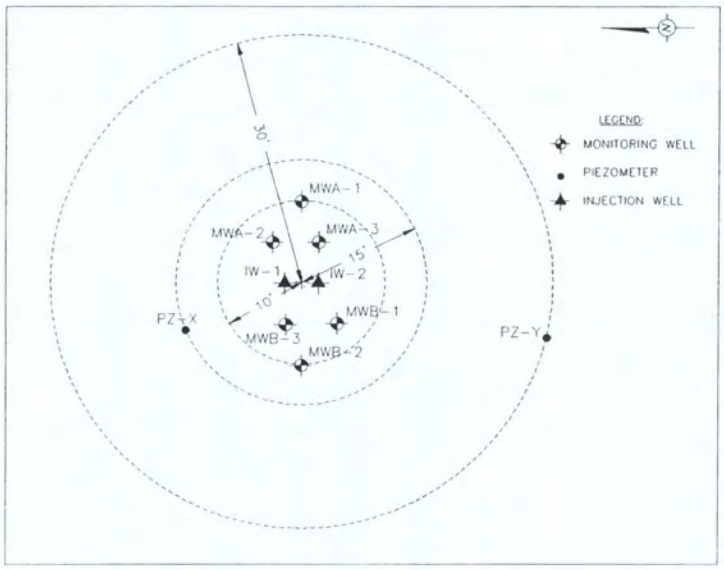


FIGURE 1: Pilot Demonstration Well Network, Layout

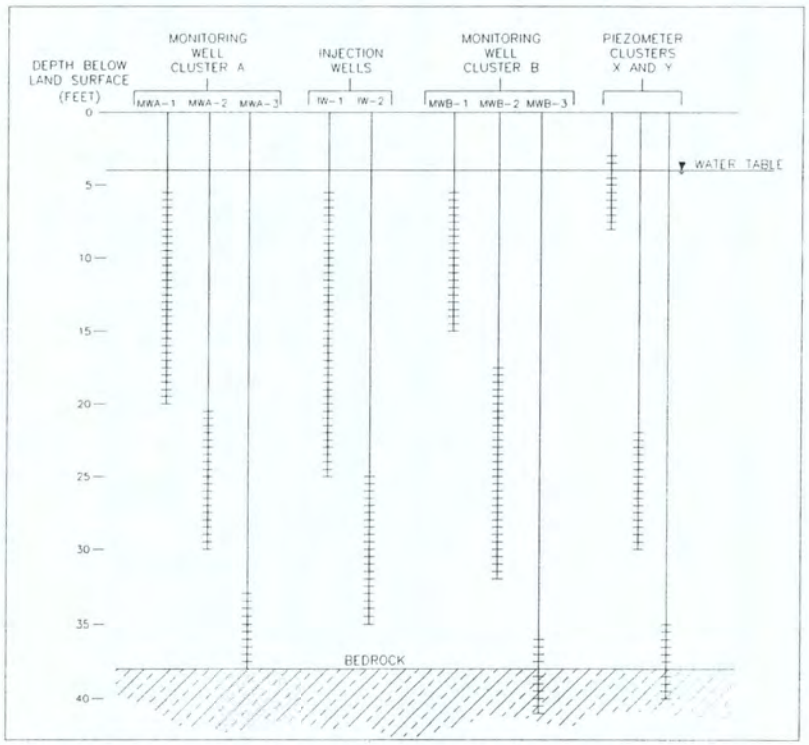
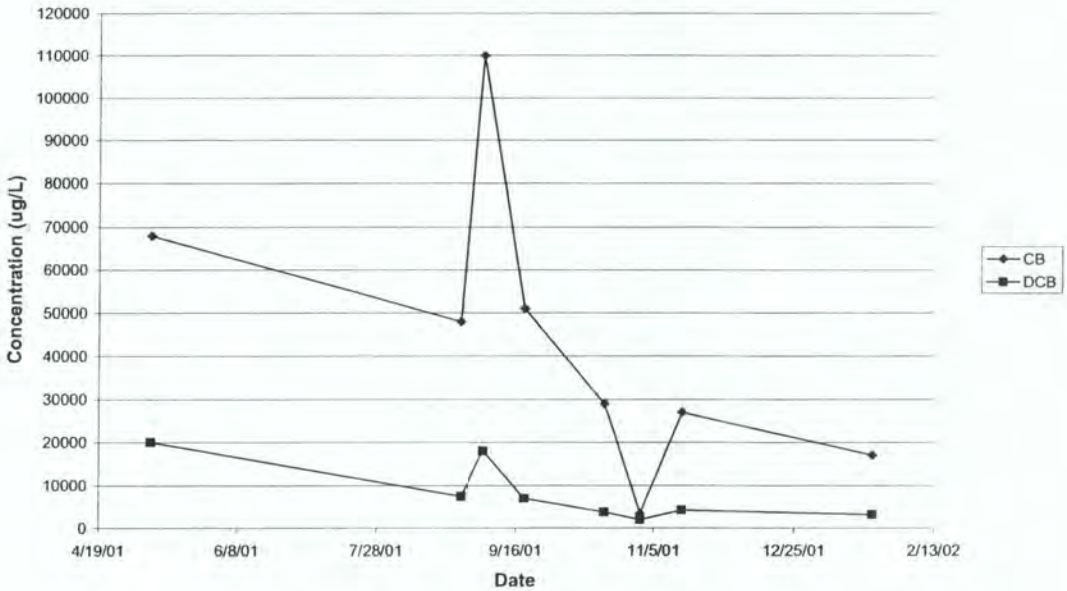


FIGURE 2: Pilot Demonstration Well Network, Profile

- The injected $KMnO_4$ was successfully delivered to the formation and distributed throughout the entire treatment area of the pilot demonstration. This is apparent based on the increase in dissolved potassium and manganese concentrations in groundwater samples collected from the monitoring wells, an increase in the specific conductivity of the groundwater at the monitoring locations, and the presence of unreacted $KMnO_4$ at the monitoring locations.
- The $KMnO_4$ was successful in overcoming the natural reductive poise (naturally occurring organic carbon and other sources of oxidant demand in the aquifer). This is evident by the significant increase in oxidation-reduction potential (ORP) throughout the treatment area.
- Evidence of the reaction between permanganate and the target compounds was observed in at least two of the monitoring well locations, as follows: 1) a 92% decrease in MCB concentration at MWB-1; and 2) a 75% decrease in MCB and 84% decrease in 1,2-DCB concentration at MWB-2 (see chart below). However, target compound concentrations in most of the pilot test monitoring wells exhibited stable to fluctuating trends, indicating that the ability of the permanganate to sufficiently react with the target compounds was limited.

MCB and DCB Concentration Trends Observed at MWB-2



CONCLUSIONS

Because the oxidation reaction associated with permanganate is dependant upon both the concentration of the target contaminant and the permanganate concentration (second order reaction), an insufficient concentration of permanganate in the subsurface would diminish its ability to react with the target compounds (Yan, 1998; Urynowicz,

2000). The low solubility of $KMnO_4$ only permitted the injection of a three percent by weight solution. Once injected, the three percent solution was further diluted in the treatment area after mixing with groundwater. This, in turn, appears to have limited the ability to sustain the desired reaction rates throughout the entire treatment area. We believe that the limited reaction between the oxidant and the target compounds can be overcome through the use of an alternate source of permanganate with a much higher solubility. Specifically, sodium permanganate ($NaMnO_4$) has a solubility ranging up to 50 percent by weight. By increasing the strength of the injected permanganate solution, the resulting in-situ permanganate concentrations should reach a point adequate to sustain sufficient reaction with the target compounds throughout the entire treatment area.

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OZONATION TREATMENT STUDIES USING DIOXIN-, FURAN- AND HYDROCARBON-CONTAMINATED WATER

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ABSTRACT: The use of ozone by municipalities to rid drinking water from certain undesirable chemicals and microorganisms that chlorine cannot destroy is well documented. As a result, the environmental industry is beginning to examine applications whereby ozonation may be useful in the treatment of organic compounds and mixtures in water.

The objectives of the treatment studies were to examine the destruction efficiency and efficacy of ozone on chemicals of concern (COC) commonly found in rhenformer wash water and contaminated groundwater. The rhenformer wash water contained a variety of dioxins, including 2,3,7,8-tetrachlorodibenzo-p-dioxin, and furans. The groundwater contained chlorinated hydrocarbons and mineral spirits. The studies were performed as bench scale tests.

This paper provides summaries of the bench scale treatment studies by describing the COC; procedures and apparatus; observations; and results. The summaries detail which applications hold promise with respect to ozonation and which ones do not. Bench test results for experiments involving chlorinated hydrocarbons and mineral spirits were relatively successful. Concentrations for the COC ranging from 300 to 3400 micrograms per liter (μg/L) were brought below levels specified for storm sewer discharge per the National Priority Discharge Elimination Systems (NPDES) permit requirements. Bench test results for the experiments involving dioxins and furans were less promising and revealed that additional processes would have to be used in combination with ozonation to bring the concentration of COC within the targeted treatment ranges. The effectiveness of ozonation was not significantly diminished by the presence of particulates to which dioxin and furan compounds were adhered.

INTRODUCTION

Ozone, hydrogen peroxide, and ultraviolet (UV) light, are presently in limited use in the environmental industry. These oxidants can be used alone or in combination with one another. Each serves as an oxidizing agent. Ozone was selected for the subject bench scale tests because it has the highest oxidation potential of these treatment agents; can be used with turbid process streams (unlike UV light); and is stable (unlike hydrogen peroxide).

Simple bench top apparatus were used to perform ozonation tests with various sample waters. The reaction vessel consisted of a single cylindrical Plexiglas cylinder with stationary-rotating agitator blades inserted within it. Once test water was placed inside the reactor vessel, ozone was injected into one end of the vessel under controlled flow. Ozone was produced on-demand in gaseous form by a small generator.

Test waters were obtained from a several sources in order to represent the mixtures encountered in the real world. Test waters were selected to provide

experimentation with chlorinated hydrocarbons, mineral spirits, dioxins, and furans. Bench tests with waters containing chlorinated hydrocarbons and mineral spirits demonstrated greater than 85% destruction efficiency, and frequently better than 99%. Bench tests involving chlorinated hydrocarbons and mineral spirits ranging from 300 to 3400 μg/L were brought below NPDES permit levels (5.0 and 50.0 μg/L, respectively). Bench tests with waters containing dioxins and furans were less successful and revealed that ozonation probably could not be used as a stand alone treatment for these COC.

PROCEDURES

This section describes the procedures employed in the scaled ozonation testing. The procedures presented herein describe the testing apparatus and laboratory methods used to confirm results.

Bench Testing. Test samples were ozonated in a cylindrical, Plexiglas reactor vessel 3 feet in length and 2 inches in diameter. Reactor orientation during testing was length-vertical. Stationary, corrosion-resistant, stainless steel agitators were inserted into the reactor to maximize ozone and process water mixing.

One liter (L) water samples were used in each test. Test samples were obtained from a refinery rhenformer washer and a groundwater pump and treat system. Prior to placing a sample into the reactor vessel it was decanted through a 100 mesh polyethylene filter to remove large debris.

Ozone, generated on-demand, was provided to the bottom of the reactor vessel through a control valve. Flow rates were recorded from an in-line gauge. Ozone flow rates ranged from 0.03 to 0.14 standard cubic feet per minute (scfm). Test durations ranged from 20 to 60 minutes. Total ozone used in a test was determined by multiplying the test duration, ozone flow rate and ozone concentration. Table 1 summarizes the ozone test conditions.

Verification Testing. Test samples were analyzed by certified commercial laboratories prior to and following ozone treatment. The laboratories used approved EPA methods, where appropriate, to report selected parameter concentrations. The variation in the use of standard EPA methods was in the analysis of total petroleum hydrocarbons as mineral spirits (TPHms). The method employed to analyze this parameter was derived from gas chromatography/mass spectrometry (GC/MS) EPA methods and may be considered an extended EPA method 8260 instrument run (Schaal, 1996). Laboratory analytical methods are summarized in Table 2.

SCALED OZONATIONATION TEST RESULTS

The samples containing dioxins and furans in Tests A through E were rhenformer wash water obtained from refinery. The samples containing chlorinated hydrocarbons and mineral spirits were obtained from a hazardous waste site. Recovered unprocessed groundwater from the site was used in Tests F and G. Air stripped groundwater from the site was used in Tests H and I.

The ozonation test results for each set of parameters are provided in Table 3. COC destruction reported as % reduction for each ozonation test is summarized in Table 4.

TABLE 1. Ozone Test Conditions

Test Identity	Test Conditions		
	Reaction Time (min)	Ozone Weight (%)	Ozone Flow Rate (scfm)
Rhenformer Wash Water #1			
Ozone Treatment A	30	1.2	0.033
Ozone Treatment B	60	1.2	0.055
Rhenformer Wash Water #2			
Ozone Treatment C	20	0.57	0.093
Ozone Treatment D	40	1.2	0.13
Ozone Treatment E	60	1.2	0.08
Recovered Groundwater			
Ozone Treatment F	20	1.2	0.12
Ozone Treatment G	60	1.2	0.09
Processed Groundwater (air stripper effluent)			
Ozone Treatment H	15	1.5	0.83
Ozone Treatment I	30	1.3	0.14

TABLE 2. Laboratory Analytical Methods

Target Parameters	Analytical Methods
Dioxins: 2,3,7,8 - TCDD OCCD Total TCDD Total HxCDD Total PeCDD Total HpCDD	EPA Method 8290
Furans: 2,3,7,8 - TCDF OCDF Total TCDF Total HxCDF Total PeCDF Total HpCDF	
Chlorinated Hydrocarbons: cis-1,2 DCE TCE 1,2 DCB PCE	EPA Method 8260
Mineral Spirits	GC/MS Fingerprinting (modified EPA method 8260)

TABLE 3. Test Results By Parameter

Sample Description	DIOXIN Test Parameters (aqueous: pg/L; solids: pg/g)					
	2,3,7,8-TCDD	Total TCDD	Total PeCDD	Total HxCDD	Total HpCDD	OCCD
Rhenformer Wash Water #1						
Control (unfiltered)	25.3	812	883	1,250	793	394
Ozone Treatment A (unfiltered)	4.6	525	800	869	514	246
Ozone Treatment B (unfiltered)	2.8	ND (<114)	130	574	404	172
Rhenformer Wash Water #2						
Control (unfiltered)	9.3	1,760	1,300	691	165	21
Filtered Aqueous	ND (<4.9)	204	92.5	46.5	16.3	39.1
Filtered Solids	816	106,000	88,100	48,000	12,200	1,860
Ozone Treatment C (unfiltered)	5.7	754	532	289	71.9	26
Filtered Aqueous	3.6	7.2	ND (<3.8)	ND (<3.6)	75.8	8.35
Filtered Solids	23.1	1,610	975	583	93.5	56.5
Ozone Treatment D (unfiltered)	ND (<5)	1,660	1,350	754	190	57.3
Ozone Treatment E (unfiltered)	ND (<5)	1,090	941	530	132	22.1

Sample Description	FURAN Test Parameters (aqueous: pg/L; solids: pg/g)					
	2,3,7,8-TCDF	Total TCDF	Total PeCDF	Total HxCDF	Total HpCDF	OCDF
Rhenformer Wash Water #1						
Control (unfiltered)	499	8,330	6,540	3,520	1,460	354
Ozone Treatment A (unfiltered)	334	5,020	4,360	2,440	866	198
Ozone Treatment B (unfiltered)	334	3,760	3,120	1,760	749	163
Rhenformer Wash Water #2						
Control (unfiltered)	312	7,700	4,740	1,750	429	38
Filtered Aqueous	60.5	833	392	156	151	345
Filtered Solids	31,000	373,000	263,000	125,000	328,000	167,000
Ozone Treatment C (unfiltered)						
Filtered Aqueous	93.2	2,730	2,110	890	224	19.9
Filtered Solids	ND (<3)	34.1	ND (<1.9)	11.5	ND (<8.1)	9.7
	703	6,560	4,690	2,380	607	204
Ozone Treatment D (unfiltered)	222	6	4,848	2,060	594	66.4
Ozone Treatment E (unfiltered)	164	4,270	3,570	1,420	352	30.6

TABLE 3. Test Results By Parameter, continued

Sample Description	HYDROCARBON Test Parameters (μg/L)				
	1,2-DCB	PCE	TCE	cis-1,2-DCE	Mineral Spirits
Recovered Groundwater					
Control (estimated)	2,500	80,000	26,000	27,000	NA
Ozone Treatment F	78	4,100	2,600	5,400	NA
Ozone Treatment G	ND (<50)	4,800	3,100	7,700	NA
Processed Groundwater (air stripper effluent)					
Control	ND (<0.5)	3,400	1,100	2,500	330
Ozone Treatment H	ND (<0.5)	2.6	ND (<0.5)	ND (<0.5)	ND (<50)
Ozone Treatment I	ND (<0.5)	3.5	ND (<0.5)	ND (<0.5)	ND (<50)

TABLE 4. Chemical Of Concern Destruction

Target Parameter	% Reduction										
	Treatment Identity										
	A	B	Un-filtered	Filtered Aqueous	Filtered Solids	D	E	F	G	H	I
Rhenformer Wash Water #1 and #2											
2,3,7,8-TCDD	82	89	39	0	97	>46	>46	-	-	-	-
Total TCDD	35	>86	57	96	98	6	38	-	-	-	-
Total PeCDD	9	85	59	>96	99	0	28	-	-	-	-
Total HxCDD	31	54	58	>93	99	0	28	-	-	-	-
Total HpCDD	35	49	56	0	99	0	20	-	-	-	-
OCCD	38	56	0	0	97	0	0	-	-	-	-
2,3,7,8-TCDF	33	33	70	>99	98	29	47	-	-	-	-
Total TCDF	40	55	65	96	98	>99	45	-	-	-	-
Total PeDCF	33	52	56	>99	98	0	25	-	-	-	-
Total HxDCF	31	50	49	93	98	0	19	-	-	-	-
Total HpCDF	41	49	48	>95	>99	0	18	-	-	-	-
OCDF	44	54	48	97	>99	0	20	-	-	-	-

TABLE 4. Chemical Of Concern Destruction, continued

Target Parameter	% Reduction										
	Treatment Identity										
	A	B	Un-filtered	Filtered Aqueous	Filtered Solids	D	E	F	G	H	I
Recovered and Processed Groundwater											
1,2-DCB	-	-	-	-	-	-	-	97	>98	N/A	N/A
PCE	-	-	-	-	-	-	-	95	94	>99	>99
TCE	-	-	-	-	-	-	-	90	88	>99	>99
cis-1,2,-DCE	-	-	-	-	-	-	-	80	72	>99	>99
Mineral spirits	-	-	-	-	-	-	-	-	-	>85	>85

The following observations were recorded during the ozonation treatment tests.

- The additional filtration of the rhenformer wash water revealed that the majority of the dioxins and furans were sorbed onto particulates present in the sample.

- During ozonation water turned from clear to black in Tests A through E and yellow-brown during test F through I, then became clear again in all tests. As the water cleared in Tests F through I sediment of the color noted accumulated on the reactor vessel bottom.

- During ozonation the water foamed mildly. The foaming ceased before the tests were completed.

- Most frequently, the ratio of ozone flow rate to ozone concentration equal or greater to 0.1 resulted in 85% or better destruction efficiency. This observation remains true regardless of test durations. The single noted exception to this is Treatment Test D. The ratio of ozone flow rate to ozone concentration for each test is provided in Table 5.

TABLE 5. Ozone Flow Rate To Ozone Concentration Ratios

Treatment Test	Ozone flow rate to ozone concentration ratio
A	0.03
B	0.04
C	0.16
D	0.11
E	0.06
F	0.1
G	0.8
H	0.05
I	0.1

COST CONSIDERATIONS

A feasibility study was not within the scope of this bench scale study. The results of this bench scale study suggest that further investigation respective to efficiency, efficacy, and feasibility appears warranted. Efficiency and efficacy have been discussed in previous sections of this paper. A limited discussion regarding cost considerations is presented below.

In a scenario in which activated carbon operation and maintenance (O&M) costs would be about $12 per 1000 gallons of water, ozonation O&M would range from $2 to $5 (Roy, 1990). Small generators are capable of producing 25 to 125 pounds of ozone per day at concentrations ranging from 2 to 5 % weight for a cost of about $30 per day (Roy, 1990). Capital costs are not addressed due to the numerous variabilities in any specific application. Typically, ozone systems comprised of a generator and reactor are commercially available from $10,000 to $200,000 for units capable of producing tens of pounds to hundreds of pounds per day, respectively. It should be noted that the equipment is durable and, therefore, can be used in subsequent applications to recoup capital costs.

CONCLUSIONS

Ozonation treatment technology warrants further evaluation. Ozonation treatment efficiencies with the chlorinated hydrocarbons and mineral spirits in stripped groundwater generally exceeded 85% and were often better than 99%. This observation supports the concept of using ozonation in post-processing stages similar to a final carbon polish. Ozone destruction of the chlorinated hydrocarbons and mineral spirits in the recovered groundwater was slightly less effective. The demonstrated 70% or greater destruction efficiency was achieved with chlorinated hydrocarbons and mineral spirits concentrations ranging from 2,500 to 80,000 μg/L is indicative that ozonation treatment holds promise as

a pre-processor. Contaminant load reduction by ozonation could extend the useful life of activated granular carbon and resin beds or assure air stripper efficiency.

Ozonation treatment efficiencies with dioxins and furans in the rhenformer wash water were varied. Destruction efficiencies ranged from almost none to better than 99%. Review of test conditions suggests that better efficiencies may have been achievable if test parameters had been set to field a higher ozone flow rate to ozone concentration ratio.

Treatment test durations varied from 20 to 60 minutes. Destruction efficiencies of 85% or better were obtained when the ratio of ozone flow rate to ozone concentration was 0.1 or greater, regardless of test duration. This suggests that reaction time beyond 20 minutes was not important and is probably an independent variable.

Treatment Test C demonstrates that oxidation with ozone can be used to process streams in which the contaminants are sorbed to particulates (Table 4). Treatment Test D is inconclusive (Table 4). The low destruction efficiencies are more likely due to sample mishandling or analytical method variability than ineffective treatment. This belief is based on the laboratory analyses in which some of the post-treatment COC concentrations were higher than pre-treatment. However, because it is not possible to substantiate this or identify any other reason for this occurrence, it is not possible to draw a formal conclusion about destruction efficiencies associated with Treatment Test D.

SUMMARY

The byproducts from complete ozonation destruction are water and carbon dioxide. Compared to other commonly used oxidizers (i.e., UV light and hydrogen peroxide), ozone has a greater ionization, may be used in turbid process streams (unlike UV) and is stable in high concentrations, (unlike hydrogen peroxide). One publication reports that O&M costs to treat 1000 gallons of water is 2 to 6 times less expensive with ozone than with activated carbon.

Based on the bench scale studies presented in this paper, ozonation for treatment of water containing chlorinated hydrocarbons, mineral spirits, dioxins, or furans appears to hold promise. The bench scale tests demonstrate better destruction efficiencies with the chlorinated hydrocarbons and mineral spirits than the dioxins and furans. Concentrations of chlorinated hydrocarbons and mineral spirits ranging from 300 to 3400 μg/L were reduced below NPDES permit requirements (5.0 and 50.0 μg/L, respectively).

Wide-ranging application for ozone treatment in pre- and post-processing appears plausible, as does stand-alone use. In pre- and post-processing applications it may serve to compliment other systems by extending their service lives or reducing loading to/from them. Applicability is a function of contaminant identities and concentrations; process throughputs; and ozone generator capacity and source gas (i.e., air or oxygen). The described bench scale studies illustrate the need to perform further controlled experiments, and possibly, pilot studies to address efficiency and efficacy in a specific application.

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Oxidation of Chlorobenzene with Fenton's Reagent

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■ The degradation of chlorobenzene and its oxidation products by hydroxyl radicals generated with Fenton's reagent was studied. In the absence of oxygen, chlorophenols, dichlorobiphenyls (DCBs), and phenolic polymers were the predominant initial products. In the presence of oxygen, DCB yields decreased markedly and chlorobenzoquinone was also formed. Chlorophenol isomers were further oxidized by OH•s to form chlorinated and nonchlorinated diols. DCBs and the phenolic polymers were also oxidized. The highest yield of product formed per mole of H_2O_2 consumed was observed in the pH range of 2–3. The pH dependence and product distributions suggest that complexes of aromatic intermediate compounds with iron and oxygen may play a role in regulating reaction pathways. At pH 3.0, approximately 5 mol of H_2O_2/mol of chlorobenzene were required to remove all of the aromatic intermediate compounds from solution.

Introduction

Chlorinated aromatic hydrocarbons (CAHs) have been introduced to the environment from a variety of sources. Many of these compounds do not readily degrade and pose a threat to biota and human populations. Concern about the potential hazards associated with these compounds has resulted in laws and policies that require the cleanup of contaminated soil, sediments, surface water, and wastewater (*1*). Treatment of these wastes necessitates the development of technologies to effectively degrade many types of CAHs.

One potentially important method of destroying CAHs is through chemical oxidation by hydroxyl radicals generated with Fenton's reagent (*2, 3*). Fenton's reagent is a mixture of hydrogen peroxide and ferrous iron (Fe^{2+}), which produces OH•s according to reaction 1 (*4*):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+}\ OH^- + OH^\bullet \qquad (1)$$

The OH•s produced in reaction 1 are capable of reacting with a variety CAHs (*5–7*). Preliminary studies for the design of waste treatment systems employing Fenton's reagent (*2, 3, 8–10*) indicate that the reaction is effective in the degradation of phenols, chlorophenols, formaldehyde, and octachloro-*p*-dioxin. However, none of these studies have focused on either the nature of intermediate products or factors affecting product yields and distributions. Furthermore, mechanistic studies on CAHs are mainly limited to systems in which oxygen is excluded and high H_2O_2 and substrate concentrations are present.

Understanding the reaction mechanism for the oxidation of CAHs under conditions relevant to waste treatment is an essential step in the design of efficient, cost-effective Fenton's reagent treatment systems. These factors are especially important for this oxidation system because product yields and distributions may be drastically affected by environmental conditions such as pH and oxidant concentrations (*11, 12*). Furthermore, identification and quantification of intermediate products is important because hydroxylated aromatic and dimeric intermediates may be recalcitrant and/or toxic.

In this study we have evaluated reactions of Fenton's reagent with chlorobenzene and its intermediate oxidation products as a function of pH, and in the presence or absence of oxygen. Through determination of intermediate products and the effect of environmental variables on product yields and distributions, we have identified possible reaction mechanisms and optimal conditions for

degrading these compounds. In addition, we have collected data that provide a basis for estimating the quantities of H_2O_2 required to oxidize all of the CAHs and aromatic intermediates.

Materials and Methods

The following chemicals were obtained from Aldrich at the specified purities and were used without further purification: benzoquinone (97%), catechol (99+%), chlorobenzene (99+%), chlorohydroquinone (technical grade), 2-chlorophenol (99+%), 3-chlorophenol (98%), 4-chlorophenol (99+%), 4-chlororesorcinol (98%), hydrogen peroxide (ACS reagent grade, 30% solution), ferric sulfate pentahydrate, ferrous sulfate heptahydrate (99+%), 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ) (97%). Dichlorobiphenyl isomers were purchased from Cambridge Isotope Laboratories.

Aqueous solutions of various organic compounds, used for oxidation reactions and as HPLC standards, were prepared with Millipore Milli-Q water. Nitrogen was bubbled through the water for at least 1 h prior to addition of solute for solutions used in reactions conducted in the absence of oxygen. Chlorobenzene solutions were stirred for at least 1 week prior to use. Solutions of chlorophenols and all other standards were prepared by dissolving the appropriate quantity in water and stirring at least 1 h. Chlorobenzoquinone standards were prepared by oxidizing a chlorohydroquinone solution with excess Fe^{3+}. Completion of the reaction was confirmed by the disappearance of the chlorohydroquinone peak on the HPLC chromatogram.

Fenton's reagent reactions were conducted in a 500-mL round-bottom flask. The flask was maintained at 25 °C with a recirculating water bath and shielded from light with aluminum foil. For reactions conducted in the absence of oxygen, a nitrogen atmosphere was maintained over the solution at a slight positive pressure and samples were withdrawn through a sampling port with a syringe. Samples were collected after 1 h unless otherwise noted.

The initial solution pH was adjusted with hydrochloric acid for reactions at pH values up to 3.0. Reactions at pH values of 4.7 and 7.0 were buffered with acetic acid and phosphoric acid buffers, respectively.

Hydrogen peroxide solutions, maintained at 25 °C with a recirculating water bath, were added to the reactor containing the solute and Fe^{2+} either in a total volume of 10 mL at the start of the reaction or at a rate of 5.0 mL/h with a metering pump.

Ferrous iron was quantified by the method of Collins et al. (*13*), which involves spectrophotometric measurements of the Fe^{2+}/TPTZ complex.

Polar compounds were quantified by HPLC using a 25-cm reverse-phase column (ODS-2; Alltech) and a mobile phase of methanol/water with 0.5 mM acetate buffer. The following gradient was used: 10% methanol (hold 4 min); ramp to 50% methanol by 15 min (hold 6 min). Compounds were detected at 280 nm and quantification was based on comparison with standards, except in the case of 4-chlorocatechol, which was estimated on the basis of the measured extinction coefficient of catechol.

Samples withdrawn from the reactor (5 mL) were also extracted three times with 10 mL of petroleum ether and 0.2 mL of saturated sodium chloride and analyzed for chlorobenzene by GC/MS (Hewlett-Packard 5890/5970). These extracts were then concentrated to 1 mL and analyzed quantitatively for dichlorobiphenyls and qualitatively for other compounds. Dichlorobiphenyls were quantified by using 2,4′,5-trichlorobiphenyl as an internal standard. Chromatographic conditions were as follows: 30-m RT_x-5 capillary column (Restek); oven programmed to start at 50 °C (hold 4 min) then ramp to 280 °C at 5 °C/min; detection with scan mode in the 50–350 mass/charge range.

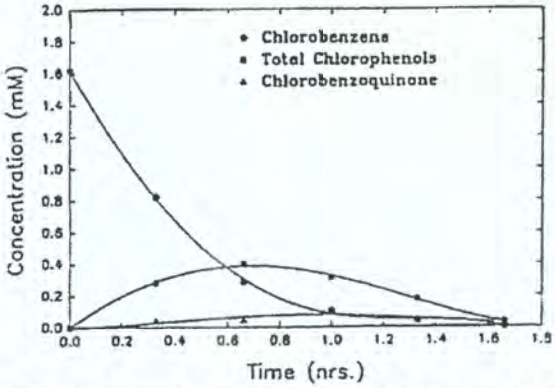


Figure 1. Oxidation of chlorobenzene with Fenton's reagent. Initial conditions: Fe^{2+}, 5.0 mM; pH, 3.0

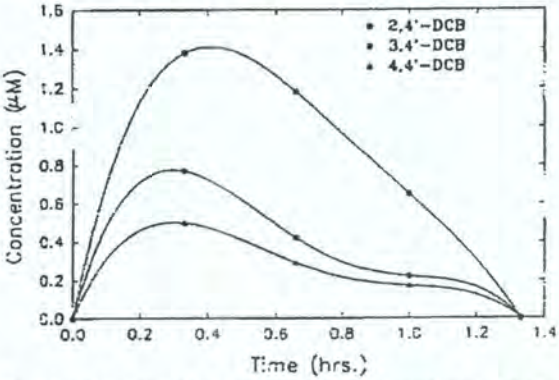


Figure 2. Formation of three dichlorobiphenyls isomers during oxidation of chlorobenzene with Fenton's reagent. 2,2′-DCB, 2,3′-DCB, and 3,3′-DCB are not shown because concentrations were significantly smaller than those observed for the other isomers. Conditions: Fe^{2+}, 5.0 mM; pH, 3.0

UV/vis spectrophotometric measurements were performed on a Varian DMS 80 spectrophotometer with a slit width of 3 nm. UV/vis scans were conducted at a scan rate of 100 nm/min.

Dissolved organic carbon (DOC) was analyzed on an automatic TOC analyzer (Model 700, OI Corp.).

Results

Results from the oxidation of chlorobenzene by addition of H_2O_2 at a rate of 5 mM/h at an initial pH of 3.0 are shown in Figures 1 and 2. Chlorobenzene and all intermediate products disappeared within the first 2 h of the reaction. The three chlorophenol isomers, chlorobenzoquinone, and the six dichlorobiphenyl isomers were identified by GC/MS (Table I) and quantified by either GC/MS or HPLC. The mass spectra and retention times for these compounds were identical with those of the standards and the mass spectra closely matched those in the NBS database. A group of compounds with retention times similar to the dichlorobiphenyl isomers were also observed. These peaks were tentatively identified as hydroxymonochlorobiphenyls or hydroxydichlorobiphenyls on the basis of the results of a computerized search of the NBS mass spectral library and similarity of their mass

Table I. Intermediate Compounds Identified from Oxidation of Chlorobenzene with Fenton's Reagent

peak	compound	RT[a]	ID[b]	quant[c]
1	2-chlorophenol	11.9	std	HPLC
2	chlorobenzoquinone	10.7	std	HPLC
3	3-chlorophenol	15.9	std[d]	HPLC
4	4-chlorophenol	17.0	std[d]	HPLC
5	2,2'-DCB	21.2	std	GC/MS
6	2,3'-DCB	25.3	std	GC/MS
7	2,4'-DCB	25.8	std	GC/MS
8	3,3'-DCB	28.7	std	GC/MS
9	3,4'-DCB	28.8	std	GC/MS
10	4,4'-DCB	29.4	std	GC/MS
11	MHClBps	many[e]	NBS	NQ[f]
12	DHClBps	many[e]	NBS	NQ[f]

[a] Retention time in minutes on column used for quantification. [b] Method of GC/MS identification: std, matched with mass spectra and retention times of standard; NBS, compared with NBS mass spectral database and spectra described by Tulp et al. (*14*). [c] Method used for quantification. [d] These chlorophenol isomers coeluted on GC/MS. Mass spectra showed characteristics of both compounds. [e] Four hydroxymonochlorobiphenyl compounds (RT = 18.5, 22.5, 24.3, and 25.1 min) and four hydroxydichlorobiphenyl compounds (RT = 26.2, 26.9, 27.5, and 27.7 min) were identified. At least 10 additional mono- and dichlorinated hydroxylated biphenyls were also identified between 29 and 31 min but could not be fully separated. [f] NQ, not quantified.

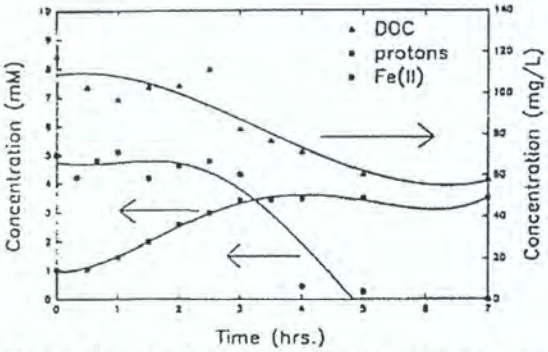


Figure 3. Changes in DOC, pH, and Fe^{2+} during oxidation of chlorobenzene with Fenton's reagent.

spectra to compounds described by Tulp et al. (*14*). Compounds with identical mass spectra and GC retention times identified in extracts from the oxidation of chlorinated biphenyls with hydroxyl radicals have been identified as hydroxychlorobiphenyls on the basis of comparison with available standards and mass spectra of methylated samples (*15*).

As the reaction progressed, UV/vis spectrophotometric scans showed a gradual increase in broad-band absorption within the visible spectral region. This increasing absorbance, which was accompanied by a decrease in solution pH, continued until approximately 4 h after the start of the reaction, at which time the solution cleared to a yellow color, Fe^{2+} decreased significantly, and pH stabilized (Figure 3). Dissolved organic carbon decreased by approximately 40% during the reaction and stabilized after approximately 5 h.

A more quantitative understanding of the initial steps of the reaction was achieved by conducting a series of experiments in which a small amount of H_2O_2 (an amount that resulted in the oxidation of less than 10% of the initial chlorobenzene) was added to a solution of chlorobenzene and Fe^{2+} at the start of the reaction (Table II). Reactions in the absence of oxygen yielded much higher concentrations of dichlorobiphenyls (DCBs) when compared to those in air. Furthermore, chlorophenol isomer distributions under nitrogen contained a higher proportion of *o*-chlorophenol than reactions performed with oxygen. When further experiments were conducted in the presence of oxygen (Figure 4), the highest yield of product formed per mole of H_2O_2 consumed was observed at pH values in the range of 2–3. Chlorophenol isomer distributions remained constant (combining the results of duplicate analyses at each pH the following mean isomer distributions and 95% confidence intervals were calculated: ortho, 35.3 ± 2.1%; meta, 19.7 ± 2.6%; para, 45.0 ± 1.7%) and DCB concentrations remained below 10^{-6} M over the entire pH range.

Table II. Chlorophenol and Dichlorobiphenyl Produced during Oxidation of Chlorobenzene with Fenton's Reagent with and without oxygen

	concn,[a] mM				
atmos[a]	ortho[b]	meta[b]	para[b]	DCBs[c]	total[d]
N_2	0.073	0.026	0.028	0.0085	0.1355
	(53.9)	(19.2)	(20.7)	(6.3)	
O_2	0.041	0.023	0.049	0.0005	0.1135
	(36.1)	(20.3)	(43.2)	(0.4)	

[a] Initial conditions: Fe^{2+}, 4.5 mM; pH, 3.0; H_2O_2, 2.7 mM; chlorobenzene, 3.8 mM. Results are average values for two experiments. [b] Concentrations of chlorophenol isomers. [c] Total concentration of dichlorobiphenyl (DCB) isomers. [d] Total amount of chlorophenols and DCBs produced. [e] Values in parentheses represent percentage of total.

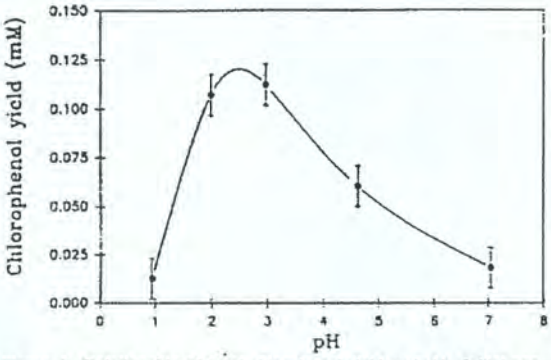
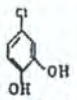
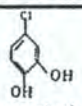
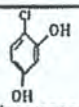


Figure 4. Relationship of total chlorphenol yield and pH. Initial conditions: Fe^{2+}, 5.0 mM; H_2O_2, 2.7 mM; chlorobenzene, 3.8 mM. Error bars represent 95% confidence intervals based on pooled variances observed in duplicate experiments at each pH.

The oxidation of pure solutions of chlorophenol isomers by Fenton's reagent was also qualitatively evaluated (Figure 5). Chlorinated diols resulting from ortho or para substitution accounted for most of the observed products identified by GC/MS. Small quantities of nonchlorinated diols (hydroquinone, catechol, and benzoquinone) were also observed. Reactions with 2-chlorophenol and 3-chlorophenol exhibited the same broad-band absorption observed for chlorobenzene. Reactions with 4-chlorophenol passed through a green-colored stage prior to onset of broad-band absorption.

Oxidation of a 4-chlorophenol solutions was followed quantitatively in the presence and absence of oxygen as depicted in Figure 6. In both cases, 4-chlorocatechol was observed as the predominant product. Compound identification was based upon analysis of mass spectra and comparison with HPLC chromatograms from Sehili et al. (*16*). Quantification was based upon extinction coefficient measurements for catechol and assumes that the UV

isomer	ortho[1]	products observed para	meta
2-chlorophenol	3-chlorocatechol catechol	chlorobenzoquinone	None detected
3-chlorophenol	3-chlorocatechol  4-chlorocatechol	chlorobenzoquinone	None detected
4-chlorophenol	 4-chlorocatechol	hydroquinone benzoquinone	 4-chlororesorcinol

[1] Location of hydroxyl addition (relative to original OH group on chlorophenol isomer)

Figure 5. Products observed from chlorophenol oxidation by Fenton's reagent. Initial conditions: Fe^{2+}, 0.5 mM; pH, 3.0; H_2O_2, 4.5 mM; chlorophenol isomer, 3.0 mM.

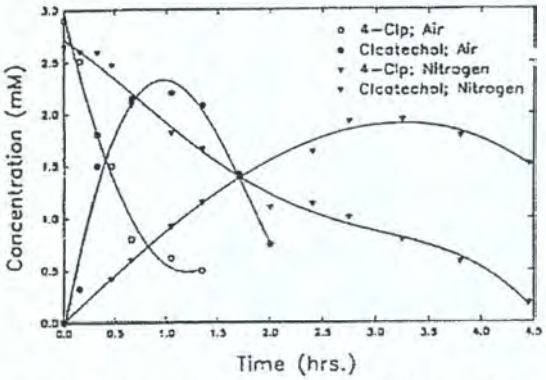


Figure 6. Oxidation of 4-chlorophenol with Fenton's reagent. Initial conditions: Fe^{2+}, 0.5 mM; H_2O_2 addition rate, 3.0 mM/h; pH, 3.0. 4-Chlororesorcinol, hydroquinone, and benzoquinone were detected at concentrations less than 0.2 mM.

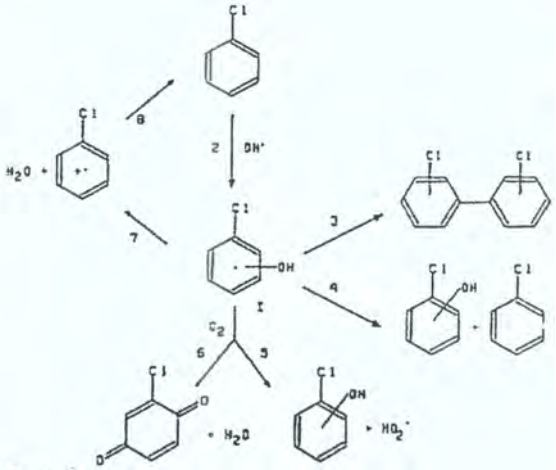


Figure 7. Proposed reaction pathway for oxidation of chlorobenzene with Fenton's reagent.

spectra of the chlorinated compound is similar to its nonhalogenated parent. Other intermediate compounds were not detected in significant quantities by GC/MS or HPLC. Results from these experiments also illustrate that oxygen almost doubles the rate of disappearance of 4-chlorophenol.

Discussion

The overall results of our experiments indicate that Fenton's reagent can effectively degrade chlorobenzene, chlorophenols, and dichlorobiphenyls. In the presence of oxygen at pH 3.0, approximately 5 mol of H_2O_2/mol of chlorobenzene is required to completely remove the aromatic intermediates from solution. Results from DOC analysis indicate that the aromatic intermediates undergo ring cleavage prior to mineralization. Cessation of the reaction after approximately 4 h, as evidenced by stabilization of DOC concentrations, pH, and Fe^{2+}, is most likely attributable the inability of many ring-cleavage intermediates to regenerate Fe^{2+}.

Chlorobenzene Reactions. By analogy to previous work on $OH^{\bullet}$ reactions with aromatic compounds and evaluation of our results, we believe that the oxidation of chlorobenzene by Fenton's reagent (Figure 7) follows a complicated reaction pathway in which products are formed via several different mechanisms controlled by factors such as oxidant concentrations and pH. The first step in the reaction sequence, $OH^{\bullet}$ attack on chlorobenzene (reaction 2), likely results in the formation of chlorohydroxycyclohexadienyl (ClHCD) radical I (*7, 17*), which may undergo one of several possible further reactions.

In the absence of oxygen, or other strong oxidants, the two predominant reactions are dimerization to produce dichlorobiphenyls (reaction 3) and bimolecular disproportionation to produce chlorophenol and chlorobenzene (reaction 4). Both of these reactions exhibit an overall stoichiometry of 2 mol of H_2O_2/mol of chlorobenzene oxidized, which is consistent with our observations (see Table II). A similar stoichiometry has been observed in the oxidation of benzene by Fenton's reagent, but biphenyl yields were as high as 50% (*18*).

In the presence of oxygen, or other strong oxidants, different product distributions are observed because several additional reactions contribute to product formation. Reactions of the oxidant (O_2) with the ClHCD radical (reactions 5 and 6) predominate because they are first

order with respect to ClHCD radical while bimolecular reactions 3 and 4 are second order with respect to the radical. Reaction of the ClHCD radical with O_2 results in lower DCB yields, different chlorophenol isomer distributions and higher chlorobenzoquinone yields than reactions under nitrogen. Reactions of ClHCD radicals with O_2 are also important because they could result in the production of hydroperoxy radicals (via reaction 5) or H_2O_2 (*19*), which could further oxidize CAHs.

The formation of chlorobenzoquinone as a result of oxygen attack on the ClHCD radical in a position para to the initial $OH^{\bullet}$ addition was expected, based upon previous experimental results with benzene (*19, 20*). However, the absence of ortho-substituted diols (catechol or chlorocatechol) observed in these reactions is unexpected given the ortho/para directing tendency of hydroxyl groups. One possible explanation is steric hindrance at the ortho position caused by an iron–oxygen complex similar to that observed in the Cu/O_2 analogue of Fenton's reagent (*20*).

The formation of chlorobenzoquinone by a pathway involving O_2 rather than via a secondary reaction of a chlorophenol isomer is strongly supported by our results. The decreased relative yields of *o*-chlorophenol observed in the presence of oxygen can be explained by a more favorable reaction of O_2 with ortho ClHCD radicals than other ClHCD radicals. Furthermore, catechol and chlorocatechol isomers were produced as primary products in reactions with solutions of the chlorophenol isomers and would presumably be present if chlorobenzoquinone was a secondary reaction product.

Chlorophenol Reactions. Hydroxyl radical attack on the chlorophenol isomers is directed by the position of the hydroxyl group, which is a stronger ortho/para director than chlorine (*22*) (Figure 5). Reactions performed with each of the chlorophenol isomers resulted almost exclusively in products of $OH^{\bullet}$ attack at a position ortho or para to the hydroxyl group. Only one product of $OH^{\bullet}$ attack at a position meta to the hydroxyl group (4-chlororesorcinol) was observed. The formation of nonchlorinated products indicates that the presence of a chlorine group did not prevent $OH^{\bullet}$ attack on the ring. Hydroxyl radical attack did however occur more readily at positions that were not occupied by chlorine groups because dechlorination occurs via a different reaction mechanism, which is probably not as efficient as reactions not resulting in dechlorination.

The visible light absorption and our inability to account for all of the reaction products [also observed by Kunai et al. (*19*)] suggest that some compounds are formed that are not amenable to HPLC analysis. The green color observed during the oxidation of 4-chlorophenol is most likely attributable to the formation of a complex of Fe^{3+} with one of the aromatic oxidation products. This green color was also observed when ferric sulfate and catechol were mixed at concentrations comparable to those observed in our experiments. Furthermore, a variety of other colored complexes have been reported when other disubstituted aromatic compounds were mixed with Fe^{3+} (*23*).

Polymerization Reactions. The broad-band visible light absorption exhibited during the oxidation of chlorobenzene and the chlorophenol isomers, which has been observed previously with benzene and phenol (*8, 19*), is most likely attributable to the formation of phenolic polymers. Formation of phenolic polymers in reactions involving $OH^{\bullet}$ was noted by Stein and Weiss (*24*) and has been implicated in the formation of humic materials (*25–27*). Hydroxychlorobiphenyls have been identified previously during the radical polymerization of 4-chlorophenol initiated by reactions with free chlorine radicals (*25*). The compounds we observed by GC/MS may result from the polymerization of phenoxy radicals or ClHCD radical cations. Alternatively, these compounds may have been produced via a secondary reaction of $OH^{\bullet}$ with the dichlorobiphenyls, as observed in the oxidation of chlorinated biphenyls by Fenton's reagent (*15*). Disappearance of the broad-band absorption and the dimers as the reaction progressed suggests that these polymers and dimers are ultimately amenable to oxidation.

pH Dependence. Optimal product yields (in terms of the amount of chlorobenzene oxidized per mole of H_2O_2 consumed) in the pH range of 2–3 have been reported previously for phenol (*8*). One possible explanation of the pH effect is acid-catalyzed base-catalyzed elimination of water from ClHCD radicals followed by reduction to chlorobenzene (reactions 7 and 8) (*18*). However, this reaction only contributes to a 50% decrease in product yield for oxidation of benzene in the absence of oxygen at pH 1 (*18*). In the presence of oxygen, the reaction should exert even less of an effect because the unimolecular elimination of water is competing with the rapid oxidation of ClHCD by O_2.

Another possible explanation for the pH effect is participation of substrate–Fe–O_2 or substrate–Fe–H_2O_2 complexes in the reaction. Kinetic results from oxidation of diols in the Fenton's reagent system (*28, 29*) and in the presence of Mn^{2+}/O_2 (*30*) do not follow predictions for a radical mechanism, but are better explained by the formation of organometallic ternary complexes. Futhermore, the stability constants for such complexes would likely favor their formation at the pH values where optimal product yields were observed, because ferric complexes with aromatic ligands are most readily formed in the pH range of 2–4 (*31*). Therefore, higher product yields in this pH range could be explained by a reaction involving the organometallic complex where either H_2O_2 is regenerated (for example, proton abstraction from chlorohydroquinone by O_2) or through increased rates of reactions in which H_2O_2 is wasted.

Conclusions

Fenton's reagent can be employed to effectively degrade recalcitrant CAHs such a chlorobenzene and chlorophenol. The most direct mechanism for CAH degradation proceeds through hydroxylation followed by ring cleavage and mineralization. Another possible reaction pathway involves the formation of dimers (such as chlorinated biphenyls and hydroxychlorobiphenyls) and colored aromatic polymers, which are oxidized by subsequent $OH^{\bullet}$ attack.

Complete mineralization of organic compounds was not observed because some of the ring-cleavage products were unable to reduce Fe^{3+}. If necessary, these ring-cleavage products could be futher oxidized by addition of more Fe^{2+}, as demonstrated in the oxidation of phenol with the electrolytic Fenton's reagent system (*8*).

Evaluation of factors affecting the reaction mechanism has also helped to define reaction conditions resulting in the greatest loss of CAHs per mole of H_2O_2 consumed. The presence of oxygen or other strong oxidants favors the more direct oxidation pathway and also follows a stoichiometry in which less H_2O_2 is required to degrade the CAHs. The reaction also follows a pH dependence and is most efficient in the pH range of 2–3.

Registry No. 2,2′-DCB, 13029-08-8; 2,3′-DCB, 25569-80-6; 2,4′-DCB, 34883-43-7; 3,3′-DCB, 2050-67-1; 3,4′-DCB, 2974-90-5; 4,4′-DCB, 2050-68-2; chlorobenzene, 108-90-7; 2-chlorophenol, 95-57-8; chlorobenzoquinone, 695-99-8; hydroxymonochlorobiphenyl, 132178-75-7; hydroxydichlorobiphenyl, 53813-74-4; oxygen,

7782-44-7; 3-chlorophenol, 108-43-0; 4-chlorophenol, 106-48-9.

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Physical Factors Influencing Winter Precipitation Chemistry

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■ Two case studies of winter precipitation events highlight the roles of transport and snow crystal riming (the capture of supercooled cloud droplets by snow crystals) in determining precipitation chemistry. In one case, passage of a cold front leads to a change in the air mass producing precipitation over the monitoring site. A simultaneous decrease in precipitation ion concentrations is observed. Correlations of the ion concentrations with the pseudoequivalent potential temperature, which serves as an air mass identifier, suggest that the decrease in ion concentrations is caused by the air mass change, rather than by washout of aerosols and gases from the atmosphere. In the second case, evidence is presented indicating that an increase in precipitation ion concentrations results from significant capture of polluted cloudwater droplets by the snow crystals. Influences on precipitation chemistry from both processes, transport and riming, can be large. In order to study other processes influencing precipitation chemistry that occur on similar time scales (minutes to hours), such as aerosol and gas scavenging or aqueous-phase oxidation, it is important to evaluate possible confounding effects of transport and riming.

Introduction

The chemical composition of precipitation is determined through the interaction of numerous chemical and physical processes. Some of the more commonly studied of these include nucleation and impaction scavenging of aerosol particles and scavenging of soluble gases within the cloud (*1–4*), below-cloud scavenging of aerosol particles and soluble gases by precipitation particles (*4–8*), and chemical reactions within the aqueous phase (*9, 10*). Our experience in studying aerosol scavenging in winter precipitation systems (*4, 7*) has revealed great variety between individual events. Processes primarily responsible for controlling precipitation chemistry in one case may play a subordinate role in another event. In this paper we will focus on two frequently ignored physical processes that we have observed playing an important role in determining the chemistry of winter precipitation in central Switzerland: an air mass change and the capture of supercooled cloud droplets by snow crystals (riming). Two case studies will be used to illustrate the influence these processes exert on precipitation chemistry.

One of the weaknesses of ground-based precipitation studies is their limited ability to provide information about the temporal evolution of parameters of interest in a moving air mass. Because the air being sampled at a fixed station is changing with time, evaluating processes like aqueous-phase sulfur oxidation or aerosol scavenging can be greatly complicated by a change in background conditions that occurs on a similar time scale. This situation may be particularly problematic during frontal passage (*4*,

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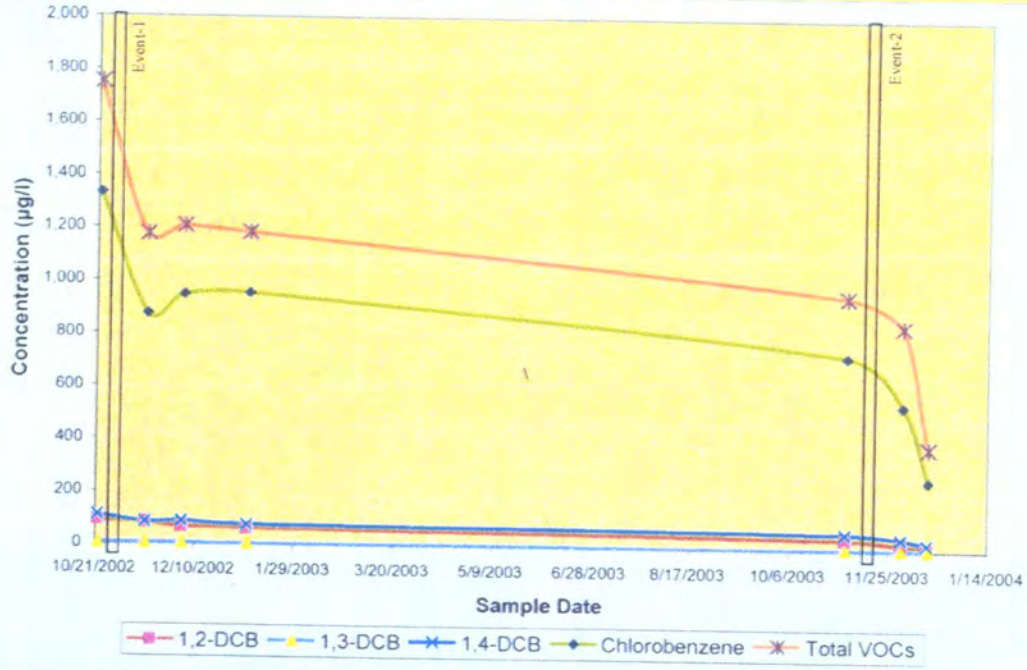
Baseline vs Post-Treatment VOC Concentrations
Former DOD Facility, New York

VOC Results (µg/l)



Date	1,2-DCB	1,3-DCB	1,4-DCB	Chloro-benzene	Total VOCs	% VOC Reduction	% Chlorobenzene Reduction
10/22/2002	94.2	5.8	111.9	1333.8	1753.1	-	-
11/15/2002	85.2	5.5	84.6	875.0	1177.2	33%	34%
12/4/2002	68.8	5.4	89.2	948.2	1207.7	31%	29%
1/6/2003	64.9	4.7	77.6	954.2	1184.4	32%	28%
11/4/2003	41.4	3.7	62.5	729.8	955.0	46%	45%
12/2/2003	22.2	2.7	45.2	545.7	845.2	52%	59%
12/15/2003	11.7	1.5	25.9	263.5	389.2	78%	80%

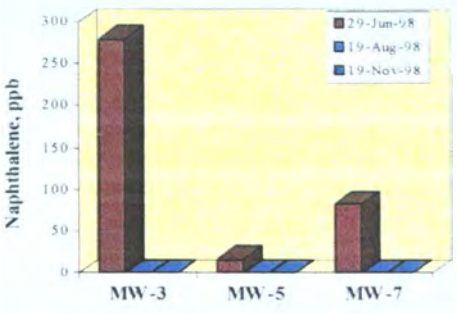
Pilot Study Event-I injections were performed in October 2002 and Event-II injections were performed in Nov-03

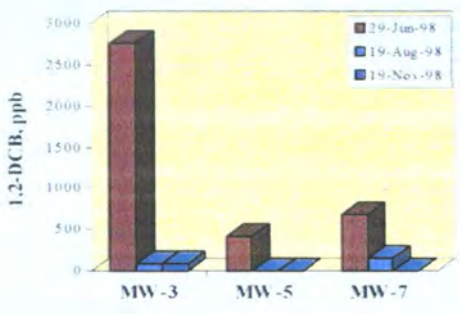
Quarry Facility

SITE LOCATION:	Sussex County, New Jersey
CONTAMINATION:	1,4-Dichlorobenzene (341 ppb); 1,2-Dichlorobenzene (2,760 ppb); Naphthalene (279 ppb)
GEOLOGY:	Fractured bedrock underlying glacial overburden of 9-20 ft thick; water table is at approximately 20-25 ft bgs within the bedrock.
AREA TREATED:	Approximately 1200 sq. ft at an interval between 20-65 ft bgs.
EFFECTIVENESS:	Site-wide groundwater contamination reduced by 98%. All COCs were treated to ND or well below NJDEP groundwater criteria.

The subject site is an active quarry facility with supplementary operations including an asphalt plant, a concrete plant, and a truck maintenance garage. The site is underlain by a glacial overburden (9 to 20 feet in thickness), and by fractured bedrock beneath the overburden containing the water table. The contamination originated from a former dry well outside the truck maintenance garage. Contaminated soil from the source area was initially excavated and natural attenuation with quarterly groundwater monitoring has been ongoing since 1992. The principal contaminants of concern were **1,4-Dichlorobenzene, 1,2-Dichlorobenzene,** and **Naphthalene**. The regulatory agency requested active remediation due to consistent groundwater contamination noted since 1992.

- An ISOTEC **laboratory study** was initially completed noting a 94% destruction of total volatile organic compounds (VOCs) found in the groundwater sample.
- **The field pilot program** was initiated in July, 1998. Results indicated approximately **97% to 100%** destruction of contaminants of concern in the groundwater plume in less than **three** months. ISOTEC's treatment during the field pilot program resulted in decreasing total site wide groundwater concentrations of **1,2-Dichlorobenzene from 3,847 ppb to 74 ppb, 1,4-Dichlorobenzene from 489 ppb to 10 ppb, and Naphthalene from 379 ppb to ND** (see figures below).
- ISOTEC is recommending site closure based on the treatment program results, which remained significantly below the applicable regulatory criteria. Approximately **$500,000.00** had been spent by the Quarry facility in monitoring costs alone since 1992. In comparison, the **ISOTEC treatment was performed for a cost of less than $100,000.00.**





NOTE:
(1) NJDEP groundwater quality criteria. 1,4-Dichlorobenzene = 75 ppb; 1,2-Dichlorobenzene = 600 ppb, and naphthalene = 300 ppb.

In-Situ Oxidative Technologies, Inc.

51 Everett Drive, Suite A-10
West Windsor, New Jersey 08550
Phone: (609) 275-8500 Fax: (609) 275-9608

5200 DTC Parkway, Suite 150
Englewood, Colorado 80111
Phone: (303) 843-9079 Fax: (303) 843-9094

Three Full-scale DNAPL Removal Projects - Was It Worth It?

Dean Williamson and Paul Favara,
CH2M HILL

Barbara Nwokike/US NAVY, Southdiv

CH2MHILL

Sites to be Discussed

- Electrical Resistance Heating for PCE Removal at a Dry Cleaner, Charleston Naval Complex
- In-situ Chemical Oxidation Using Fenton's Reagent for a Dichlorobenzene Site, Charleston Naval Complex
- In-situ Chemical Oxidation Using Fenton's Reagent for a TCE site, Naval Training Center Orlando

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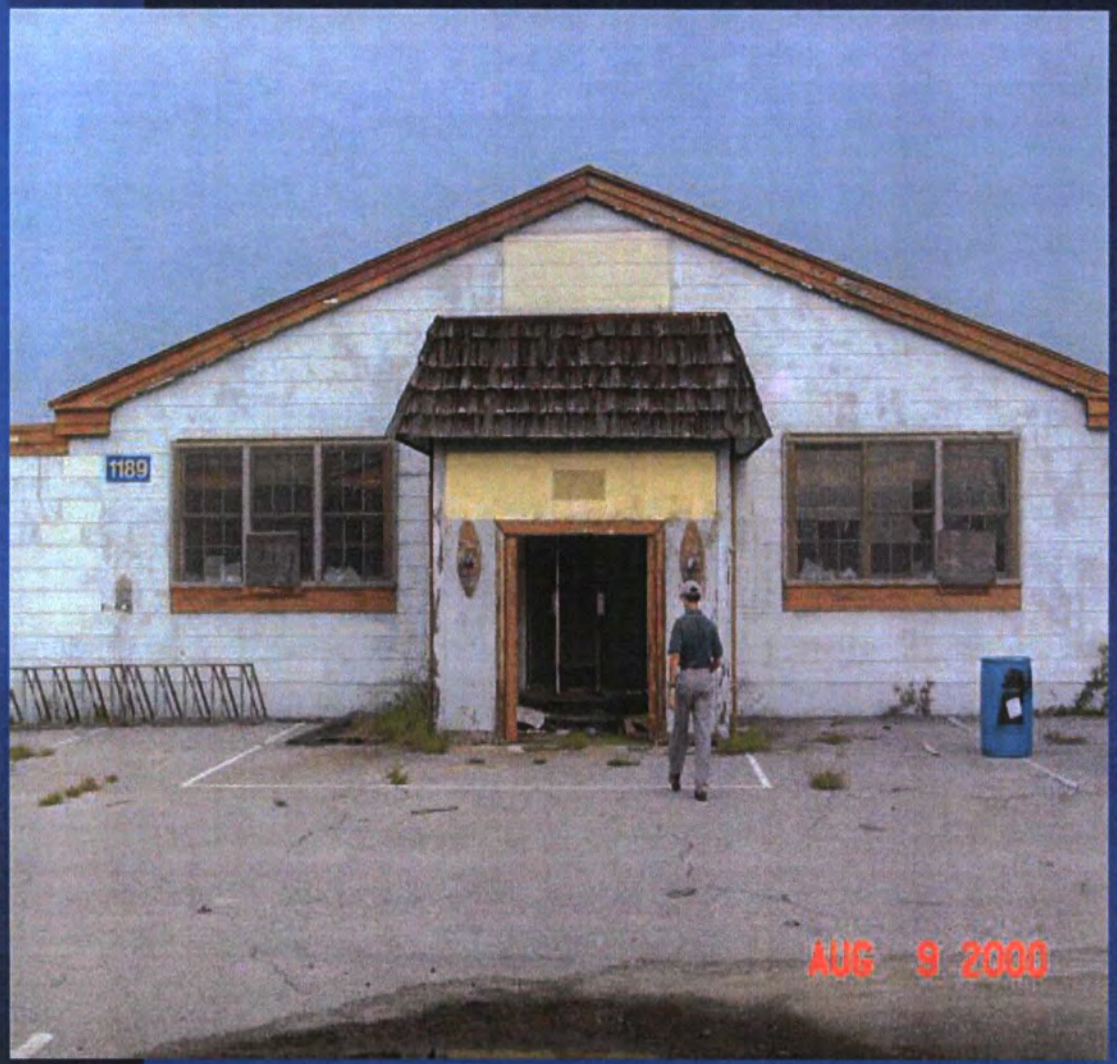
AOC 607 - A Former Dry Cleaner Impacted by PCE



- Dry cleaner operated from 1942 to 1995
- PCE in groundwater above 26,000 ug/L
- Groundwater contaminated primarily from 5 to 12 ft bgs
- Clay aquitard at ~ 11 to 12 ft
- Site groundwater hydraulically influenced by sanitary sewer
- IM goal was PCE DNAPL mass removal and 95% reduction of dissolved phase

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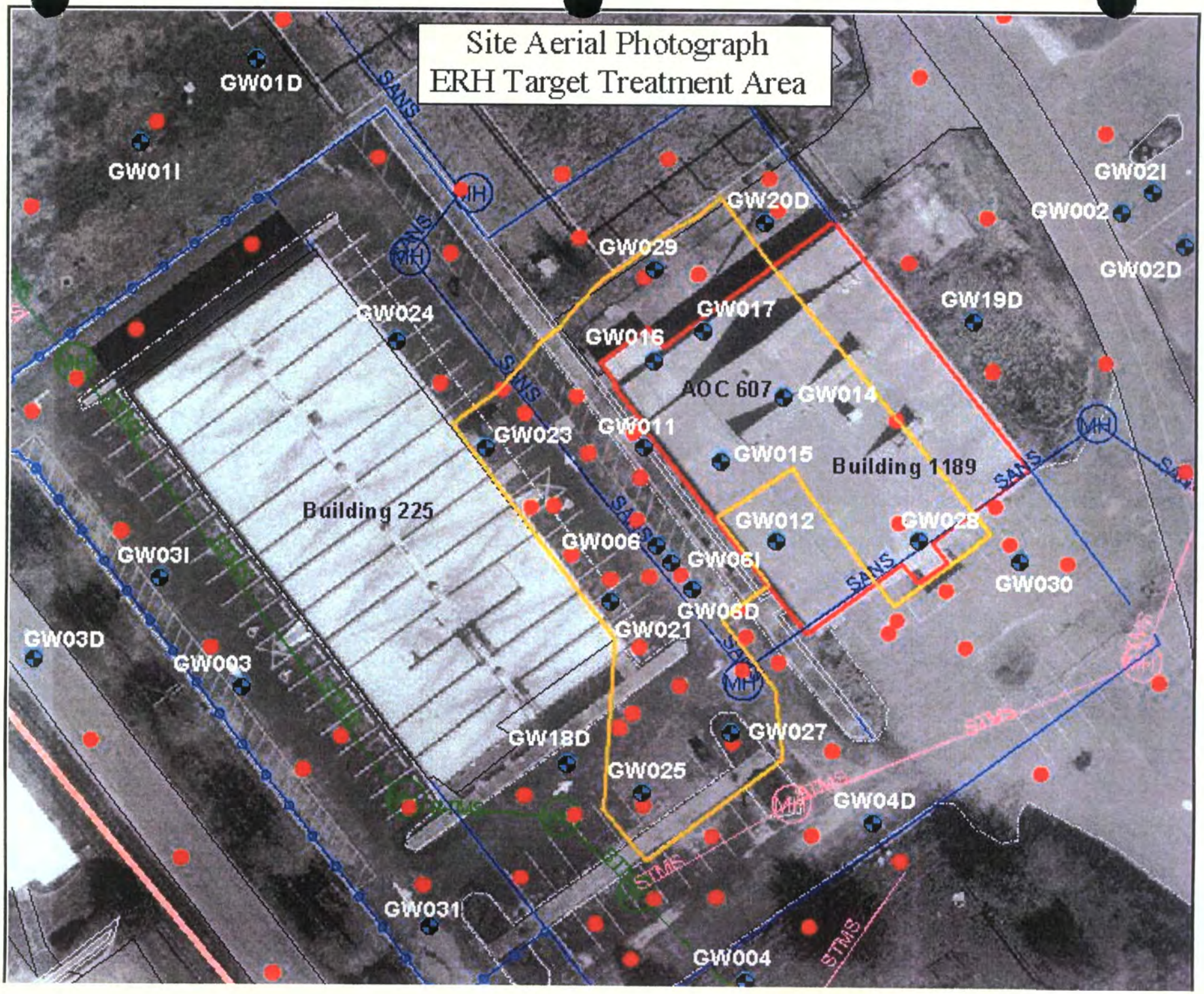
Site Aerial Photograph
ERH Target Treatment Area
GW01D
GW01I
GW02I
GW002
GW02D
GW20D
GW029
GW019D
GW017
GW016
GW024
AOC 607
GW014
GW023
GW011
GW015
Building 1189
Building 225
GW012
GW028
GW006
GW031
GW030
GW03I
GW03D
GW003
GW021
GW027
GW18D
GW025
GW04D
GW031
GW004
SANS
STMS
MH

Overview of ERH IM at AOC 607

- Thermal Remediation Services, Inc. - ERH Subcontractor - Design, Construction, and O&M
- Target Treatment Area (TTA)
  CVOC Concentrations > 2,000 μg/L Footprint ~ 16,525 ft^2
- Treatment Interval From Groundwater Table to 12 ft bls
- Start-Up - October 2001
- Anticipated System Operation of 124 Days
- 97 Electrodes; Two 500 KVA Power Control Units

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ERH Electrode Field at AOC 607

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ERH Results at Shutdown

- 279 Days of Operation (October 2001 to July 2002)
- Maintained Boiling Temperature of PCE at 7 ft bls (89°C) for 77 Days and at 11 ft bls (92°C) for 23 Days
- 5 of 12 Monitoring Wells - Total CVOC Reduced > 88 %
- 247 Pounds of CVOCs and 234 Pounds of PCE Recovered
- 21 Percent Reduction in Total CVOCs (dissolved) in the TTA; 65 Percent PCE Reduction (dissolved) in the TTA
- CVOC Rebound in Half of the Monitoring Wells - January 2003

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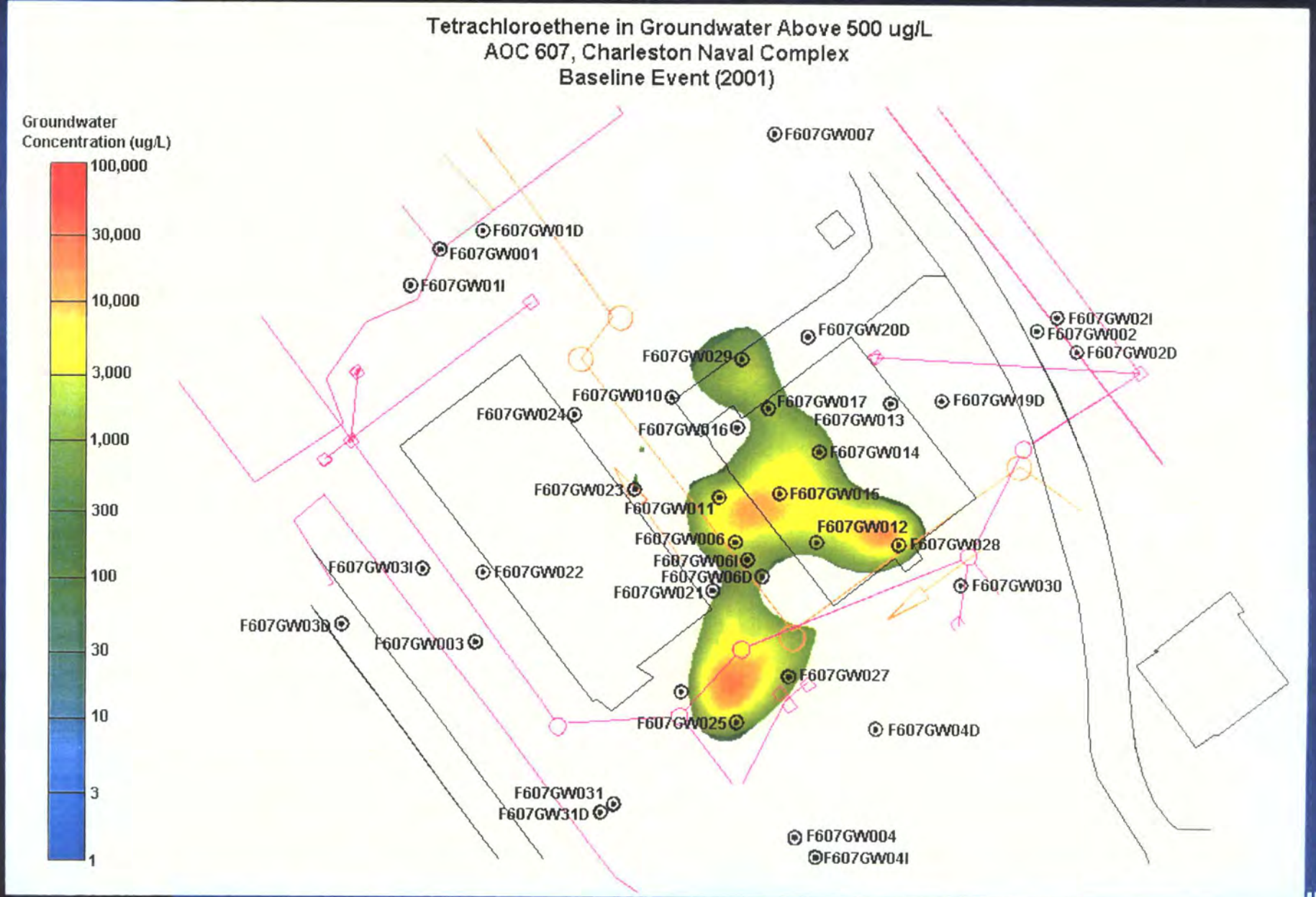
Baseline PCE > 500 ug/L at AOC 607



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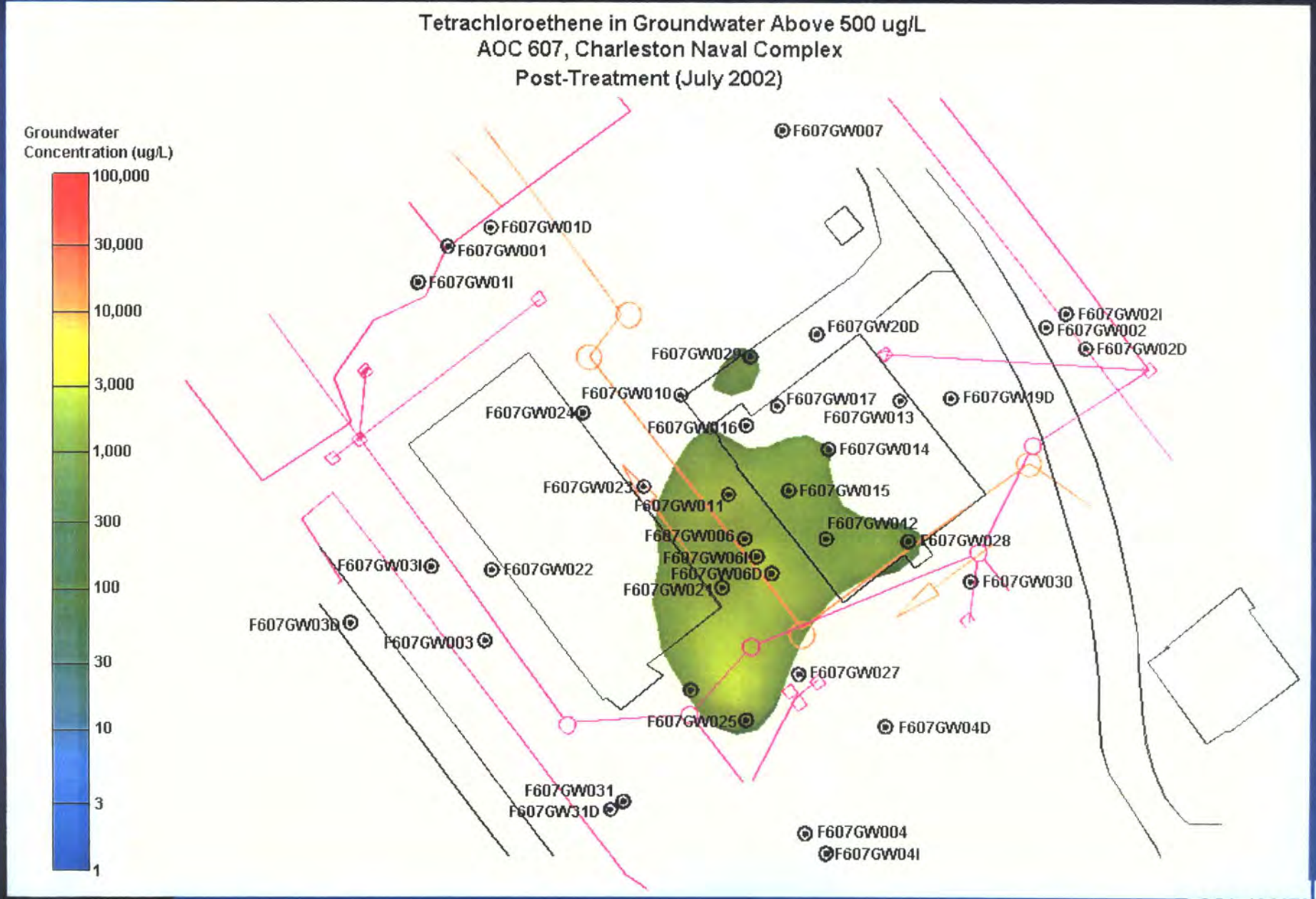
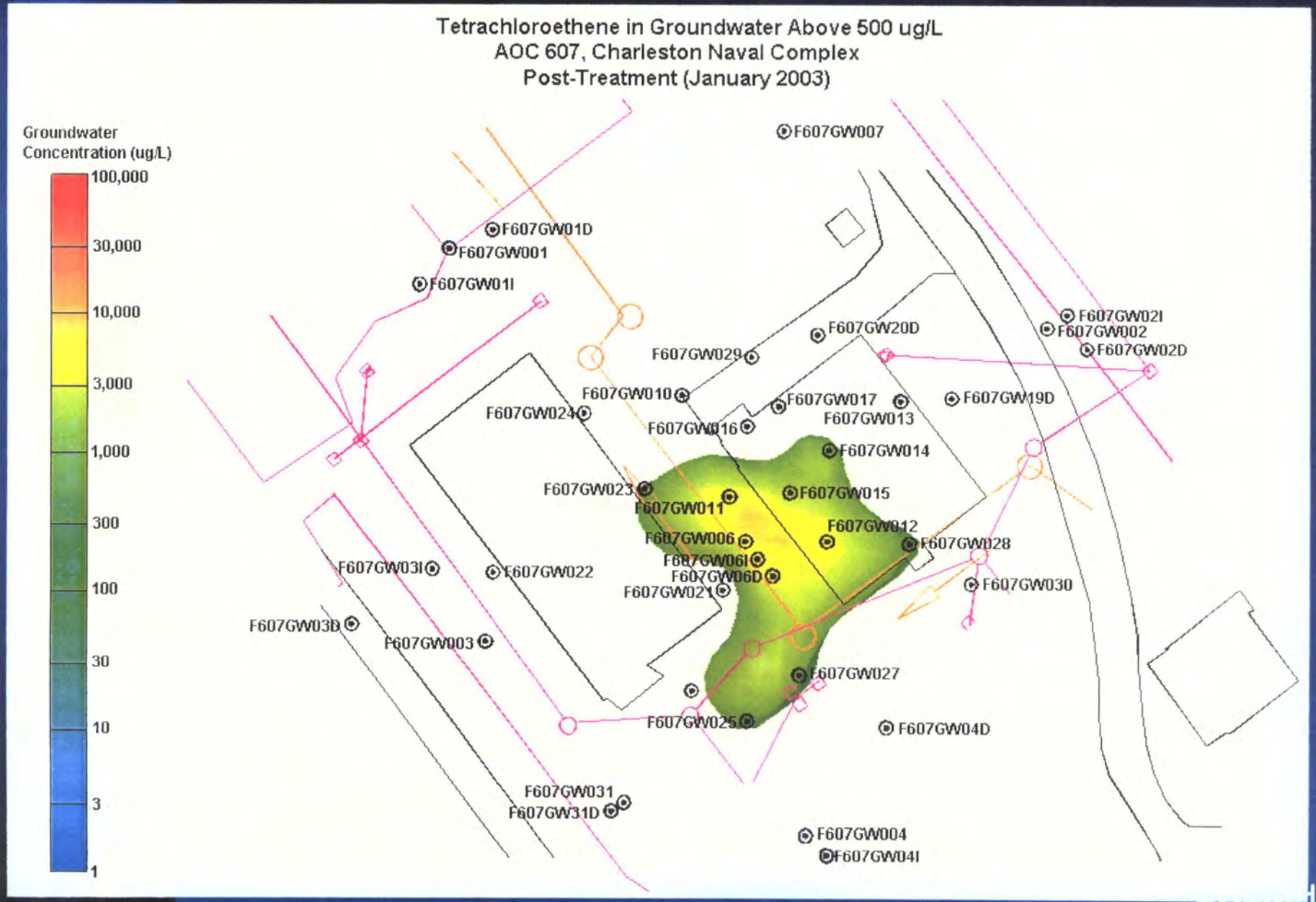
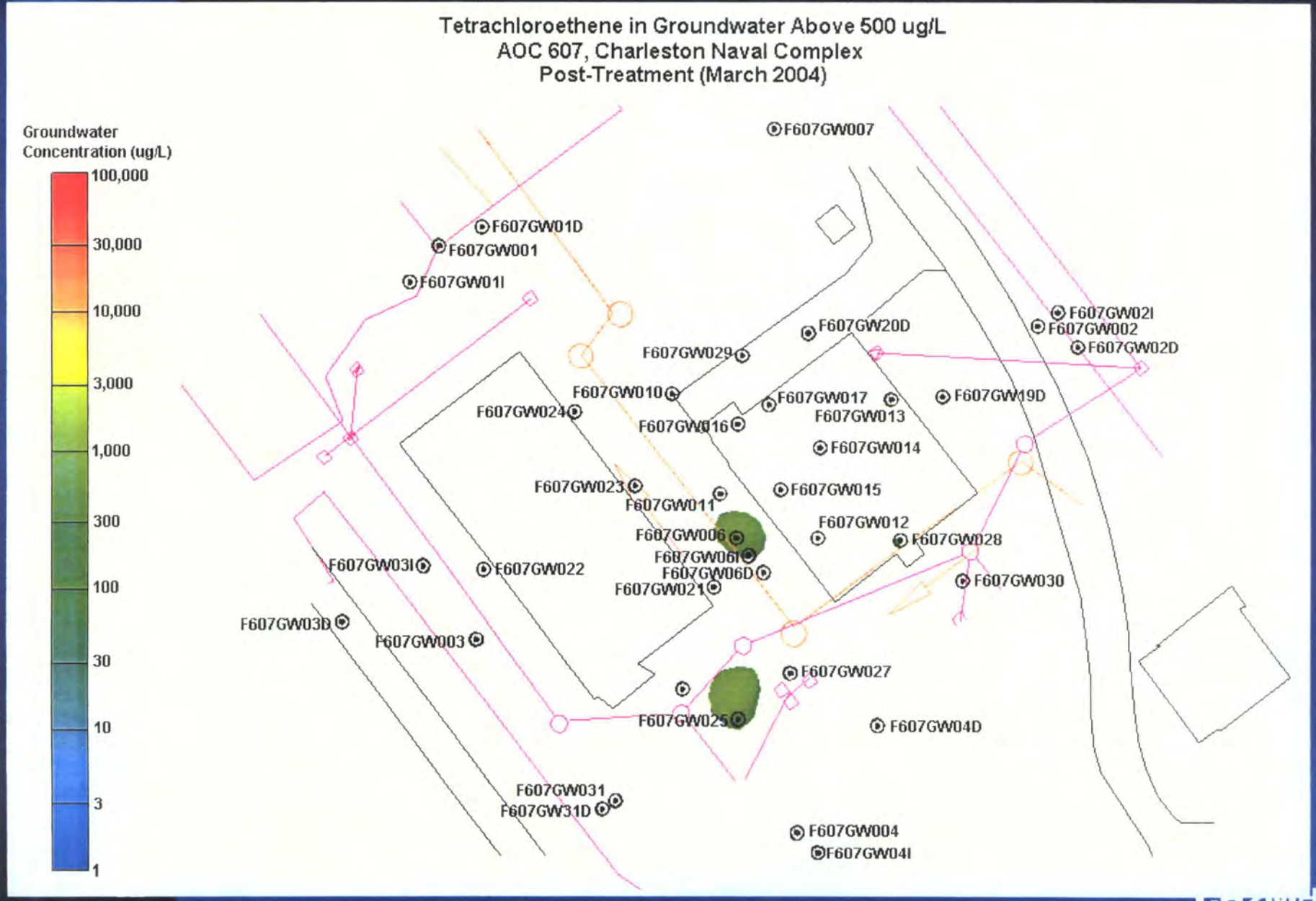
July 2002 PCE > 500 ug/L



January 2003 PCE > 500 ug/L



March 2004 PCE > 500 ug/L



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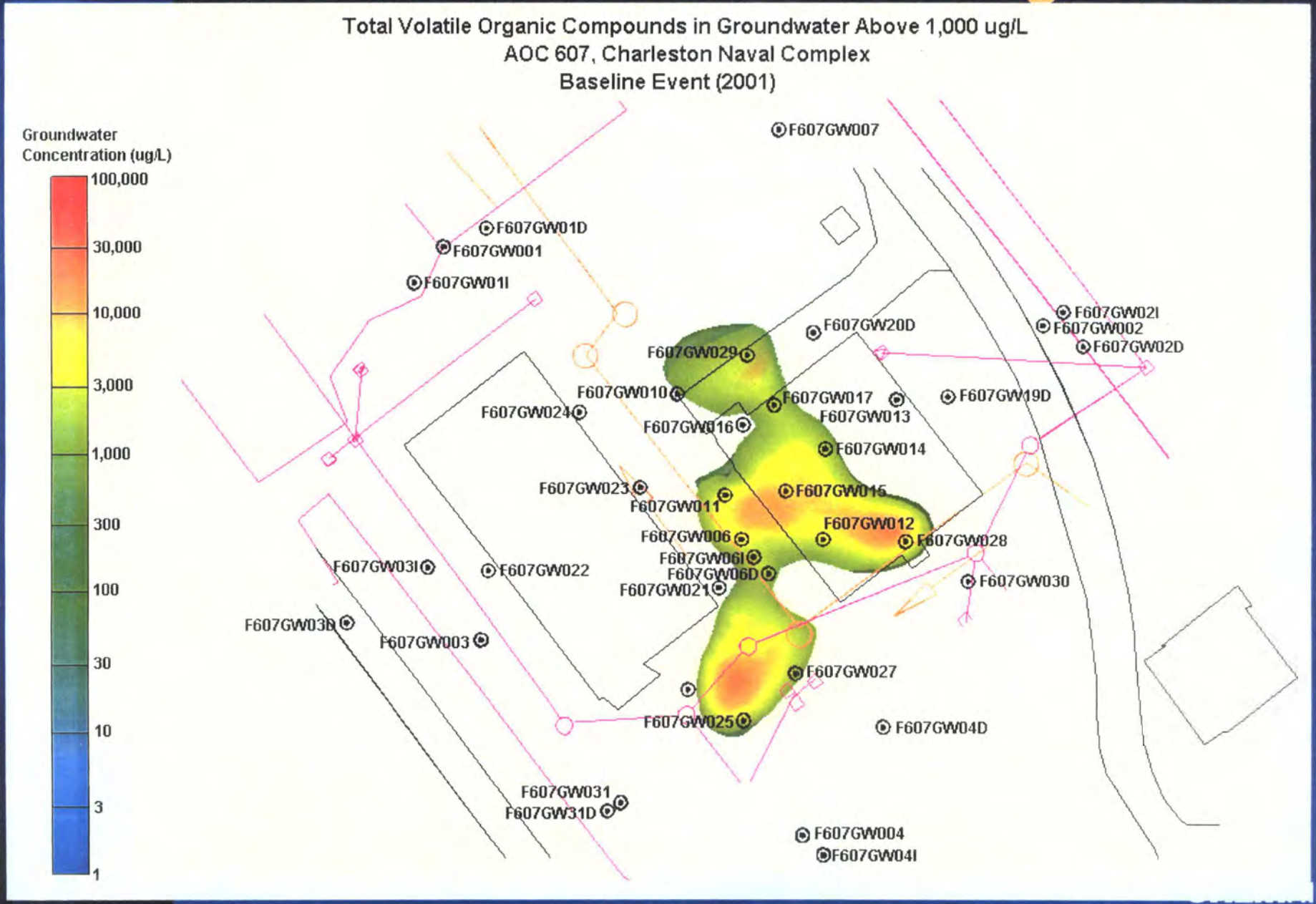
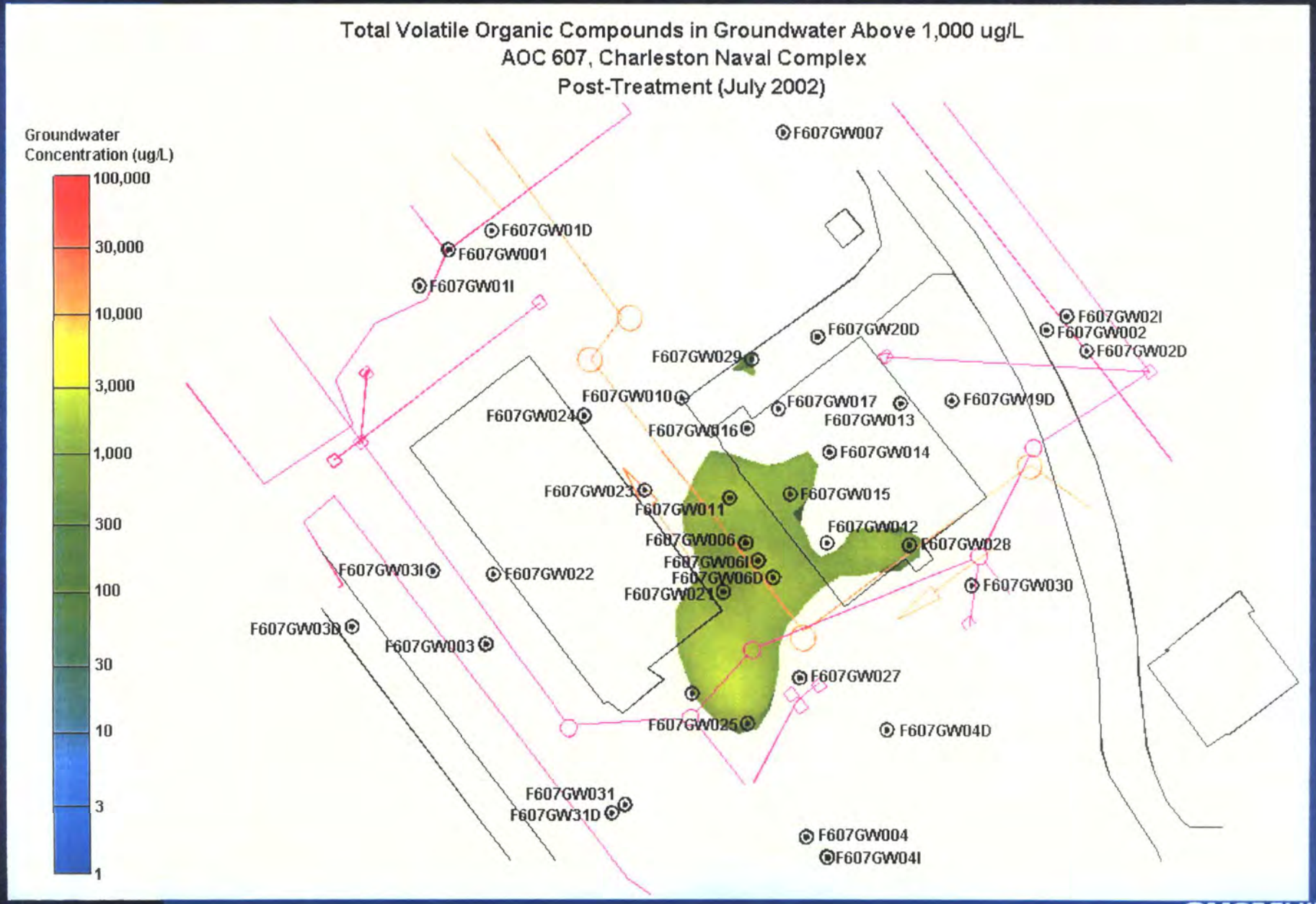
Baseline CVOC Plume > 1000 ug/L 2001



July 2002 CVOC Plume > 1000 ug/L



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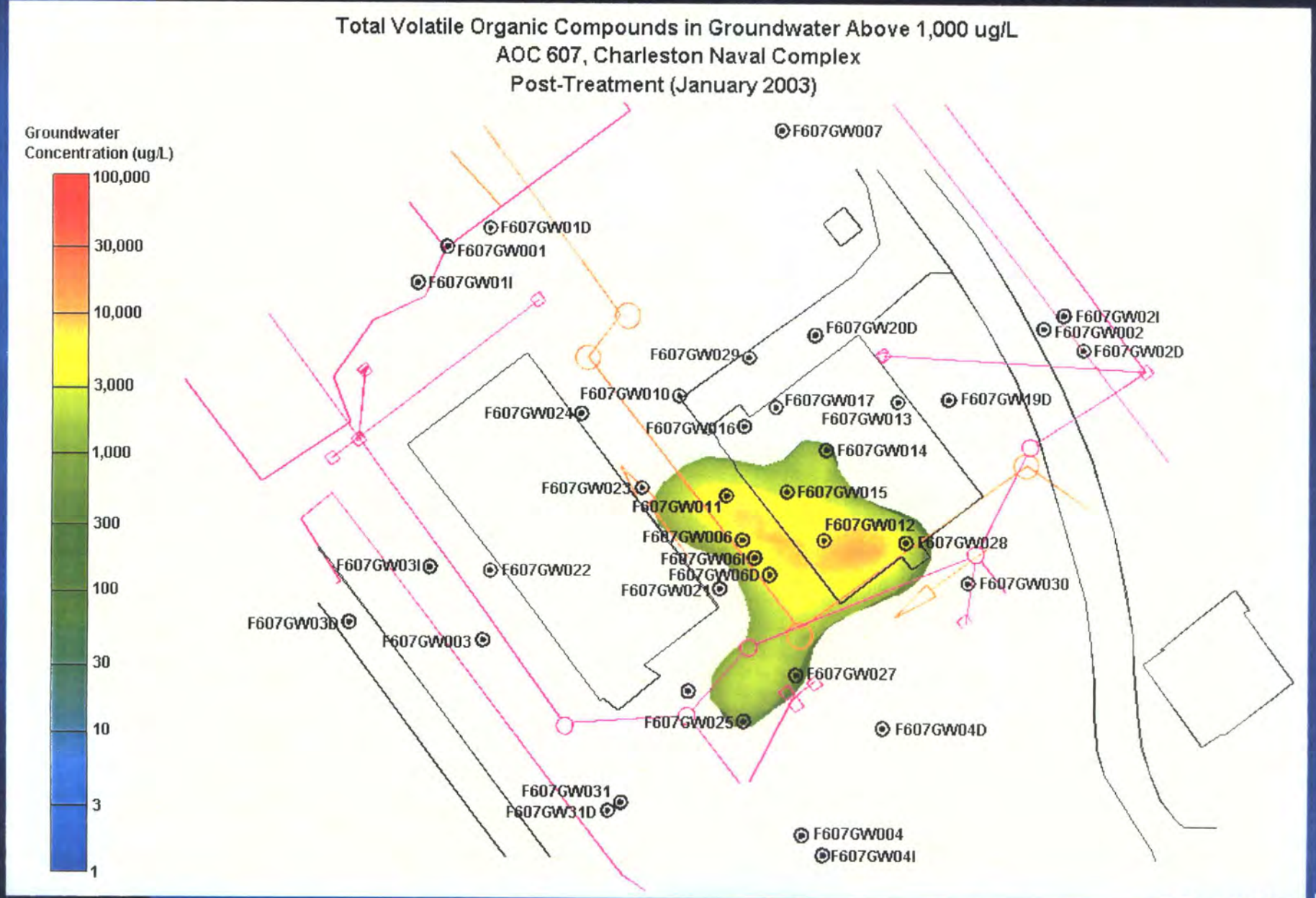
January 2003 CVOC Plume > 1000 ug/L



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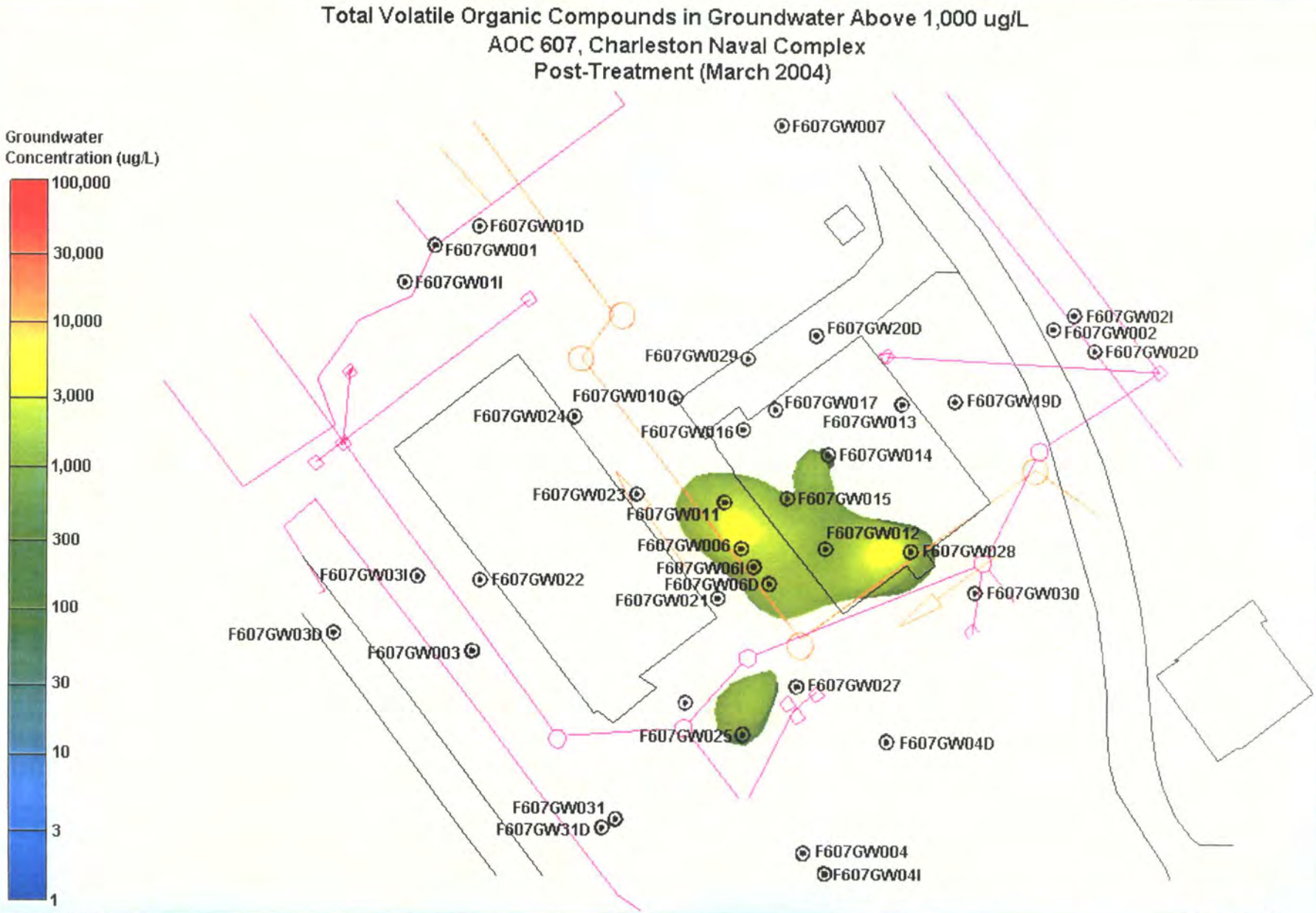
March 2004 CVOC Plume > 1000 ug/L



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Changes in VOC Concentrations After ERH; Well F607GW011, Charleston Naval Complex

	Prior to ERH (ug/L) 7/2001	After ERH (ug/L) 3/2004	% change
PCE	5600	283	-95%
TCE	430	520	+20
Cis-DCE	440	1060	+140
VC	<250	6.3	
Total VOC	6470	1066	-83%

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ERH Results at AOC 607

- 247 Pounds of CVOCs and 234 Pounds of PCE Recovered During ERH Operation
- 94% reduction in dissolved phase PCE, 66% reduction of total dissolved CVOC
- Greater proportions of TCE, DCE, and VC now compared to PCE that prior to ERH
- Dehalococcoides genetic material detected in site groundwater using 16S RNA PCR
- Pilot biostimulation currently underway using potassium lactate

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SWMU 196 - A Site Impacted with Chlorobenzene and Dichlorobenzenes

Chlorobenzene and Dichlorobenzenes greater than 10,000 ppb, from unknown source

Groundwater contaminated from 5 to 15 ft bgs

Marsh clay aquitard at 15 ft

Shipyard Creek immediately adjacent to site and required monitoring to evaluate potential for mobilization of contaminants

Goal was 90% reduction of dissolved phase

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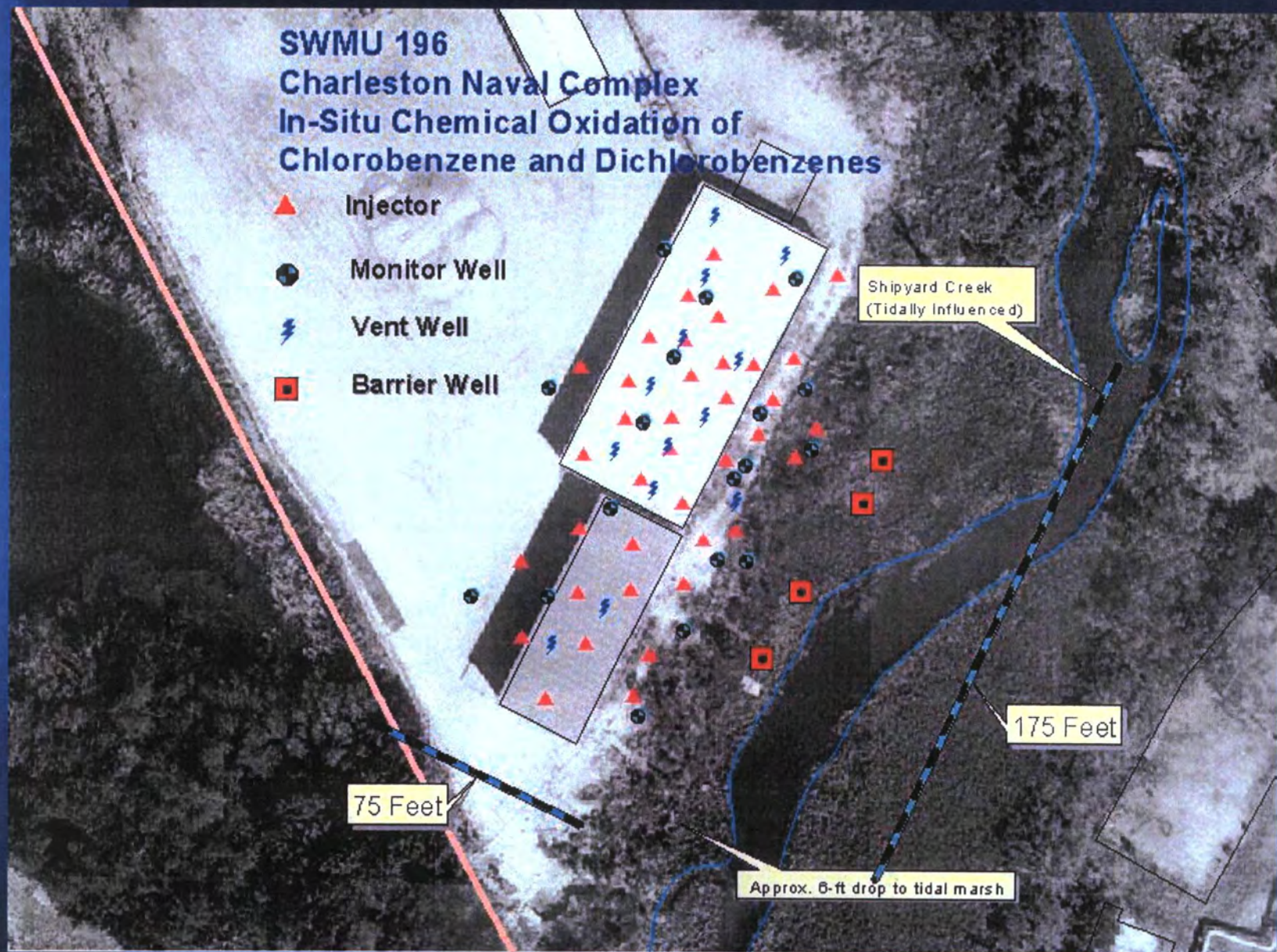
ISCO Applied Via Closely Spaced Injectors



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ISCO Using Fenton's Reagent Was Implemented in 3 Phases

- Phase 1 - Nov 2001; 11 injectors at 2 elevations with 3 ft screens, 32,600 lbs of 50% H_2O_2 injected
  - minimal change in dissolved phase concentration noted
- Phase 2 - Mar 2002; 28 additional injectors, 50,000 lbs of 50%H_2O_2 injected
  - 56 % reduction in dissolved phase concentration noted
- Phase 3 - Jul 2002; 6 additional injectors, 31,000 lbs of H_2O_2 injected
  - 82 % reduction in dissolved phase concentration noted in Sept 2002
  - But only 54 % reduction noted in December 2002

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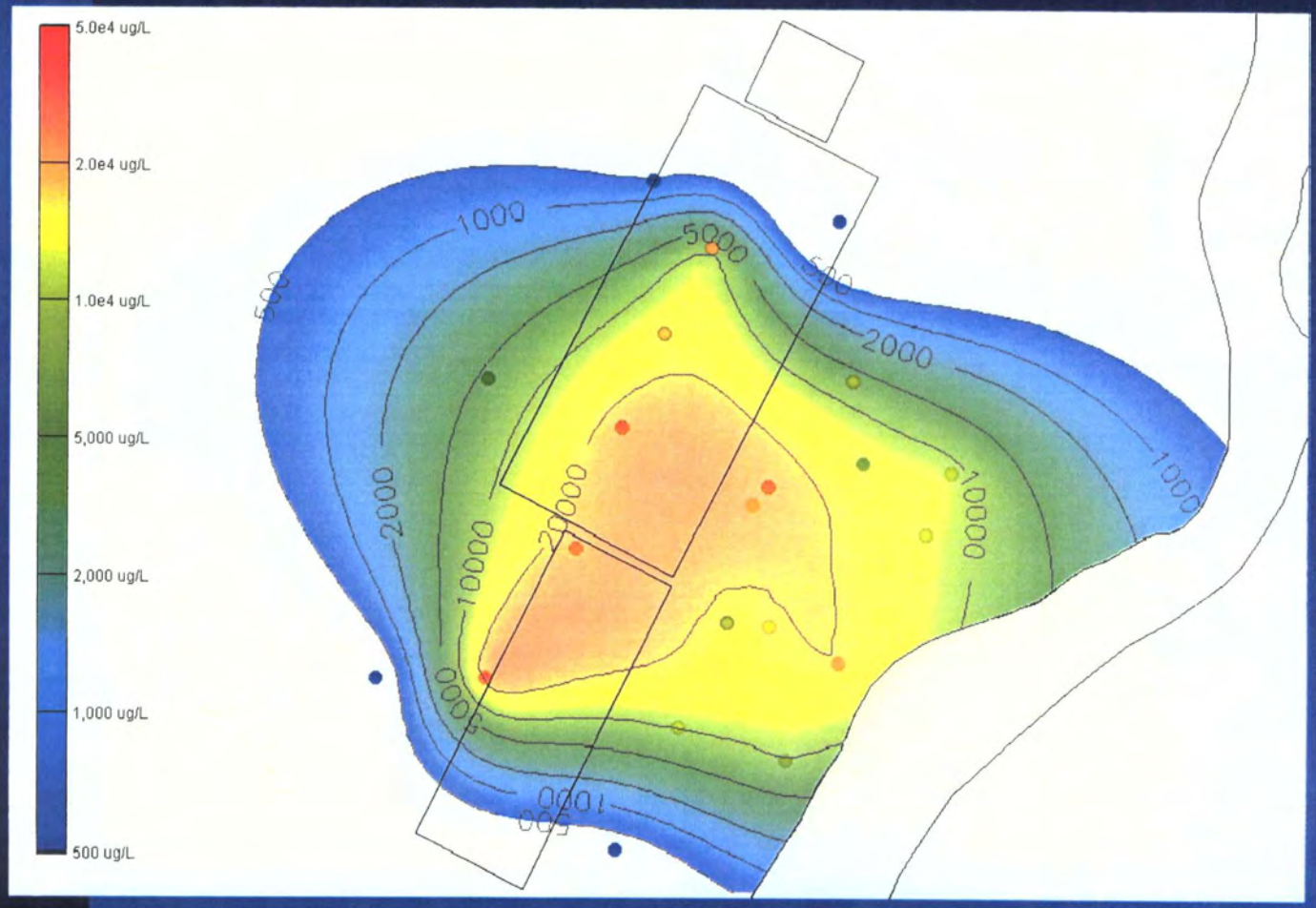
Total Chlorobenzenes - March 2002



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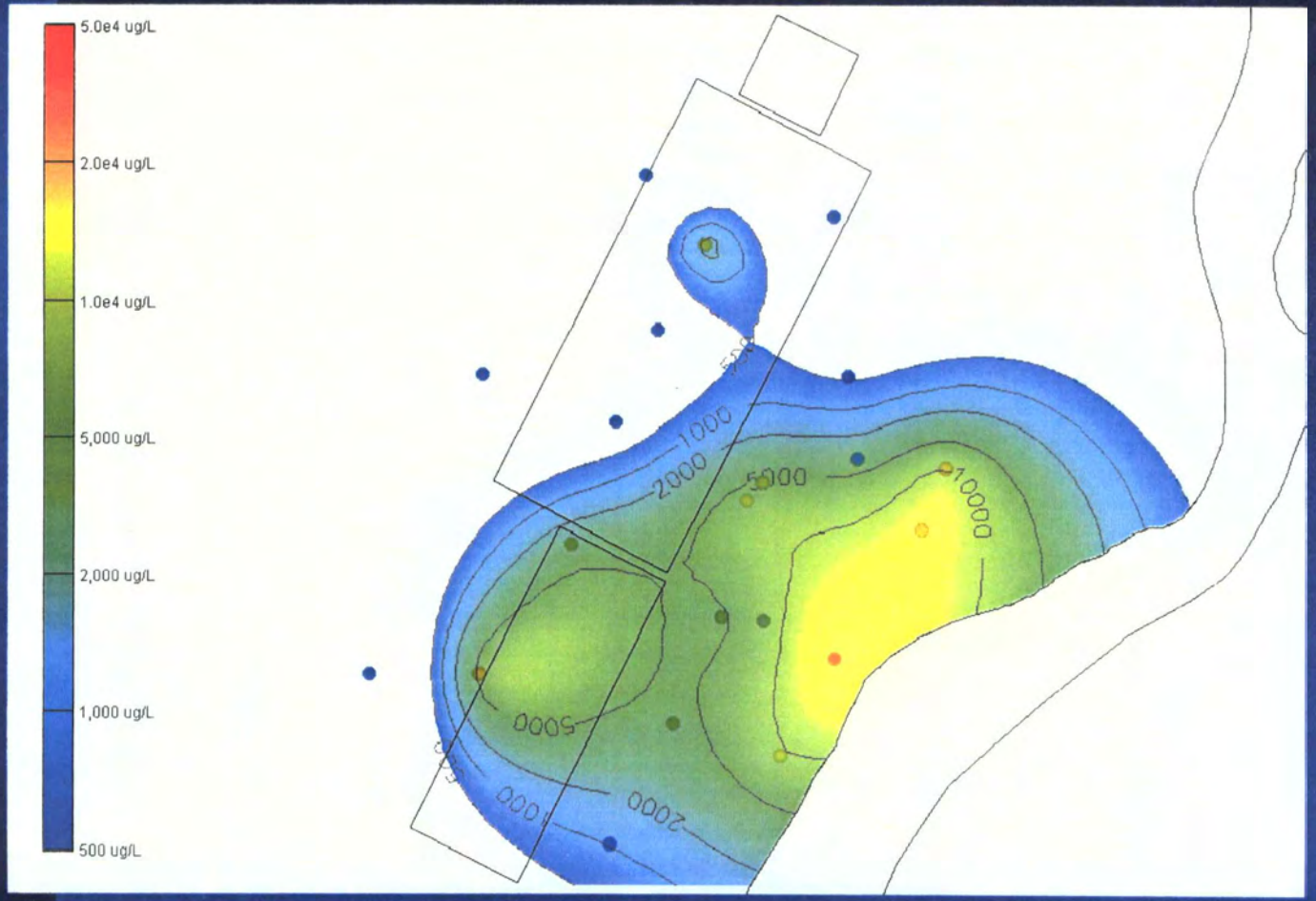
Total Chlorobenzenes - Sept 2002



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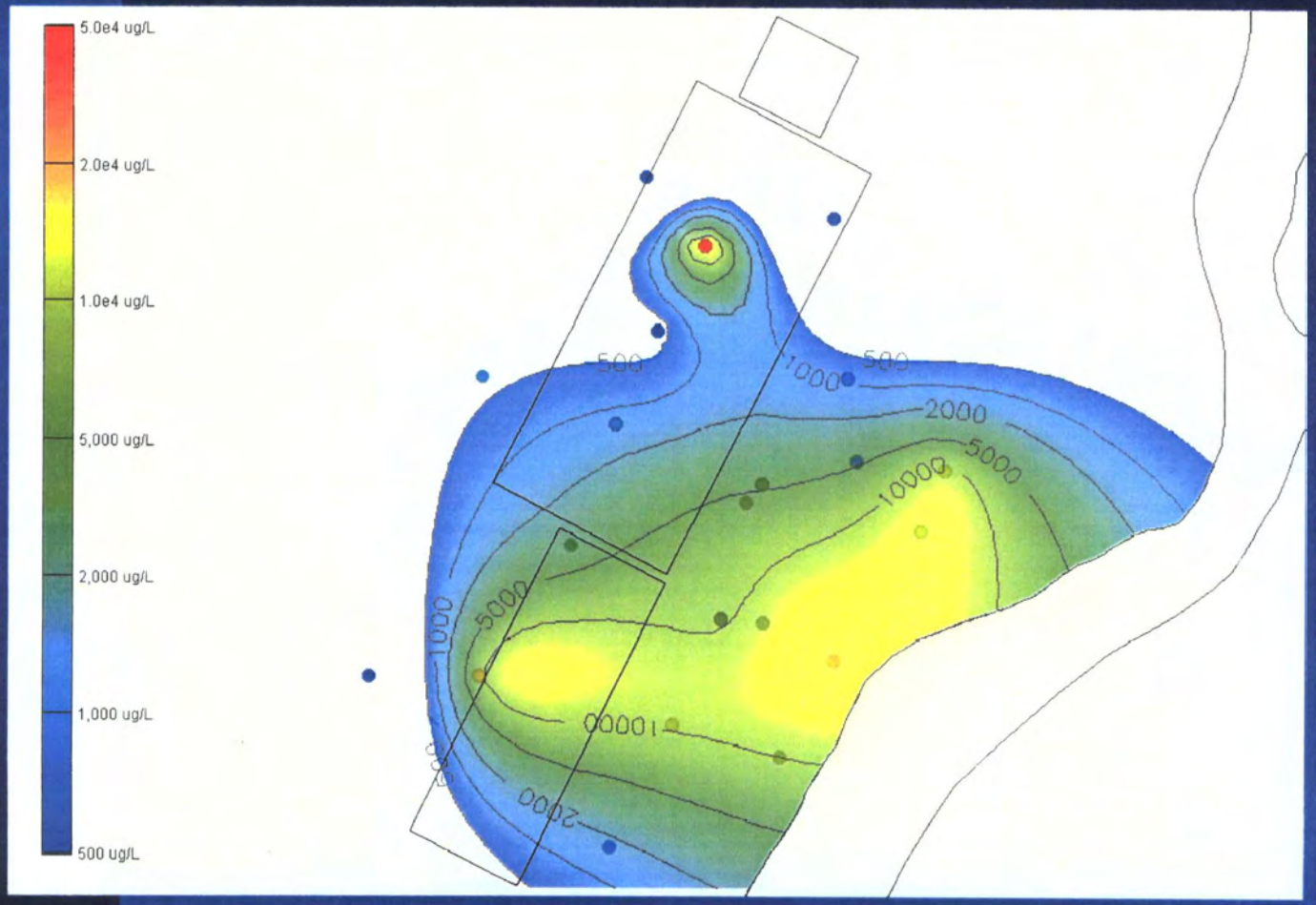
Total Chlorobenzenes - Dec 2002



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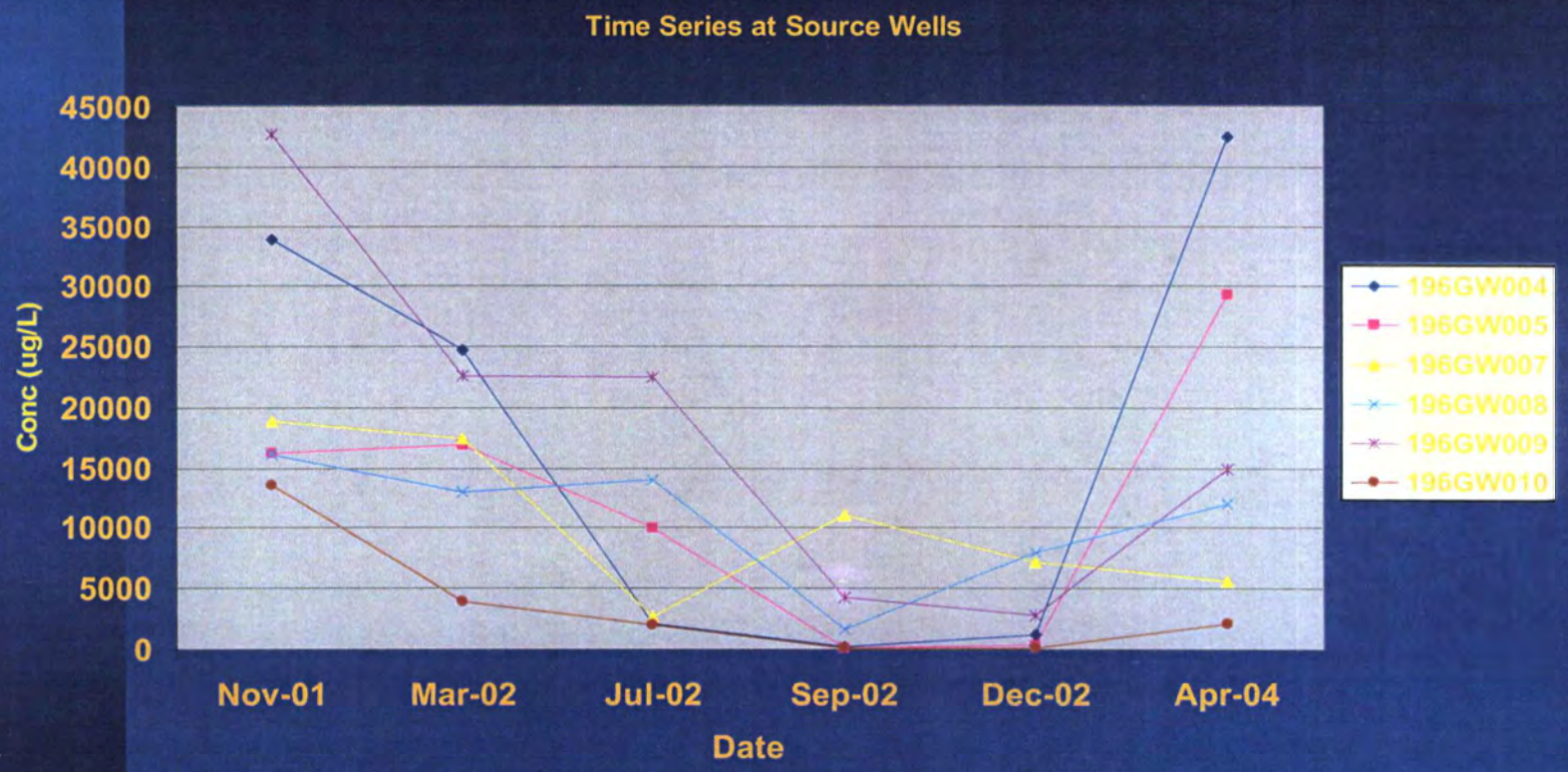
Response of Multiple Wells in Source Area Over Time Shows Some Rebound



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Conclusions for SWMU 196

- ISCO was effective in partial mass reduction, though expectations were not achieved
- Treatment was aggressive but could not prevent rebound in some source area wells
- Downgradient wells that have not exhibited rebound to-date may show an increase in concentrations as source area GW moves towards them
- Additional treatment (aerobic biostimulation) in process of being implemented.

SA17 - NTC Orlando

- 9-acre site formerly served as Defense Property Disposal Office (DPDO)
- High concentrations of TCE and daughter products in soil and groundwater
- Depth To GW about 5 ft bls
- Aquifer consists of interbedded sands and clays
- Most Contamination located between 10 and 40 ft bls

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SA 17 Site Cross Section

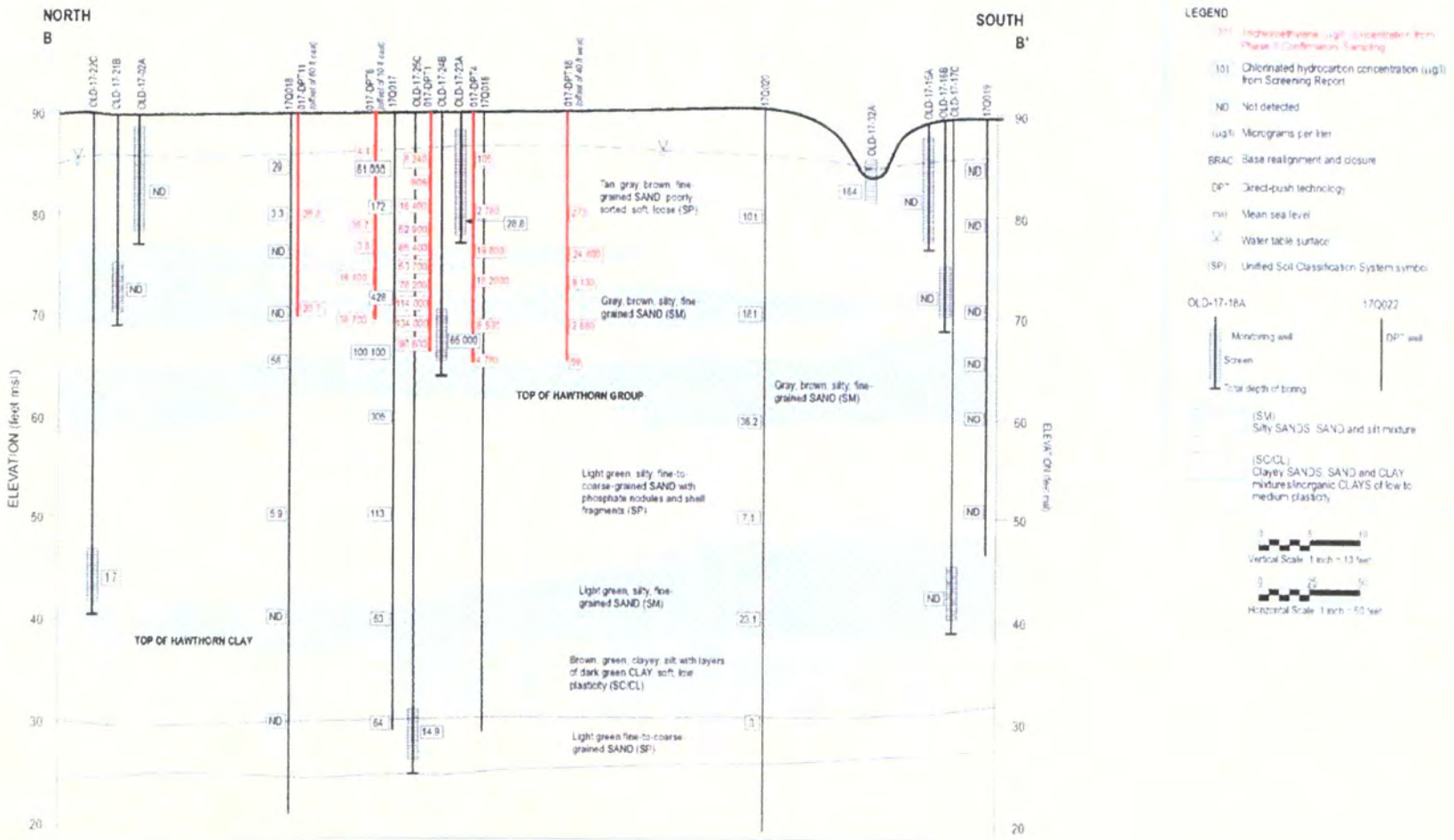

FIGURE 1-2
Lithologic Cross Section
Studay Area 17, Naval Training Center
Orlando, Florida

Overview of ISCO Treatment and Sampling at SA17

- Injection Events
  - Nov '00 and Jan '01 as Phase 1 (shallow)
  - Mar 2002 - Focus on Deeper Zone
  - Aug 2002
  - Sep 2002
- Sampling Events
  - Base Line
  - Post-Phase 1
  - Mar '02
  - Apr '02
  - Jul '02
  - Oct '02
  - Jan '03
  - Jun '03

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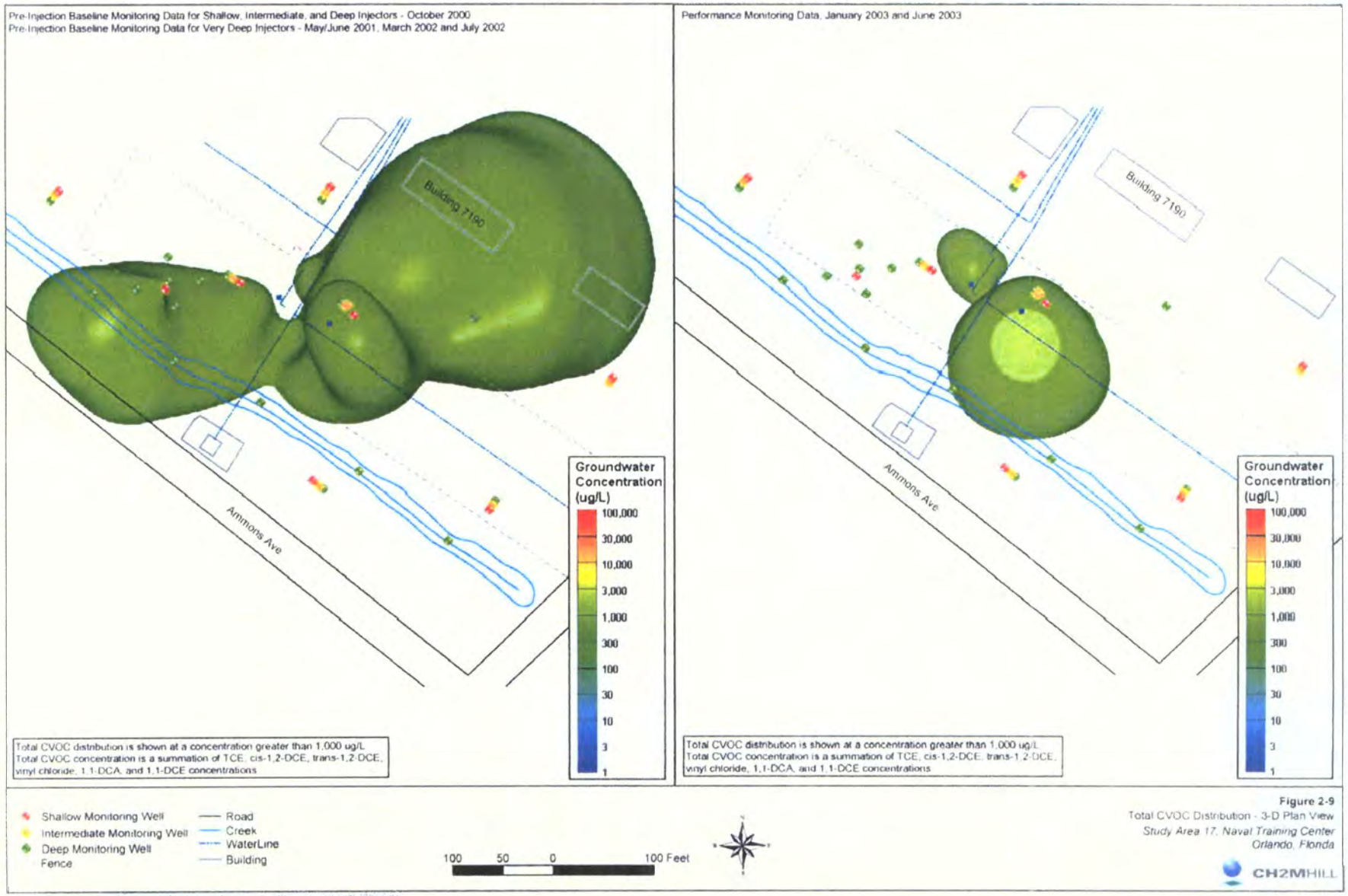
CVOCs > 1000 ug/L Before and After ISCO at SA 17



Recent Source Area Delineation Efforts

- 45 MIP Locations to focus on specific areas and provide additional information on lithology
- Seven groundwater borings - four to five groundwater samples per boring
- 10 soil borings - five soil samples per boring

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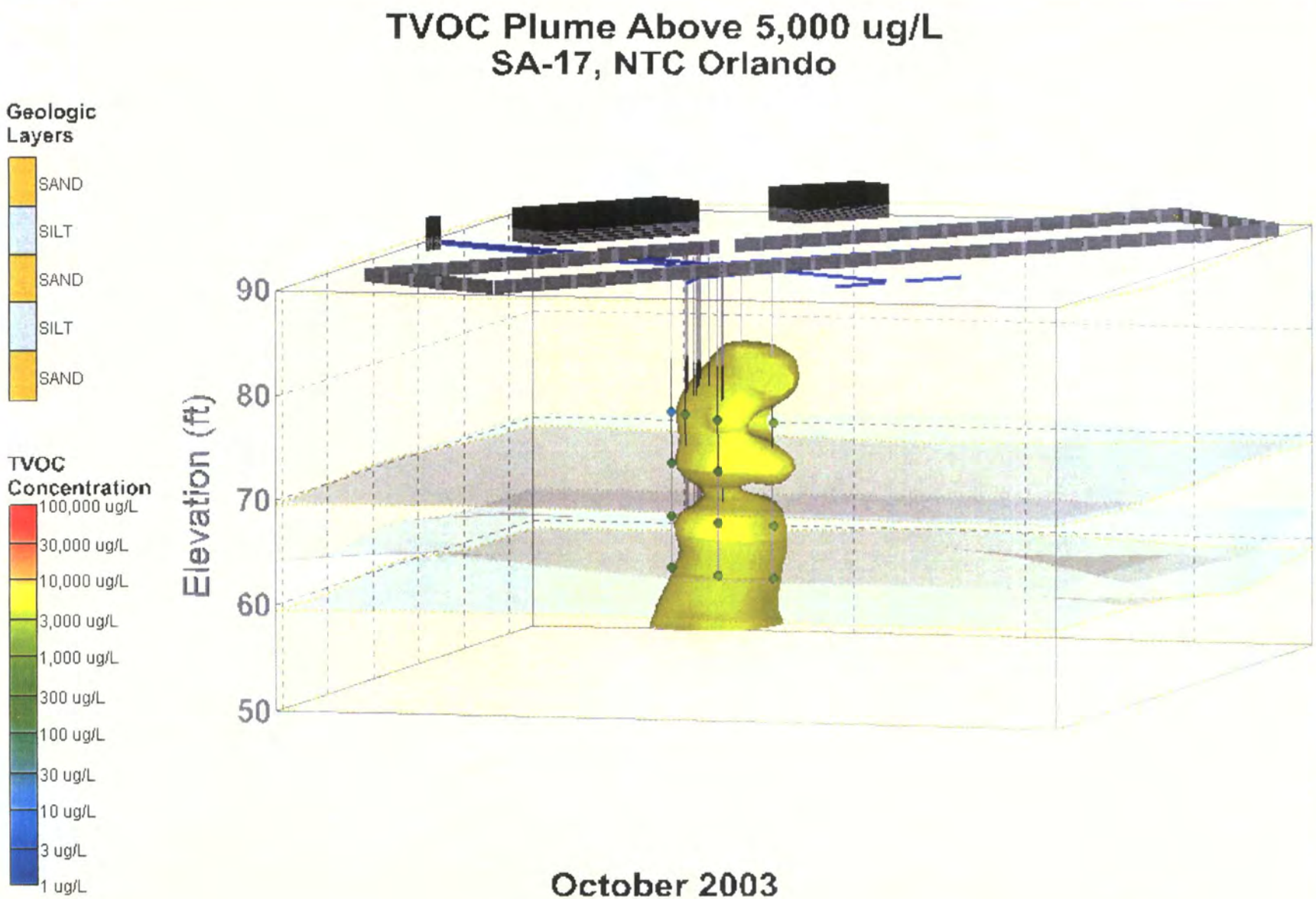
Source area still remains at SA 17



ISCO Assessment at SA 17

- Partial mass removal accomplished
- Dissolved phase plume TCE concentrations reduced by 88 percent
- ISOC unable to treat some portions of source area
  - reasons include lack of hydraulic connection, preferential flow paths
- Residual source area continues to release TCE to groundwater

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Current Status for SA 17

- Diffuse portion of plume treated to levels that allows MNA
- Defined source area exists in tighter soils at several discrete depths
- Alternate source area actions (e.g., excavation, other chemical type treatment) being evaluated

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Conclusions for Three Sites - Was it Worth It?

- ERH at AOC 607 - Probably Worth It
  - latest results are promising, may allow for site closure within foreseeable future (10 - 15 years?)
  - Relatively expensive IM (>$1MM)
- ISCO at SWMU 196 - Maybe/Maybe Not
  - Partial mass removal but substantial source area and plume remain
  - May have reduced ultimate source lifetime somewhat
- ISCO at SA 17 - Probably Worth It
  - Plume size reduction and partial mass removal achieved but substantial source area remains
  - May have reduced ultimate source lifetime somewhat

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AEROBIC BIOREMEDIATION TREATABILITY STUDIES

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Variability of biological degradation of aromatic hydrocarbons in an aerobic aquifer determined by laboratory batch experiments

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ABSTRACT

The biological aerobic degradation of 7 aromatic hydrocarbons (benzene, toluene, *o*-xylene, *p*-dichlorobenzene, *o*-dichlorobenzene, naphthalene and biphenyl) was studied for 149 days in replicate laboratory batch experiments with groundwater and sediment from 8 localities representing a 15 m × 30 m section of an aerobic aquifer. Compared to biologically deactivated control experiments all compounds were biologically degraded. Degradation curves were very reproducible for some compounds (benzene, toluene, *o*-xylene, *o*-dichlorobenzene and *p*-dichlorobenzene) and less reproducible for other (naphthalene and biphenyl). Based on observed length of lag phases, length of the degradation periods and percent degradation, the variation among the 8 localities appears to be modest. However, detailed examination of the degradation rates revealed statistically significant variation among localities for benzene, toluene, naphthalene and biphenyl, but not for *o*-xylene, *o*-dichlorobenzene and *p*-dichlorobenzene. The maximum variation in degradation rates was 15 times in the case of biphenyl. Significant co-variation in degradation rates was found between benzene and toluene, and between *p*- and *o*-dichlorobenzene.

INTRODUCTION

During recent years comprehensive research has been performed on the biological degradation of specific organic compounds in aquifers (e.g., Ghiorse and Wilson, 1988; van Beelen, 1990). Most of the reported investigations have focused on biological degradation under aerobic conditions and have, in most cases, involved laboratory batch experiments with groundwater and/or sediment from actual aquifers. In general, the reported investigations show that many organic compounds can be degraded in aerobic aquifers, but

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hardly any investigations have addressed the variability of the biological degradation within the aquifer. How different would the results have been if the groundwater and/or aquifer sediment for the experiment had been obtained, within the same aquifer, a few meters away from the actual sampling point?

The usefulness of evaluating biological degradation in an aerobic aquifer on the basis of laboratory experiments involving one or two groundwater and/or sediment samples of the entire aquifer seems dubious in view of the emerging documentation of small-scale heterogeneities of aquifers with respect to hydrogeology (Sudicky, 1986; Bjerg et al., 1992), hydrogeochemistry (Pedersen et al., 1991; Bjerg and Christensen, 1992) and microbiology (Albrechtsen and Winding, 1992). The realized hydrogeological, hydrogeochemical and microbial variations could support variations in degradation of organic compounds due to variations in transport and availability of bacteria, substrate, nutrients and electron acceptors.

The purpose of this study is to investigate the variability in biological degradation of 7 aromatic compounds in laboratory batch experiments representing 8 localities within a small section (15 m × 30 m) of an aerobic aquifer. Each locality is represented by duplicate experiments in order to sort out experimental uncertainty and variations of the aquifer with respect to degradation. The question on how well laboratory batch experiments represent the actual degradation processes in the aquifer is not specifically addressed in this study, but the study used a laboratory batch experimental method, involving a combination of groundwater and the fine particles of the aquifer sediment, that previously has been reported to resemble actual conditions in the aquifer fairly well. Holm et al. (1992) compared in situ methods and laboratory methods (full sediment and groundwater, fine sediment particles and groundwater, and groundwater only) for the same aquifer as used in this study and found that the laboratory batch experiments with fine aquifer particles and groundwater gave little experimental uncertainty and results comparable to results obtained in in situ microcosms as described by Nielsen et al. (1992). The importance of the fine particles is probably related to the fact that the majority of the bacterial biomass in aquifers is associated with the silt and clay fraction of the sediment. Albrechtsen (1994) showed for the actual aquifer that 80–95% of the bacteria were associated with the fine fraction of this aquifer sediment (< 55 μm).

MATERIALS AND METHODS

Description of the aquifer

The study was performed with sediment and groundwater from a shallow,

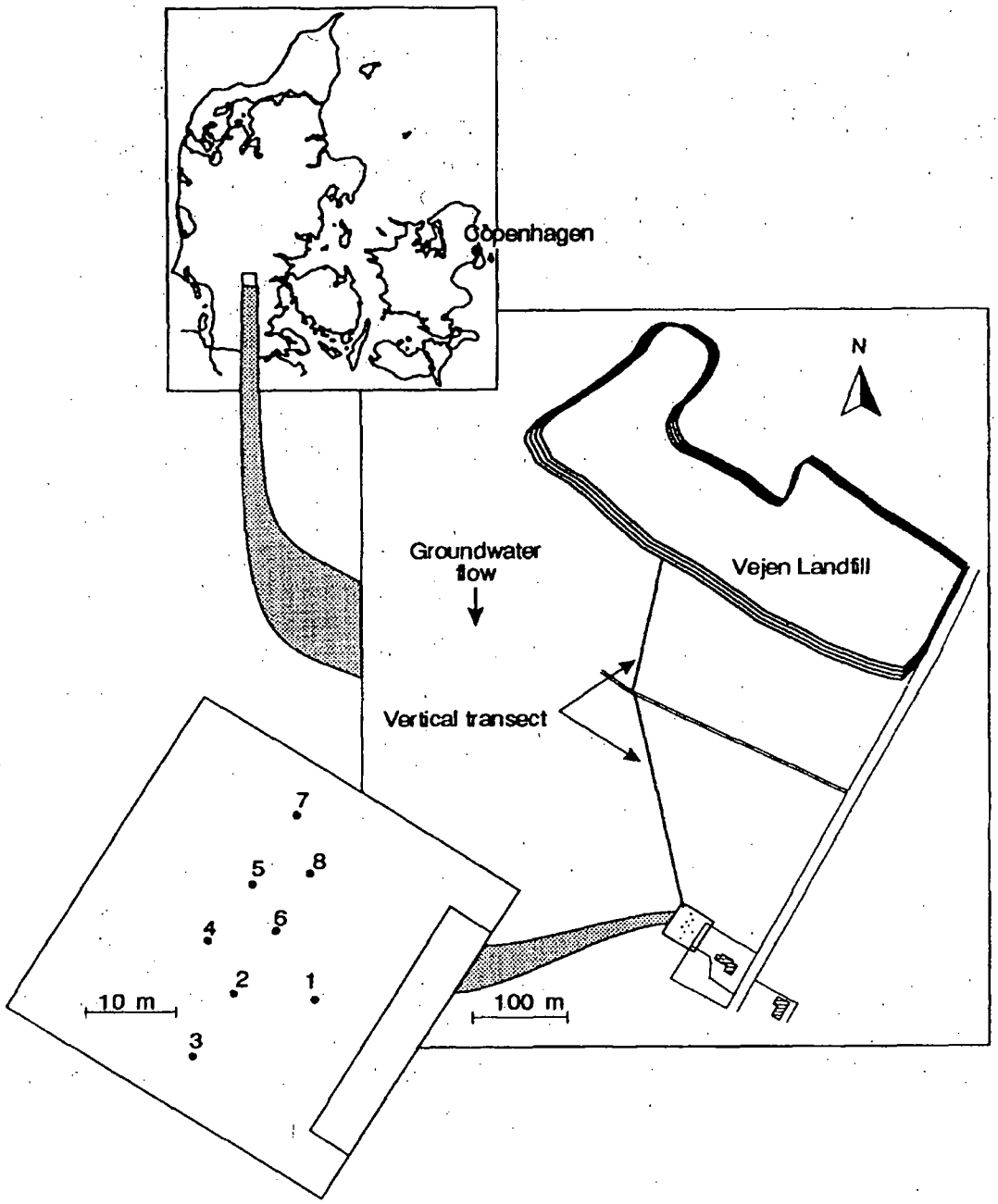

Fig. 1. Geographical location of Vejen in Denmark and location of the sampling points in the aerobic aquifer.

unconfined, glaciofluvial sandy aquifer 1 km north of Vejen City in Jutland, Denmark (Fig. 1). The thickness of the aquifer is ~ 10 m and the water table is located 3–5 m below the ground surface. The bottom of the upper aquifer consists of strata of clay and silt. The annual precipitation in the area is ~ 700–900 mm and the groundwater pore flow velocity is on the order of

150–200 m yr^{-1}. The hydrogeochemistry and the hydrogeology of the aquifer are described in detail by Bjerg and Christensen (1992) and Bjerg et al. (1992), respectively. The studied part of the aquifer is influenced by farming activity, resulting in increased concentrations of NO_3^- and K^+ in the groundwater (Pedersen et al., 1991). The Vejen Landfill is located ~ 400 m upgradient of the study area, but does not significantly affect this part of the aquifer, which is fully aerobic (Lyngkilde and Christensen, 1992a, b).

Field sampling

Location. Groundwater and sediment samples were taken at the same depth (1.5–2 m) below the groundwater table from the aerobic aquifer in 8 localities, within an area of 15 m × 30 m, as shown in Fig. 1.

Groundwater sampling. One-inch (2.54 cm) iron pipes equipped with an iron tip, a 10-cm screen and a Teflon® check valve were driven into the ground by a Cobra® jackhammer. A 10-mm-I.D. Teflon® tube was lowered into the iron pipe, and groundwater was pressed through the Teflon® tube to the ground surface by nitrogen pressure, for further details consult Lyngkilde and Christensen (1992a). The well was developed by discarding 10 borehole volumes of water before groundwater sampling. Groundwater samples were stored at 10°C in brown 2.5-L glass bottles with plastic caps. Bottles and caps were washed in acid and consecutively dry-sterilized and autoclaved. Groundwater samples were collected to measure concentrations of organic and inorganic compounds and to provide water for the microcosms.

Sediment sampling. After groundwater sampling, the iron pipe was removed, and a sediment sample was collected in the same point as the groundwater sample. Sediment samples were collected by manual equipment (Eikelkamp®) in a 10-cm-cased borehole with a stainless-steel bailer. Sediment samples were stored at 10°C in 2.5-L polyethylene buckets for 1 week. Samples were collected for characterization of the 8 localities and for providing sediment for the microcosms.

Preparation, loading and sampling of microcosms

The laboratory batch microcosms were made in 2.5-L glass bottles equipped with a glass valve used in sampling (Fig. 2). Groundwater was saturated with O_2 by bubbling atmospheric air through a diffuser for ~ 1 h in order to ensure aerobic conditions throughout the experimental period. A suspension of sediment and groundwater was made by mixing 1 kg of wet sediment with 1 L of groundwater in a dry-sterilized 5-L bottle. After 1 min of

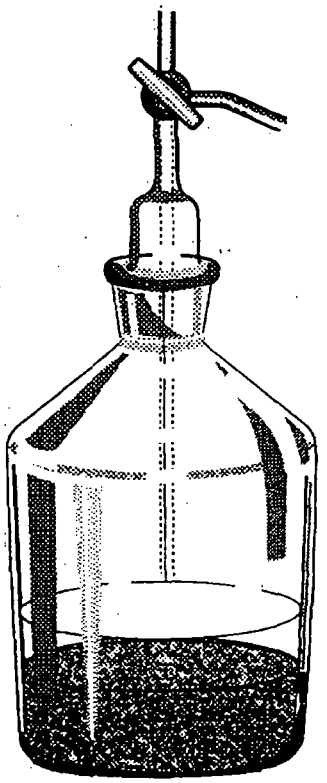

Fig. 2. Laboratory batch microcosm. Glass bottle of 2.5 L closed by a glass stopper equipped with a glass tube. Fine sediment particles from 1 kg of groundwater sediment and 1 L of groundwater is supplied to the bottle for the laboratory degradation experiments.

sedimentation, groundwater and suspended clay and silt particles were transferred to the microcosm bottle. Again 1 L of groundwater was mixed with the sediment in the 5-L bottle and the procedure was repeated to yield a microcosm containing ~ 5 g of clay and silt and 2 L of groundwater. This procedure was previously used by Holm et al. (1992). After preparation of the microcosm, a mixture of specific organic contaminants dissolved in water was added to the suspension. The specific organic compounds included ~ 150 μg L^{-1} (±20%) each of phenolic hydrocarbons (phenol, *o*-cresol, *o*-nitrophenol, *p*-nitrophenol, *2,6*-dichlorophenol, *2,4*-dichlorophenol, *4,6-o*-dichlorocresol, pentachlorophenol), chlorinated aliphatic hydrocarbons (*1,1,1*-trichloroethane, trichloroethene, tetrachloromethane, tetrachloroethene, *1,1,2,2*-tetrachloroethane) and aromatic hydrocarbons (benzene, toluene, *o*-xylene, *p*-dichlorobenzene, *o*-dichlorobenzene, naphthalene, biphenyl, nitrobenzene, phenanthrene, dibenzothiophene, fluorenone).

The microcosms were incubated in the dark in a slowly rotating box at 10°C for a period of 149 days. During this period, samples were collected for analysis of specific organic compounds, O_2, NO_3^- and dissolved organic carbon (DOC). A slight overpressure was maintained in the microcosm by

forcing atmospheric air into the microcosm with a syringe. Before sampling, sediment was allowed to settle. When opening the valve, a water sample was pushed out of the microcosms into a sample bottle by the over pressure.

For each of the 8 localities 2 replicate batch microcosms were established. Including the 2 biologically deactivated control batch microcosms a total of 18 experimental batch microcosms were included in the study. Each microcosm was sampled 24 times to establish well-defined degradation curves. Biologically deactivated control experiments were made by poisoning two microcosms with 250 mg L^{-1} of formaldehyde.

Analytical procedures

Groundwater characterization. Samples for DOC, NH_4^+, Fe^{2+} and Mn^{2+} analysis were preserved with sulphuric acid and those for NO_3^- and NO_2^- determination were preserved with mercury chloride. Samples for SO_4^{2-} and Cl^- analysis were not preserved. All samples were kept at 4°C until analysis. pH and specific conductivity were measured in the field by electrodes (pH: WTW SenTix *96*®; specific conductivity: Hanna HI *8733*®). Dissolved O_2 was measured by Winkler titration (modified for 12-mL volumes). DOC analysis was performed on a Dohrmann DC-*80*® total organic carbon (TOC) analyzer, whereas NH_4^+, NO_3^-, NO_2^-, SO_4^{2-} and Cl^- were quantified by standard autoanalyzer routines (Technicon® Autoanalyzer II). Metals were analyzed on a Perkin Elmer® *370* atomic absorption spectrophotometer.

Sediment characterization. Samples of 250 g wet sediment from the aquifer was suspended in 1 L 0.002 *M* $Na_4P_2O_7$ solution. The suspension was sieved through sieves of 2, 0.2 and 0.075 mm. The coarse fraction of sediment (> 0.075 mm) was dried, and weighed. The fine fraction (< 0.075 mm) was centrifuged at 3000 rpm, dried, weighed, and resuspended in 20 mL 0.002 *M* $Na_4P_2O_7$ solution. The solution was characterized by sedigraphy (Micromeritics® *5000* ET sedigraph). After termination of the degradation studies sediment from 4 microcosms were also suspended in 1 L 0.002 *M* $Na_4P_2O_7$ solution and characterized by sedigraphy in the same way as sediment from the aquifer.

Specific organic compounds. During the experimental period, samples were analyzed for concentrations of specific organic compounds. In this paper results from 7 aromatic hydrocarbons are presented. The aromatic compounds analyzed include benzene, toluene, *o*-xylene, *o*-dichlorobenzene, *p*-dichlorobenzene, naphthalene and biphenyl. Samples of 10 mL were

obtained directly into a 10-mL measuring flask and 10 μL of 10 *M* NaOH were added. Afterwards the samples were extracted with 100 μL of pentane containing internal standards (isopropylbenzene, heptane and hexadecane). The organic compounds were detected on a Carlo Erba Mega *500*® gas chromatograph with N_2 as carrier gas (10 mL min^{-1}). The aromatic compounds were analyzed by injection of 3 μL pentane into a 30-m J&W DB-*5*®, 0.32 mm (I.D.) capillary column with a film thickness of 1.5 μm, and detected by flame ionization detector. Initial oven temperature was 40°C for 5 min followed by an increase to 115°C by 15°C min^{-1}. This temperature was held for 1 min and followed by an increase of 20°C min^{-1} to 250°C for 1 min.

Statistics. The statistic analysis (one-way analysis of variance (ANOVA) and correlation analysis) on overall degradation rates were made in Statgraphics© based on the assumption that the overall degradation rates are normally and independently distributed, have the same variance, and are homogeneous within replicates.

RESULTS AND DISCUSSION

Groundwater and sediment characteristics of the 8 localities

Table 1 presents the groundwater and sediment characteristics of the 8 localities. The significant concentrations of oxygen and the insignificant concentrations of NH_4^+ and Fe^{2+} prove that all 8 localities are aerobic. The other parameters do show some variation, but large horizontal variations have previously been reported for the same aquifer (Bjerg and Christensen, 1992). Sediment from all localities was sandy with a large fraction of coarse sand (> 80%) and very low content of clay and silt (max. 1%). The sediment show only minor variation among the 8 localities with respect to texture. The variations observed are in general only modest and indicate no systematic differences among the 8 localities.

Control of aerobic conditions during the experiment

The addition of atmospheric air to the microcosm as part of the sampling procedure ensured aerobic conditions during the 149-day-long experimental period. Oxygen was measured 8 times during the experiment and no values were below 9 mg L^{-1}. The concentrations of NO_3^- and Fe^{2+}, as well as pH, were measured frequently (data not shown), and were constant, indicating that neither NO_3^- reduction nor Fe(III) reduction were of significance in the microcosms.

TABLE 1

Characteristics of groundwater and sediment in 8 localities sampled for the laboratory degradation experiments

	Locality number							
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
Groundwater:								
Chloride (mg L^{-1})	27	49	27	45	43	39	39	47
Sulphate (mg L^{-1})	48	31	65	32	90	95	98	35
Spec. cond. (μS cm^{-1})	381	292	355	288	281	289	287	288
Oxygen (mg L^{-1})	2.1	4.8	2.6	5.9	3.5	2.2	3.0	6.1
Nitrate (mg L^{-1})	44	19	40	22	27	36	40	21
Ammonia (mg L^{-1})	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Iron(II) (mg L^{-1})	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Manganese(II) (mg L^{-1})	0.11	0.3	< 0.1	0.33	0.44	0.18	0.23	0.21
pH	6.1	5.4	5.7	4.9	5.3	5.0	5.3	4.6
DOC (mg L^{-1})	1.0	2.6	1.2	2.2	3.4	2.2	2.3	3.3
Sediment:								
Gravel, > 2 mm (%)	0	9.4	5.3	1.8	1.9	0	0	2.3
Coarse sand, 0.2–2 mm (%)	88	84	91	79	77	92	88	73
Fine sand, 0.02–0.2 mm (%)	12	6.0	3.4	18	20	7.5	12	24
Silt, 0.002–0.02 mm (%)	0.18	0.16	0.25	0.23	0.34	0.17	0.23	0.29
Clay, < 0.002 mm (%)	0.13	0.23	0.44	0.46	0.68	0.15	0.33	0.57

Fine particles in the microcosms

The amount of fine particles (< 75 μm) in the microcosms varied between 1 and 3 g L^{-1} but was identical within replicates (relative standard deviation: 5%). Microcosms representing localities with high contents (%) of clay and silt in the sediment also tended to have high contents (g L^{-1}) of fine particles (< 75 μm) in the microcosms, but substantial scatter was observed (not shown). This is probably due to the fact that the microcosms preparation method involved sedimentation of large particles that also might have consisted as aggregates of smaller particles, as no dispersing agents were used. Dispersing agents were used in the determination of the sediment texture (refer to section on Materials and Methods).

Examples of degradation curves

Fig. 3 presents benzene, *o*-xylene, *p*-dichlorobenzene and biphenyl

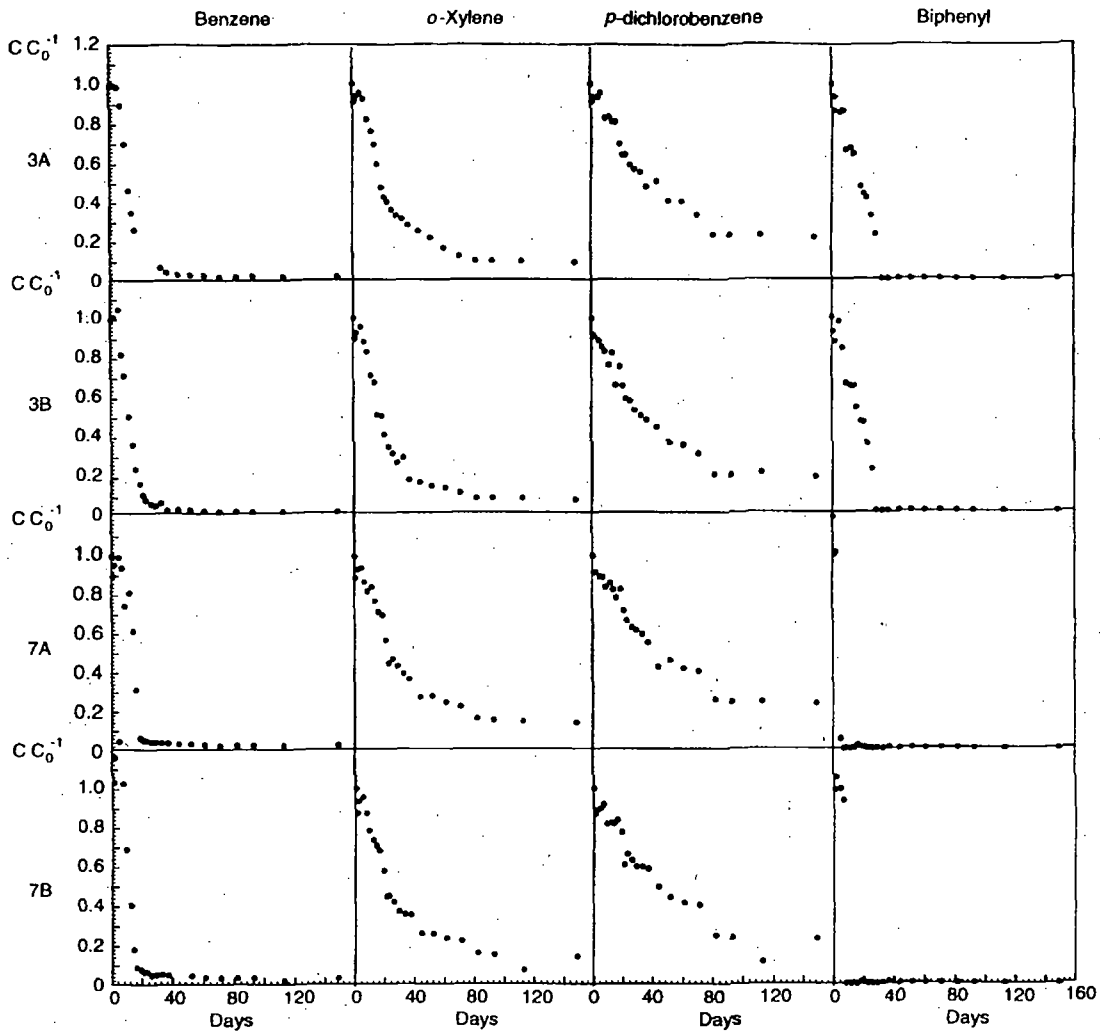

Fig. 3. Normalized concentrations of benzene, *o*-xylene, *p*-dichlorobenzene and biphenyl as a function of time in laboratory batch microcosms with sediment from localities *3* and *7* including replicates (*A* and *B*). The concentrations are normalized by the initial concentration.

degradation curves for localities *3* and *7* including replicates (*A* and *B*). The 16 degradation curves presented are representative examples of the 112 total degradation curves (7 compounds, 8 localities, 2 replicates).

In the biologically deactivated control microcosms concentrations of the 7 compounds were stable and no signs of significant degradation or sorption to the sediment appeared (data not shown). Sorption of specific organic compounds to sediment from the Vejen aquifer has been discussed in detail by Brusseau et al. (1991) and Larsen et al. (1992 a, b, c). Sorption to sediment was not important in this experiment as concentration of sediment in the microcosms was only 5 g L^{-1} and the fraction of organic carbon in the sediment was very low (typically 0.025%). It can be calculated that ~ 1% of the most

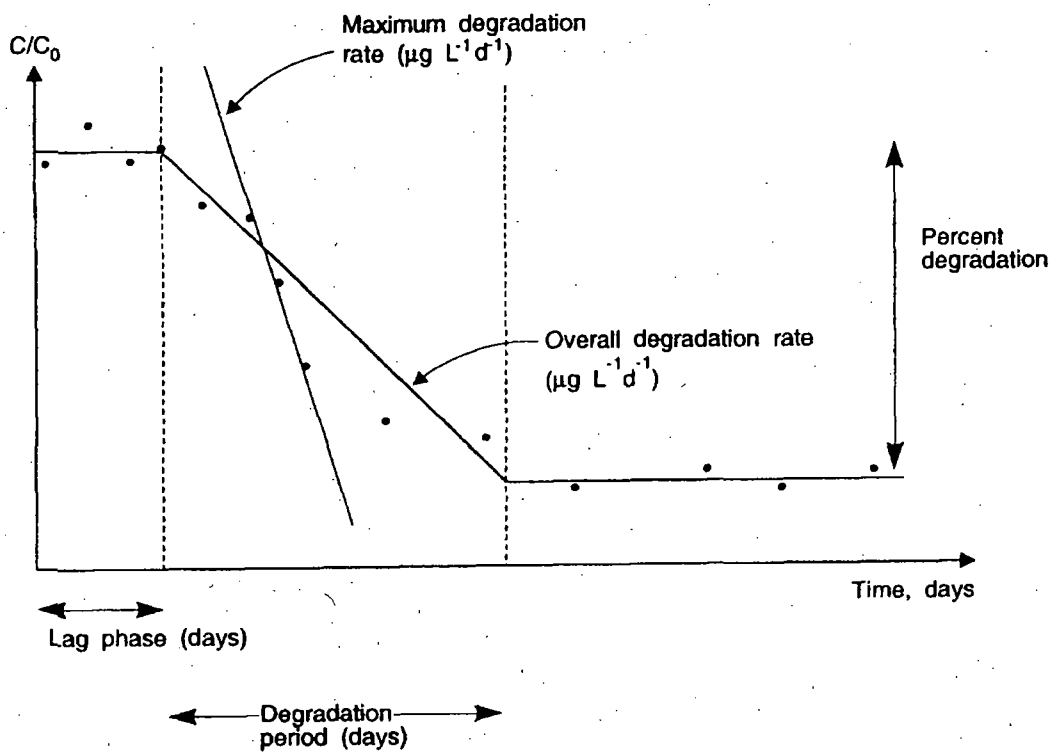

Fig. 4. Sketch of degradation pattern showing lag phase, degradation period, percent degradation, overall degradation rate and maximum degradation rate.

hydrophobic compound (biphenyl) was associated with the sediment in the microcosms.

In biological active microcosms, benzene was degraded to < 2 μg L^{-1} within 30 days in both replicates of localities *3* and *7*. The shape of the degradation curves are very similar and the only difference is the slightly faster degradation of benzene in locality *7* than in locality *3*. *o*-Xylene and *p*-dichlorobenzene were degraded $\sim$ 90% and $\sim$ 80%, respectively, in both replicates of localities *3* and *7* within the experimental period of 149 days. The shapes of the degradation curves of *o*-xylene and *p*-dichlorobenzenes are very similar. Biphenyl was degraded to < 2 μg L^{-1} in both replicates of localities *3* and *7* within 40 days. The replicates of locality *3* are very similar, whereas the replicates of locality *7* exhibit some variation. However, biphenyl degradation seems to be somewhat faster in locality *7* than in locality *3*.

Quantification of degradation patterns

Lag phase (days), degradation period (days), percent degradation, maximum degradation rate (μg L^{-1} day^{-1}) and overall degradation rate (μg L^{-1} day^{-1}) were estimated by subjective measurements as illustrated in Fig. 4 to compare all degradation curves for all localities and replicates.

TABLE 2

Degradation results for 7 aromatic hydrocarbons in 16 149-day laboratory batch microcosm experiments

	Initial concentration[a] (μg L^{-1})	Lag phase ±stand. dev. [Range]	Degradation period ±stand. dev. [Range]	Percent degradation ±stand. dev. [Range]
Benzene	140	4.6 ± 1.4 [2–7]	31.5 ± 12.9 [16–61]	97.8 ± 0.7 [97–98]
Toluene	143	4.1 ± 1.8 [2–7]	26.6 ± 11.0 [16–44]	99.8 ± 0.2 [99–100]
o-Xylene	141	4.7 ± 1.9 [2–7]	82.0 ± 0.0[b] 82	86.9 ± 5.3 [83–95]
p-Dichlorobenzene	120	4.9 ± 3.3 [0–7]	82.0 ± 0.0[b] 82	78.3 ± 5.9 [75–78]
o-Dichlorobenzene	119	4.5 ± 2.6 [0–7]	82.0 ± 0.0[b] 82	81.0 ± 5.2 [79–82]
Naphthalene	150	4.5 ± 2.3 [2–9]	15.2 ± 8.4 [9–44]	99.9 ± 0.1 100
Biphenyl	152	4.5 ± 2.2 [2–7]	29.7 ± 34.3 [5–149]	100.0 ± 0.0 100

Lag phases (days), degradation periods (days) and percentage degradation are for each compound average values of 16 degradation curves.
[a]Concentration of each compound was similar in all microcosms.
[b]Degradation stopped between day 75 and day 82 in all the 16 experiments.

Table 2 summarizes initial concentrations, lag phases, degradation periods and percent degradation for all 7 compounds based on degradation curves from the 16 microcosms. The lag phases were all very short (2–9 days) and very similar in all localities and all replicates for all 7 compounds, whereas the degradation period and percentage degradation differed for the different compounds. Benzene, toluene, naphthalene and biphenyl were all degraded to <2 μg L^{-1} within 1 month whereas the degradation of *o*-xylene, *p*-dichlorobenzene and *o*-dichlorobenzene continued for a period of $\sim$3 months until 5–20% of the compound were left. The three compounds were degraded to approximately the same degree in all microcosms. Sampling was once per week in this period and degradation stopped between day 75 and day 82 in all microcosms. Biphenyl was degraded fast in some localities (e.g., locality *7*) and slower in other localities (e.g., locality *3*), but <2 μg L^{-1} was left in all experiments.

In general, the variations among the 8 localities seem relatively moderate. Where the largest variation is observed (biphenyl), the degradation is fairly rapid, thus reducing the environmental significance of the variation. However, a closer examination of the degradation rates does reveal some statistically

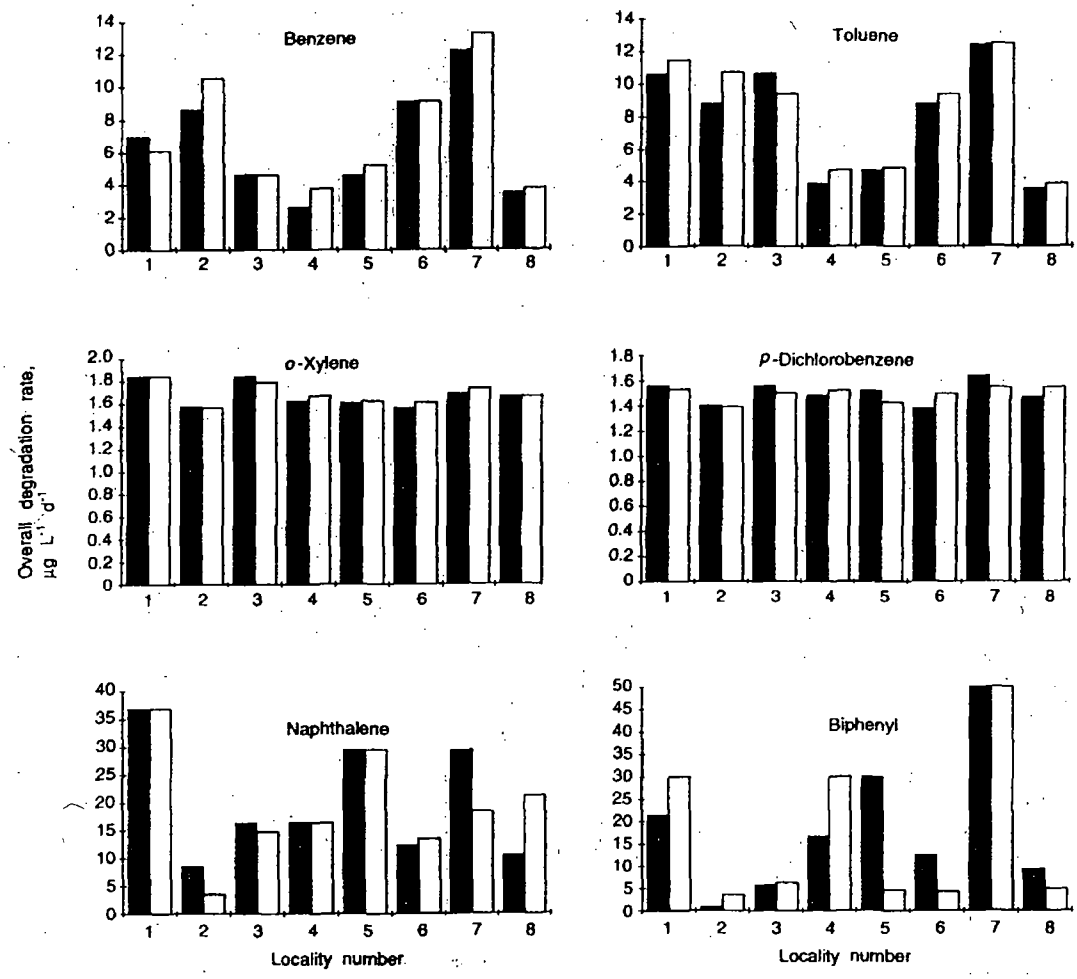

Fig. 5. Overall degradation rates for 6 aromatic hydrocarbons in 8 localities in a 15 m × 30 m area of an aerobic aquifer (*solid bars* = replicate *A*; *open bars* = replicate *B*).

significant variations. The overall degradation rates for all compounds (excluding *o*-dichlorobenzene which in terms of degradation rates is very similar to *p*-dichlorobenzene) are for all experiments, shown as bar diagrams in Fig. 5.

Small uncertainties in sampling of microcosms and in gas chromatography analysis caused significant variation in maximum degradation rates (cf. Fig. 4) because they often were estimated from only 2 or 3 observations. Overall degradation rates were usually estimated from much more observations and were preferred for the comparison of degradation patterns.

Overall degradation rates: variation among localities

Fig. 5 shows three features with respect to variation in overall degradation

TABLE 3

Correlation matrix (r) among overall degradation rates for 7 aromatic hydrocarbons in 8 replicated laboratory batch experiments

	Benzene	Toluene	*o*-Xylene	*p*-Dichlorobenzene	*o*-Dichlorobenzene	Naphthalene	Biphenyl
Benzene	1	0.77	−0.14	0.03	−0.06	−0.09	0.34
Toluene		1	0.42	0.26	0.23	0.11	0.30
o-Xylene			1	0.65	0.69	0.54	0.27
p-Dichlorobenzene				1	0.85	0.59	0.66
o-Dichlorobenzene					1	0.41	0.37
Naphthalene						1	0.55
Biphenyl							1

rates (see Fig. 4 for definition): (1) for benzene and toluene, the experimental variation among replicates is very small, although the variation among localities with respect to overall degradation rates is both substantial (up to a factor of 4) and statistically significant (5%); (2) for *o*-xylene, *o*-dichlorobenzene (data not shown) and *p*-dichlorobenzene, the experimental variation is also very small, but the localities showed no statistically significant differences with respect to overall degradation rates; and (3) for naphthalene and biphenyl, the experimental variation is substantial, but the differences (up to a factor of 15 for biphenyl and 6 for naphthalene) among localities are statistically significant (5%). The experimental variation with respect to naphthalene and biphenyl is to some extent due to the fast degradation of these compounds, complicating the exact estimation of the overall degradation rates.

The localities studied are too few to allow for a geostatistical analysis of the spatial variations in the overall degradation rates observed for benzene, toluene, naphthalene and biphenyl.

Overall degradation rates: correlation among compounds

Table 3 presents the correlations (r) observed among the 7 compounds with respect to overall degradation rates. The only important correlations are between the two dichlorobenzenes ($r^2 = 0.72$) and between benzene and toluene ($r^2 = 0.59$). Fig. 6 presents the corresponding overall degradation rates for benzene and toluene. The correlation is close for all localities except localities *1* and *3*, where toluene degradation is much faster than benzene degradation in both replicates (Fig. 6). Since the replicates are very similar, it appears that localities *1* and *3* may differ from the other 6 localities. Locality *1* and *3* are both located in the south part of the sampling area (Fig. 1) and

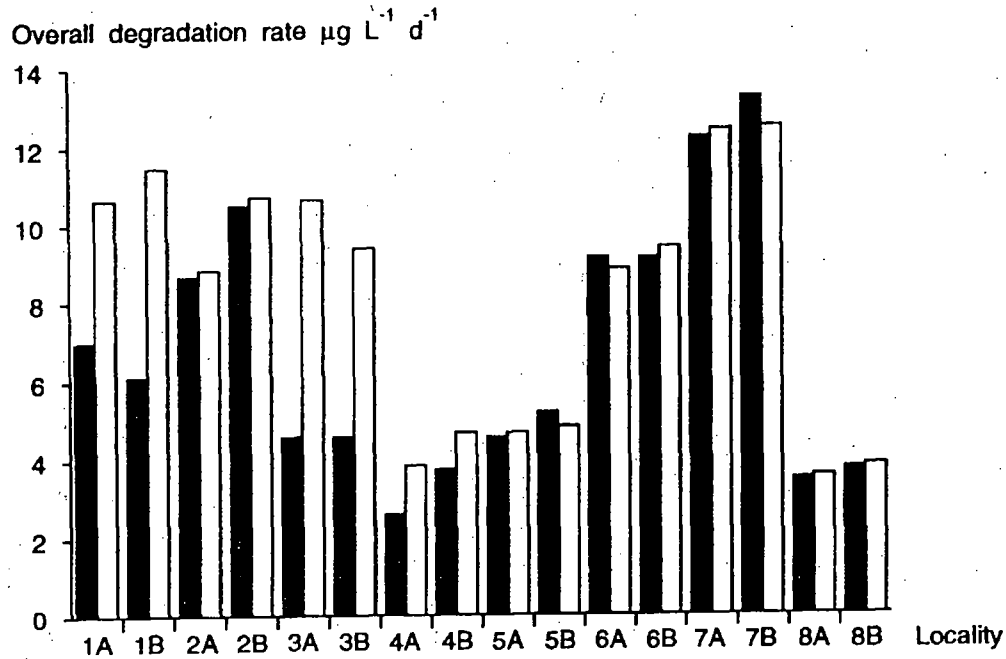

Fig. 6. Overall degradation rates for benzene and toluene in 8 localities in a 15 m × 30 m area of an aerobic aquifer (*solid bars* = benzene; *open bars* = toluene). *A* and *B* are replicates.

according to Table 1 these two localities may have slightly different groundwater composition than the other localities: pH is slightly higher, the specific conductivity is slightly higher, and chloride is slightly lower. However, many other factors may also vary, e.g. the microbial population, and no conclusions can be made as to the reasons for this apparent deviation.

CONCLUSIONS

Based on the results of the 149-day-long laboratory degradation experiment, the following conclusions can be made:

Benzene, toluene, *o*-xylene, naphthalene, biphenyl, *p*-dichlorobenzene and *o*-dichlorobenzene were biologically degraded in 8 localities representing a 15 m × 30 m section of an aerobic aquifer. All compounds showed short lag phases (max. 9 days). Benzene, toluene, naphthalene and biphenyl were degraded to < 2 μg L^{-1} in all replicates from the 8 localities and *p*- and *o*-dichlorobenzene were degraded to $\sim$ 80% in all replicates of the 8 different localities, whereas *o*-xylene was degraded $\sim$ 85% in all microcosms.

The laboratory batch microcosm technique was very reproducible for some compounds (benzene, toluene, *o*-xylene, *p*- and *o*-dichlorobenzene) and less reproducible for other compounds (naphthalene and especially biphenyl).

The overall degradation rate of benzene, toluene, naphthalene and biphenyl

varied significantly among localities (up to a factor of 15 for biphenyl), whereas no variation among localities was observed for *o*-xylene, *o*-dichlorobenzene and *p*-dichlorobenzene.

The overall degradation rates for *p*- and *o*-dichlorobenzene and for benzene and toluene, respectively, showed significant correlation.

The performed laboratory experiments showed a fairly modest variation among the sampling points with respect to degradation of aromatic hydrocarbons under aerobic conditions. The study showed that all eight sampling sites in the aquifer had the potential to degrade the studied compounds but some variations with respect to degradation rates were observed for some of the compounds in the completely mixed batch reactors. Variations in actual degradation rates in the field may differ from the variations documented in the laboratory experiments because in the field, additional variations may be caused by local variations in mass transfer of compounds and nutrients.

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NATURAL ATTENUATION OF CHLORINATED BENZENES AT A FORMER DISPOSAL SITE

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Abstract: This case study examines a former military waste disposal site at Kelly Air Force Base (AFB), Texas, where the surficial aquifer is contaminated with dichlorobenzenes (DCBs) and chlorobenzene (CB) from past degreasing activities. An investigation was completed to assess whether DCBs and CB were being attenuated via biodegradation, and to evaluate the implementability of monitored natural attenuation (MNA) as an alternative in ongoing feasibility studies and corrective measure studies for the site. This paper reviews the biochemistry and microbiology of chlorinated benzene biodegradation, the results of microcosm studies for the site, current and historic chemical concentration trends, and geochemical trends, biodegradation rates, and modeling results. The areal extent of the current groundwater plume is stabilized due to the combined effects of aerobic and anaerobic biodegradation. Evidence suggests that DCB is reductively dehalogenated to CB, while CB is removed from groundwater by aerobic biodegradation at the plume perimeter. MNA will provide protection of potential downgradient receptors, although source treatment would decrease the length of time required for long-term monitoring.

INTRODUCTION

Natural physical, chemical, and biological processes often provide beneficial stabilization and destruction of groundwater contaminants. The measurement and utilization of these natural processes in a managed remedial approach is referred to as MNA. Chlorinated benzenes in groundwater appear to be well-suited to the application of MNA because they are selectively biodegradable under aerobic and anaerobic conditions, and exhibit biodegradation behaviors similar to those of chlorinated ethenes, which have been the subject of much study. This paper describes the natural attenuation of a mixed DCB and CB groundwater plume at Site S-1, Kelly AFB, San Antonio, Texas. The work was performed as part of an ongoing study sponsored by the United States Air Force Research Laboratory to conduct site characterization and groundwater modeling to evaluate the scientific defensibility of MNA as a remedial option for groundwater contaminated with chlorinated benzenes (Parsons Engineering Science, Inc., 1999).

CHLORINATED BENZENE BIODEGRADATION

Chlorinated benzene biodegradation has been documented in the laboratory, but little information is available regarding biodegradation of these compounds in the environment. CB and polychlorinated benzenes up to and including tetrachlorobenzene (TeCB) have been shown to be biodegradable under aerobic conditions (Spain, 1997). Nishino *et al.* (1994) note that aerobic bacteria able to metabolize CB have been detected at a variety of CB-contaminated sites, but not at uncontaminated sites. Spain (1996) notes that this provides strong evidence that the bacteria are selected for their ability to adapt and to derive carbon and energy from *in situ* chlorinated benzene biodegradation.

For the highly chlorinated benzenes (e.g., hexachlorobenzene and pentachlorobenzene, as well as TeCB, and trichlorobenzene [TCB]), reductive dechlorination in anaerobic environments is the most likely biodegradation mechanism (Holliger *et al.*, 1992; Ramanand *et al.*, 1993; Suflita and Townsend, 1995). The chlorinated benzenes most likely act as electron acceptors as other sources of carbon and energy are being utilized by microbes or microbial consortia (Suflita and Townsend, 1995). As these compounds are dechlorinated, the daughter products become more resistant to further reductive dechlorination (Fathepure *et al.*, 1988; Bosma *et al.*, 1988; Holliger *et al.*, 1992), but are increasingly amenable to aerobic biodegradation (Schraa *et al.*, 1986; Spain and Nishino, 1987; Ramanand *et al.*, 1993). The reductive dechlorination of CB has not been documented; however, the structurally similar compound chlorotoluene has been observed to be dehalogenated to toluene in methanogenic soil slurries (Ramanand *et al.*, 1993).

Numerous studies have documented the existence of chlorinated benzene-degrading bacteria at contaminated sites. However, studies suggest that indigenous bacteria in uncontaminated ecosystems typically are not capable of metabolizing chlorinated benzenes, but become capable through the exchange and incorporation of genetic information between two separate bacterial types (van der Meer *et al.*, 1998). Indigenous microorganisms aerobically degrade CB and DCBs in groundwater after an acclimation period. The length of the acclimation period may determine when and where biodegradation begins at a CB spill site. Selective enrichments from soil and water samples have taken from 6 to 14 months to develop the ability to degrade 1,3-DCB, 1,4-DCB, 1,2-DCB, and 1,2,4-TCB (de Bont *et al*, 1986; Schraa *et al.*, 1986; Spain and Nishino, 1987; Haigler *et al.*, 1988; and van der Meer *et al.*, 1987).

SITE S-1 DESCRIPTION

Kelly AFB is located in south-central Texas, 7 miles southwest of the center of San Antonio. Site S-1 was used as an intermediate storage area for mixed solvents, carbon cleaning compounds, and waste petroleum, oils, and lubricants from the 1960s until 1973 (Figure 1). Wastes were stored in aboveground tanks that were located in an open pit, or sump area. Turco Carbo Strip was used extensively by the Air Force for removal of carbon from jet engine parts. This solvent was composed of 1,2-DCB and 25-percent cresylic acid. It is probable that Kelly AFB used similar solvent formations for various industrial

operations, though a history of the sources of CB and DCB is unavailable for Site S-1.

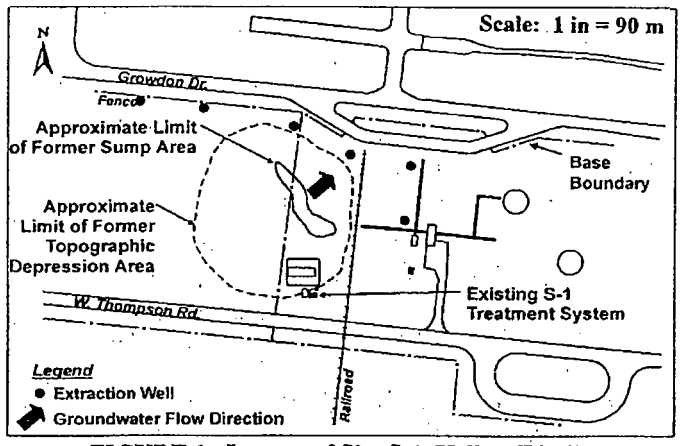

FIGURE 1. Layout of Site S-1, Kelly AFB, TX.

Geology and Hydrogeology. The shallow aquifer overlying the Navarro Clay aquitard is composed of coarse-grained alluvial sand and clayey gravel. The saturated thickness of the alluvial aquifer within the source area in March/April 1998 ranged from approximately 1 to 5 feet (0.3 to 1.5 m). The hydraulic conductivity of the alluvial sands ranges from 7.1×10^{-3} cm/sec to 6.7×10^{-1} cm/sec. The groundwater velocity in the former sump area was estimated to be 4.6 ft/day (1.4 m/day), decreasing to approximately 0.5 ft/day (0.2 m/day) to the northeast (downgradient). An interim pump-and-treat system installed to prevent off-Base migration influences groundwater flow directions and rates; however, the thinness of the saturated zone limits the radius of influence of this system.

Contaminant Source. Free and residual product within an area of approximately 2.2 acres (9,000 m^2) constitutes the source of chlorinated benzene contamination at Site S-1. At the center of the former sump area, large volumes of product are present. A fluctuating water table and the relatively high groundwater velocities have caused vertical smearing and downgradient migration of free product from the sump. The average thickness of the smear zone along the water table is 7 to 10 feet (2 to 3 m). Free product primarily consists of CB and DCBs with smaller fractions of fuel hydrocarbons.

FIELD INVESTIGATION AND AEROBIC MICROCOSM SETUP

Groundwater samples were collected from 25 monitoring wells to assess trends in natural chemical attenuation over time. In addition to the site contaminants, all groundwater samples were analyzed for a suite of natural attenuation indicator parameters.

Aquifer solids and groundwater also were collected from the downgradient portion of the plume (CB concentration of approximately 45 μg/L).

These materials were combined in a column to create an aerobic microcosm matrix. Filter-sterilized groundwater was sparged with oxygen, and the CB content was adjusted to 7.3 mg/L to serve as the feed reservoir. The influent was delivered to the bottom of the column and exited at the top of the column.

NATURE AND EXTENT OF CHLORINATED BENZENE CONTAMINATION IN GROUNDWATER

Of the three DCB isomers detected at Site S-1, 1,2-DCB was present at the highest concentrations in both free product and groundwater. The maximum 1,2-DCB concentration of 10,000 µg/L was detected in the anaerobic source area (Figure 2). The rapid disappearance of all DCB isomers downgradient from the source area, and the presence of elevated CB concentrations, suggest that DCB is being reductively dechlorinated to CB. The DCB plume is approximately 140 feet (43 m) wide by 200 feet (61 m) long. The amount of CB attributable to reductive dechlorination of DCB cannot be determined because CB concentrations also are elevated in free product samples, suggesting that CB also was a source contaminant disposed of at Site S-1.

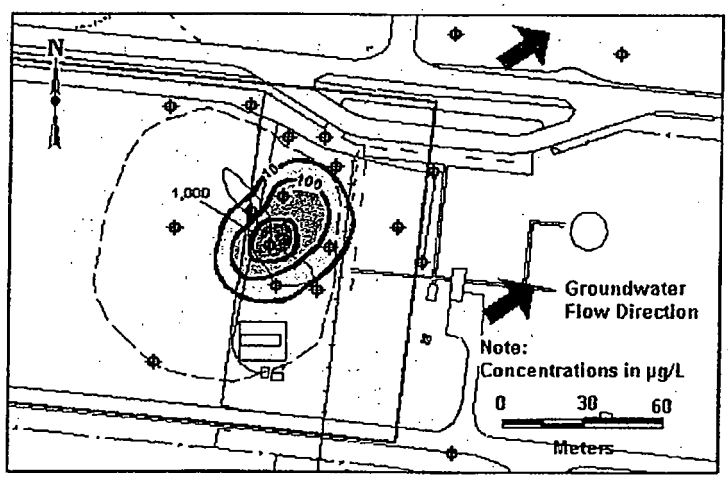

FIGURE 2. 1,2-DCB plume in groundwater, March/April 1998.

The areal extent of DCB in groundwater is relatively small compared to that of CB (Figure 3). The CB groundwater plume emanates from the former sump area and extends 2,000 feet (610 m) to the northeast. The groundwater extraction wells do not appear to be entirely preventing the downgradient migration of dissolved CB. The maximum CB concentration of 45,000 µg/L was detected within the former sump area. The groundwater CB plume at Site S-1 appears to be approximately 1,000 feet (305 m) shorter than was observed a decade ago, indicating a receding plume. Substantial reductions in CB concentrations at downgradient wells between 1989 and 1995, prior to the

installation of the groundwater extraction system, indicate that source weathering and natural attenuation of dissolved CB were occurring during this period.

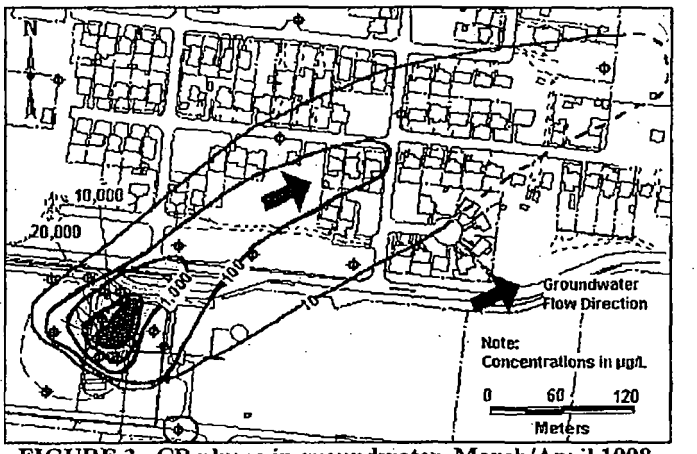

FIGURE 3. CB plume in groundwater, March/April 1998.

Although CB contamination has been present at Site S-1 for at least three decades, it is possible that significant biodegradation did not begin to destroy contaminant mass until the 1980s. Microbial acclimation to CB contamination through the process of genetic recombination requires an extended period of time. Such acclimation may have taken several decades at Site S-1, although historical data are insufficient to support this observation.

GROUNDWATER GEOCHEMISTRY

Groundwater geochemical data support the presence of anaerobic, reducing conditions in the source area and throughout most of the plume. Dissolved oxygen (DO) concentrations ranged from 0.1 to 7.0 mg/L, with the highest concentrations measured at wells crossgradient from the plume. Throughout the plume, DO concentrations generally were less than 0.5 mg/L. The low oxygen concentrations in the plume area relative to uncontaminated areas are a strong indication that microbial activity stimulated by the presence of anthropogenic hydrocarbons (e.g., CB, DCBs, benzene, and other fuel constituents) is depleting DO and creating reducing conditions conducive to DCB dehalogenation.

The area of depleted DO concentrations also is characterized by low oxidation/reduction potentials (ORPs); depleted nitrate and sulfate concentrations; elevated chloride, ferrous iron, methane, and carbon dioxide concentrations; and elevated alkalinity. The observed depletion of electron acceptors and production of metabolic byproducts supports the microbial consumption of anthropogenic organic carbon (e.g., fuel hydrocarbons) in the plume area and indicates that conditions are favorable for reductive dehalogenation of DCBs, especially in the source area.

BIODEGRADATION RATE ESTIMATES

Methods described by Buscheck and Alcantar (B&A) (1995) and Moutoux *et al.* (1996) were used to estimate first-order, field-biodegradation rate constants for chlorinated benzenes at Site S-1. The total destructive attenuation rates estimated using the B&A method for CB downgradient from the source area ranged from 7.9×10^{-4} to 2.2×10^{-3} day^{-1}. Total destructive attenuation rates for CB in the source area ranged from 1.4×10^{-2} to 1.9×10^{-2} day^{-1}. Decay rates computed for DCB in and immediately downgradient from the source area using the Moutoux *et al.* (1996) method indicated a reductive dechlorination rate of 4.6×10^{-3} day^{-1}, compared to a B&A rate estimate of 6.7×10^{-2} day^{-1}.

AEROBIC MICROCOSM STUDY RESULTS AND DISCUSSION

The aerobic microcosm results indicated that viable CB-degrading bacteria were present in the subsurface materials, and that an acclimation period of 3 days was required to establish substantial CB biodegradation rates. Based on the short acclimation period, CB degradation appeared to be caused by induction of an existing CB-degrading microbial population, rather than through a new genetic recombination. A significant microbial population that can acclimate rapidly to degrade CB appears to exist at the fringes of the plume. The results listed in Tables 1 and 2 indicate a substantial capacity for CB degradation, and suggest that the rate might be limited only by the mass transfer of CB and the availability of oxygen.

TABLE 1. Chlorobenzene in various pumped volumes of the soil column operated in intermittent mode.

Days of Operation	Chlorobenzene in Feed Water (mg/L)	Chlorobenzene at 20-mL Pumped Effluent Volume (mg/L)	Chlorobenzene at 120-mL Pumped Effluent Volume (mg/L)
0	7.3	7.9	6.9
1	7.3	6.2	6.5
3	7.4	3.1	5.6
5	5.8	1.7	4.7
6	5.5	1.2	5.0
7	5.6	0.7	4.7

TABLE 2. Chlorobenzene in soil column effluent during continuous feeding.

Flow rate (mL/hour)	Hours of Operation at Specified Flow Rate	Chlorobenzene in Effluent (mg/L)[a]
35	0.5	0.7
35	14.5	0.0
40	1	0.0
75	1	0.0
130	1	1.6
130	1.5	1.2
200	2.0	2.0
200	2.5	1.1

[a] Chlorobenzene in influent = 5.5 mg/L.

Acclimated CB-degrading bacteria were detected in significant population numbers at Site S-1 during a previous study (Nishino *et al.*, 1994). Onsite bioreactors installed at Site S-1 by Nishino *et al.* (1994) removed most of the aromatic compounds from the influent groundwater within a 40-minute hydraulic residence time. After a 7-day acclimation period, the federal drinking water standard for CB of 100 µg/L was achieved in the reactor at hydraulic residence times as short as 30 minutes. This confirms that a viable CB-degrading microbial population had pre-existed, or preacclimated, to CB at the site. No changes in CB degradation rates were observed when supplies of inorganic nutrients were discontinued to the reactors, indicating that site groundwater had sufficient nutrients to maintain rapid aerobic biodegradation rates of CB and other compounds in the reactors. When a foreign CB-degrading strain of bacteria (JS150) was added to the reactors, these bacteria did not survive, but were displaced by more viable populations of indigenous Site S-1 bacteria. This result indicated that artificial inoculation of other known strains of CB-degrading bacteria would not be beneficial relative to the natural, preestablished Site S-1 microbial community.

GROUNDWATER MODELING

A numerical groundwater model was developed to predict future plume trends under the influence of natural attenuation and other planned source-reduction actions. The model code Bioplume III (USEPA, 1998) was used to estimate the future fate and transport of dissolved CB under the influence of advection, dispersion, sorption, and biodegradation.

A focused feasibility study performed for Site S-1 (CH2M Hill, 1997) identified limited source excavation and subsequent soil vapor extraction as the preferred remedy to reduce leaching of chlorinated benzenes into the groundwater. Therefore, a source-reduction scenario was simulated that considered the effects of these activities on the longevity of the groundwater plume. The simulation assumed that the source product would be reduced by at least 90 percent during a 4-year treatment period beginning in 1999, followed by natural weathering of the remaining source at a potentially conservative geometric rate of 3 percent per year. The interim groundwater pump-and-treat system was assumed to cease operation in 2000.

By 2004, dissolved CB concentrations were predicted to be one to two orders of magnitude below the 1999 concentrations at most locations (Figure 4), and the CB plume was predicted to recede toward the source area. The model predicted that 36 years after initiation of source-reduction activities would be required before CB concentrations at all off-base wells are below the Federal Drinking Water Standard of 100 µg/L. If source remediation is not conducted at Site S-1, the estimated time for the attainment of this regulatory level at all off-base wells is anticipated to exceed model predictions by decades. Overall, the groundwater model predicted that receptor exposure pathways involving shallow groundwater are not complete under current conditions, nor will the CB plume expand to impact potential downgradient receptors under worst-case (no engineered source reduction) conditions.

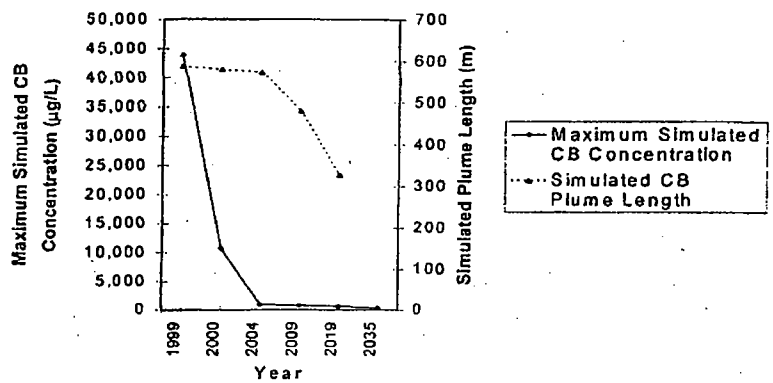

FIGURE 4. Simulated CB plume length and maximum CB concentrations.

DISCUSSION

Aerobic biodegradation of CB should become more important with time as the ratio of dissolved anthropogenic carbon per unit mass of DO decreases through engineered remediation and weathering, resulting in increasing DO concentrations across the site. The results obtained from Kelly AFB suggest that many sites with chronic chlorinated benzene contamination may be suited for the application of MNA because indigenous microbial populations can degrade these compounds. Recent releases of CB into an aquifer could experience a lengthy lag time before CB degradation could occur. However, once microbial communities have adapted to the presence of CB, the biodegradation of CB may be limited only by the availability of electron acceptors and the prevailing site geochemistry.

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BIOREMEDIATION OF NITROCHLOROBENZENE, NITROANILINE, CHLOROANILINE AND OTHER ORGANICS IN GROUNDWATER

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ABSTRACT: The uppermost aquifer beneath a chemical plant contains residual concentrations of o-nitrochlorobenzene from a tank car spill, as well as other plant-related organic compounds of concern (COC), including 2-nitroaniline and o-chloroaniline. The aquifer consists of low permeability clays and silts, and produces only a few gallons of groundwater per day from a shallow recovery well previously installed for remediation. Soil removal was the principal mechanism to treat the tank car spill. Subsequent recovery of residual groundwater contamination has been ineffective for more than 10 years due to low aquifer yield, and the recalcitrant nature of the COC. Aerobic treatment was facilitated using the Oxygen Release Compound (ORC®). The treatment area was approximately 80 square meters and the depth of treatment was approximately 6 meters of aquifer profile. The DO and ORP measurements were highly variable, but trended up for the first three months following ORC injection. The DO and ORP trends began to decrease approximately six months following injection. The DO ranged between 3.5 mg/l and 10.7 mg/l, and the ORP ranged between 291 mV and 367 mV during this six month period. Maximum contaminant concentration reductions observer during the pilot test varied from 28% to 83%, and rebound was detected following the effective life of the ORC. The relatively low sorption of the compounds to soil, and the influx of contaminated groundwater into the pilot test area indicate that a permeable bioremediation-barrier represents the most effective remedial option for this site.

INTRODUCTION

A field-scale pilot study to evaluate *in-situ* treatment of the compounds of concern (COC) was performed. Aerobic treatment of various COC in soil systems has been reported to be highly variable (Abou-Rizk et al., 1995; Myers et al., 1995; Zappi et al., 1995), and the goal of the pilot test was to establish that aerobic bioremediation of the COC was a viable option at this site. Oxygen Release Compound (ORC®), manufactured by Regenesis Bioremediation Products in San Juan Capistrano, California, is a patented formulation of magnesium peroxide that slowly releases molecular oxygen when hydrated, thereby facilitating aerobic bioremediation of the COC. Numerous remedial options were evaluated, and ORC was identified as the preferred method to oxygenate the aquifer. The ORC releases oxygen slowly over a period of 6 to 9 months, which corresponded to the scheduled testing period.

MATERIALS AND METHODS

The ORC design/loading rates were based on dissolved organic compound mass in the treatment area, as well as dissolved oxygen (DO) concentrations and oxidation-reduction potential (ORP) measurements. The ORC was injected in a grid pattern around the recovery well which continued to extract groundwater, thereby enhancing the rate of oxygen movement through the treatment area.

Baseline COC sampling was performed prior to ORC injection, and the post-treatment monitoring protocol included DO and ORP in addition to the COC. A supplementary investigation is planned to measure the potential for the contaminants to partition from the adsorbed phase into the dissolved phase. A soil core will be obtained from the site during pending investigation efforts to facilitate this analysis.

RESULTS AND DISCUSSION

Table 1 depicts the efficacy of the six month bioremediation process at this site for the COCs. Figures 1 to 3 illustrate the reductions over time in the COCs as measured in monitoring well F-2, which is located in the central portion of the pilot test area. Figure 4 illustrates the changes in dissolved oxygen (DO) and Figure 5 describes the oxidation-reduction potential (ORP) at the site during the pilot test.

CONCLUSIONS

The bioremediation process effectively reduced dissolved masses of o-nitrochlorobenzene, 2-nitroaniline and o-chloroaniline, and also reduced dissolved mass of other COCs. Rebound of the COC concentrations were observed after the oxygen from the initial ORC treatment was spent. The project will be expanded to include a long-term barrier design using ORC to continuously deliver oxygen to the aquifer, and eliminate the potential for off-site migration of dissolved COC.

TABLE 1. Maximum decrease in dissolved compounds of concern concentrations following ORC treatment.

Compound	% Concentration Reduction
1,2-dichloroethane	28.3
1,2-dichloropropane	61.0
chlorobenzene	63.5
naphthalene	54.5
2-chlorophenol	38.7
2-nitroaniline	82.1
nitrobenzene	54.5
o-chloroaniline	82.8

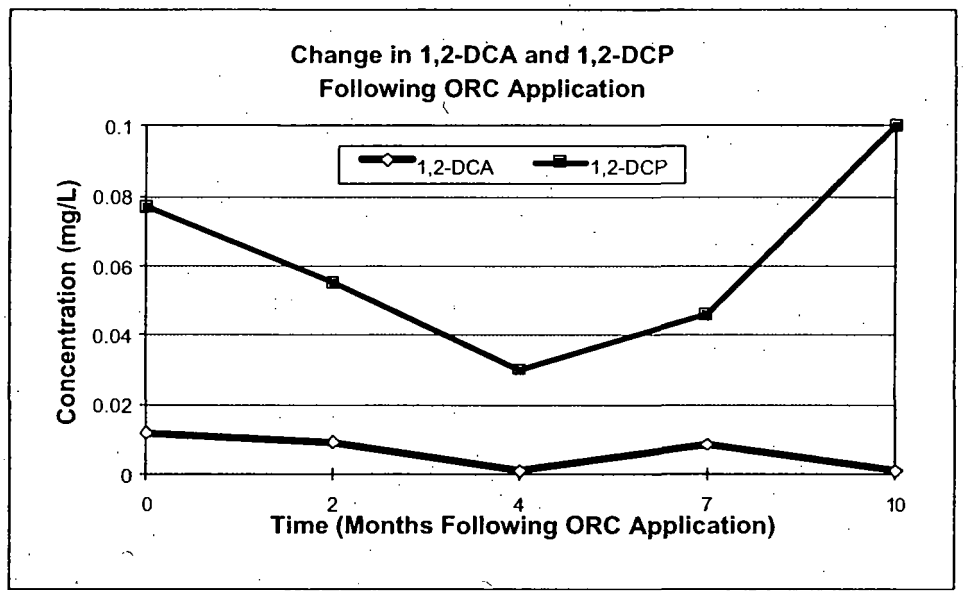

FIGURE 1. Change in 1,2-DCA and 1,2-DCP concentrations following ORC application.

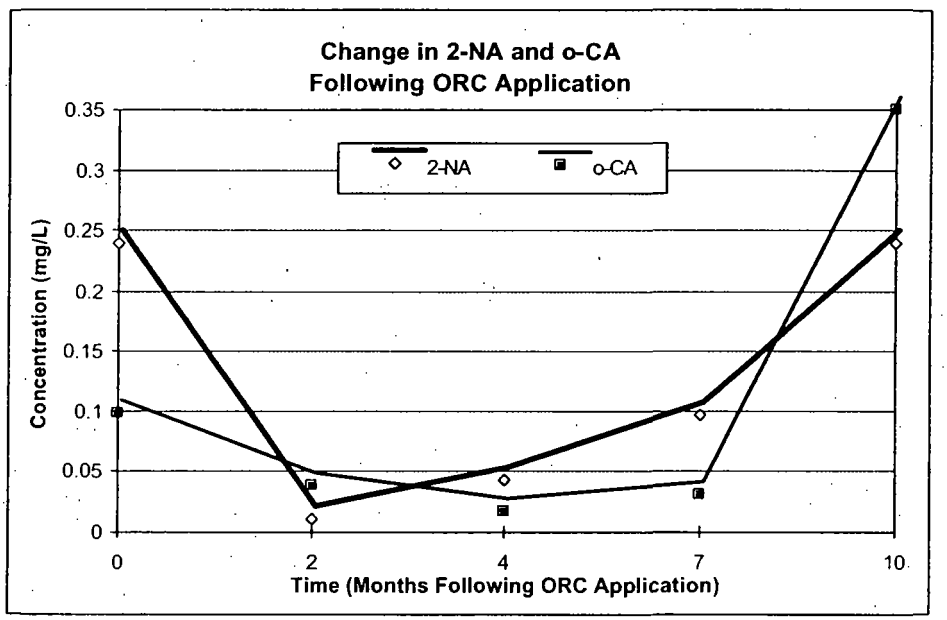

FIGURE 2. Change in 2-nitroaniline and o-chloroaniline concentrations following ORC application.

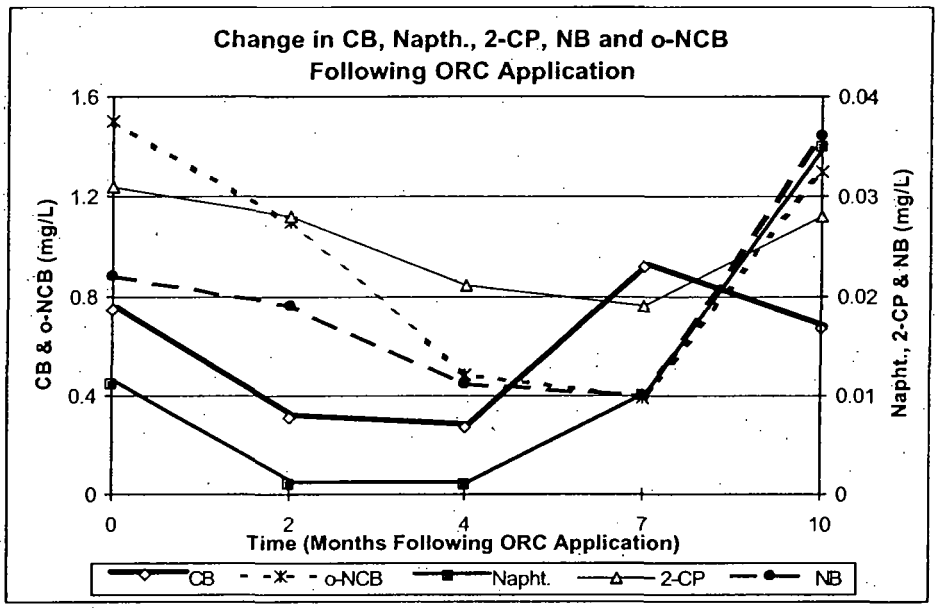

FIGURE 3. Change in chlorobenzne, nitrobenzene, o-nitrochlorobenzene, naphthalene and 2-chlorophenol concentrations following ORC application.

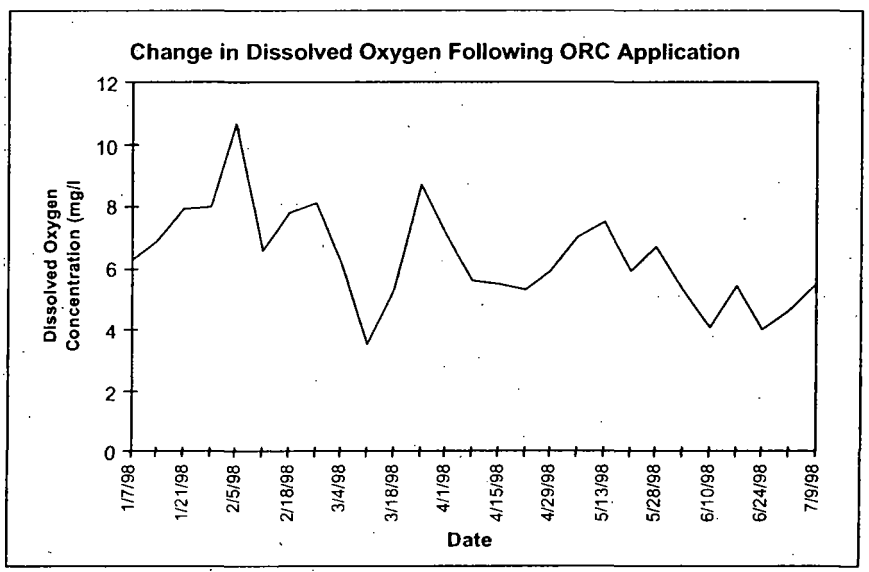

FIGURE 4. Change in dissolved oxygen following ORC application.

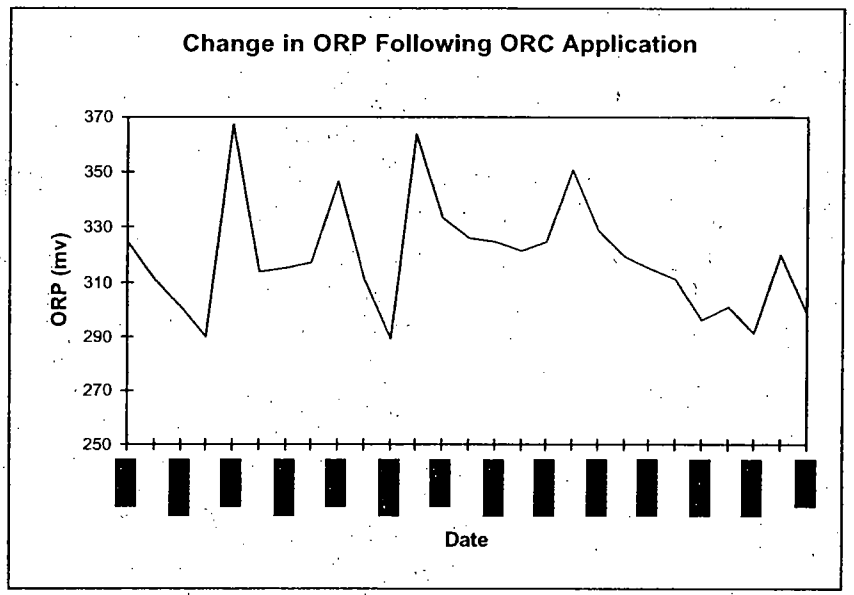

FIGURE 5. Change in ORP following ORC application.

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Bioremediation of chlorobenzene-contaminated ground water in an in situ reactor mediated by hydrogen peroxide

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Abstract

New in situ reactive barrier technologies were tested nearby a local aquifer in Bitterfeld, Saxonia-Anhalt, Germany, which is polluted mainly by chlorobenzene (CB), in concentrations up to 450 μM. A reactor filled with original aquifer sediment was designed for the microbiological remediation of the ground water by indigenous bacterial communities. Two remediation variants were examined: (a) the degradation of CB under anoxic conditions in the presence of nitrate; (b) the degradation of CB under mixed electron acceptor conditions (oxygen + nitrate) using hydrogen peroxide as the oxygen-releasing compound. Under anoxic conditions, no definite degradation of CB was observed. Adding hydrogen peroxide (2.94 mM) and nitrate (2 mM) led to the disappearance of CB (ca. 150 μM) in the lower part of the reactor, accompanied by a strong increase of the number of cultivable aerobic CB degrading bacteria in reactor water and sediment samples, indicating that CB was degraded mainly by productive bacterial metabolism. Several aerobic CB degrading bacteria, mostly belonging to the genera *Pseudomonas* and *Rhodococcus*, were isolated from reactor water and sediments. In laboratory experiments with reactor water, oxygen was rapidly released by hydrogen peroxide, whereas biotic-induced decomposition reactions of hydrogen peroxide were almost four times faster than abiotic-induced decomposition reactions. A clear chemical degradation of CB mediated by hydrogen peroxide was not observed. CB was also completely degraded in the reactor after reducing the hydrogen peroxide concentration to 880 μM. The CB degradation completely collapsed after reducing the hydrogen peroxide concentration to 440 μM. In the following, the hydrogen peroxide concentrations were increased again (to 880 μM, 2.94 mM, and 880 μM, respectively), but the

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oxygen demand for CB degradation was higher than observed before, indicating a shift in the bacterial population. During the whole experiment, nitrate was uniformly reduced during the flow path in the reactor.
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Keywords: Aquifer; Chlorobenzene; Enhanced natural attenuation; Degradation; Hydrogen peroxide; Nitrate reduction

1. Introduction

Until 1990, the soil and ground water in the Bitterfeld/Wolfen district (Saxony-Anhalt, Germany) were steadily contaminated as a result of open cast lignite mining and related chemical industries pursued for more than a century. The contaminated area is about 25 km^2 in size and has a total volume of approximately 200 million m^3. The main contaminants are halogenated aliphatic (e.g. chlorinated ethenes) and aromatic (e.g. chlorinated benzenes) compounds. A local aquifer nearby the town of Bitterfeld was chosen to develop and test new in situ reactive barrier technologies under the German ground water remediation project SAFIRA (Merkel et al., 2000; Weiss et al., 2001). In situ reactive barriers, which are considered to be more efficient and cost-effective than traditional pump-and-treat methods, allow the passage of ground water while promoting the degradation or removal of contaminants. Most techniques are currently at the development stage (Radisav and Frederick, 1996; Weiss et al., 2001). The reactive barrier technologies tested in the Bitterfeld pilot plant are based on various chemical, physical and biological processes. The whole on-site pilot plant in Bitterfeld consists of five shafts spaced 19 m apart, each with a depth of 23 m and a diameter of 3 m, housing a total of 20 reactors (Merkel et al., 2000; Weiss et al., 2001). Two reactors of shaft 5, both 12 m long and filled with original aquifer sediment, were designed for the microbiological remediation of the ground water by indigenous bacterial consortia (Vogt et al., 2002a). Since the ground water at the test site is principally contaminated by chlorobenzene (CB), remediation mainly means the in situ degradation of CB. Two different remediation approaches were tested in a long-term study: (a) CB degradation under anoxic conditions in the presence of nitrate, since the results of preliminary degradation experiments under these conditions in microcosms and on a semi-technical scale had been encouraging (Wuensche et al., 2000); (b) CB degradation under mixed electron acceptor conditions (oxygen + nitrate). The latter variant is based on the aerobic oxidation of CB, using hydrogen peroxide as oxygen-releasing compound. Nitrate was added as supplementary electron acceptor, the idea being to create mixed electron acceptor conditions (nitrate + oxygen) in zones of low dissolved oxygen concentrations in order to save oxygen.

Over the last 10 years, many aromatic compounds have been shown to be mineralizable under anoxic denitrifying conditions by bacterial isolates or mixed cultures, e.g. benzene (Burland and Edwards, 1999; Coates et al., 2001), toluene (Dolfing et al., 1990), ethylbenzene (Rabus and Widdel, 1995), xylene isomers (Dolfing et al., 1990; Rabus and Widdel, 1995), phenolic compounds (Schink et al., 2000), 3-chlorobenzoate and 4-chlorobenzoate (Haeggblom et al., 1993, Haeggblom and Young, 1999). For the

chloroaromatic compounds 2-chlorobenzoate and 2-chlorophenol, a non-reproducible degradation was observed (Haeggblom et al., 1993, 2000). However, no report exists to date which convincingly describes the degradation of CB under anoxic denitrifying conditions. In contrast, aerobic degradation and mineralization of CB by pure bacterial strains has been demonstrated by several authors (Reineke and Knackmuss, 1984; de Bont et al., 1986; Schraa et al., 1986; Spain and Nishino, 1987; Haigler et al., 1988; Sander et al., 1991; Stoecker et al., 1994; Zaitsev et al., 1995; Kiernicka et al., 1999). Most of the CB degrading strains mentioned were isolated from field sites with a history of CB pollution. In this context, Nishino et al. (1994) observed that the capability to degrade CB was solely linked to CB-contaminated sites, and van der Meer (1998) revealed that horizontal gene transfer and genetic recombination of existing genes between indigenous microorganisms were the mechanisms for the evolution of CB degrading bacterial strains on such a site.

Successful treatment of CB-contaminated ground water in aerobic bioreactors was reported by Nishino et al. (1994) and Klěcka et al. (1996); the latter used a granular activated carbon fluid-bed bioreactor with high removal efficiency. However, to our knowledge there are no reports describing an enhanced in situ bioremediation technology for CB. For the test reactors, we decided to apply hydrogen peroxide as an oxygen-releasing compound for the following reasons: the substance is (a) cheap, (b) easy to dose, and (c) rapidly decomposes. Decomposition occurs in subsurface systems by the action of microbial enzymes and several inorganic catalysts to give 0.5 mol oxygen per mol of hydrogen peroxide consumed, with microbiologically mediated catalytic reactions by the enzyme catalase being described as the most substantial (Spain et al., 1989; Pardieck et al., 1992; Anid et al., 1993; Fiorenza and Ward, 1997; Zappi et al., 2000). Thus, hydrogen peroxide provides an oxygen supply several orders of magnitude more concentrated than that achievable from saturating water with pure oxygen, when added to the environment in an elevated concentration (Pardieck et al., 1992).

In the present study, results of both remediation approaches tested in one reactor (reactor 1b) are shown.

2. Material and methods

2.1. Area description

The test site is located south east of the town of Bitterfeld. The subsurface consists predominantly of gravel, which is embedded in lignite, and Bitterfeld mica sand. The upper 3 to 4 m of the sediments are water free (vadose zone). Beginning at a sediment depth of approximately 20 m, the aquifer is separated by a lignite seam into a Quaternary and a Tertiary aquifer (Dermietzel and Christoph, 2001; Weiss et al., 2001). The upper strata contain lignite particles as well, the highest amounts being in regions near the seam (Weiss et al., 2001). Overall, three aquifers are separated by watertight layers. The reactors of the in situ pilot plant were supplied exclusively with ground water from a deeper zone (19.5 m) of the Quaternary aquifer in which the contaminants are strongly stratified: ground water from a depth of 5–9.5 m is almost non-polluted; at a depth of 9–16 m, CB is

the dominating contaminant, with a concentration of approximately 18 μM; at a depth of 16–22 m, CB concentrations increase to as much as 450 μM. The electrolytic conductivity is not uniformly distributed either: in the lower, highly polluted zone, conductivity is between 1500 and 2700 μS m^{-1}, compared to only 900 μS m^{-1} close to the surface. The ground water, with an average temperature of 14 °C and a pH of 6.6–6.8, was collected from a depth of 19.5 m by a horizontal well (HW 5). The ground water is rich in SO_4^{2-} (7–9 mM) and Cl^- (up to 13 mM), and contains NH_4^+ (300–400 μM) and PO_4^{3-} (80–120 μM). The oxygen concentration is below 1 μM, H_2S and NO_3^- are below the detection limit (Vogt et al., 2002a). Total cell counts were in the range of 10^6 cells ml^{-1}.

2.2. Reactor design

Reactor 1b (R. 1b) of shaft 5 is made of stainless steel, 12 m long and has a diameter of 600 mm (Fig. 1). Original aquifer sediment was used to fill the reactor. Besides gravel and Bitterfeld mica sand, the sediment contains 0.31–0.65 mass% iron, and up to 12.5 mass% lignite (Vogt et al., 2002a). Before filling, the sediment was stored for 6 weeks in two tanks flooded with ground water from the contaminated zone of the Quaternary aquifer, and covered by a foil made of polyethylene. The reactor was operated in flow-through mode from bottom to top at a flow rate of 4.7 l h^{-1}, leading to a residence time of approximately 10 days for water according to a conductivity tracer test (data not shown). Auxiliary substances (concentrated hydrogen peroxide and/or nitrate solution) were stored in tanks (filling quantity: 60 l) made of stainless steel, and added to the inflowing ground water by a flexible-tube pump and feed lines made of stainless steel at a rate of 0.043 l h^{-1}.

Reactor sediment and reactor water were sampled anoxically from reactor sample ports using specially designed lances (UIT, Dresden, Germany). Sediment samples were immediately transferred into sterile sample bags and stored in an anaerobic jar (Anaerocult® A, Merck, Germany). Reactor water was collected brimful in screw plug flasks. Both sediment and reactor water samples were stored at 4 °C until further processing in the laboratory. Further processing was carried out within 24 h.

2.3. Microbiological and biochemical methods

Total cell counts in the ground water were determined by staining using 4′,6-diamino-2′-phenylindol-dihydrochlorid (DAPI; Porter and Feig, 1980). Ground water was treated with ultra sound (3 min, 30 W) to extract bacteria from particles, stained with DAPI (1 μg ml^{-1}) for 15 min and subsequently concentrated onto black polycarbonate filters (0.2 μm pore size; Corning Costar, No. 110656). The filter was washed with particle-free water and mounted on a glass microscope slide in 10 μl phosphate-buffered saline/glycerol. DAPI-stained cells were identified and enumerated by means of a fluorescence microscope (Zeiss Axioskop equipped with a filter set for UV-excitation). It was not possible to determine the total cell counts in reactor water because particles interfered.

Viable cell counts (MPN) for CB degrading and aerobic bacteria were determined in ground water, reactor water and reactor sediments as described by Vogt et al. (2002a). Reactor water and ground water samples and were directly diluted without prior preparation.

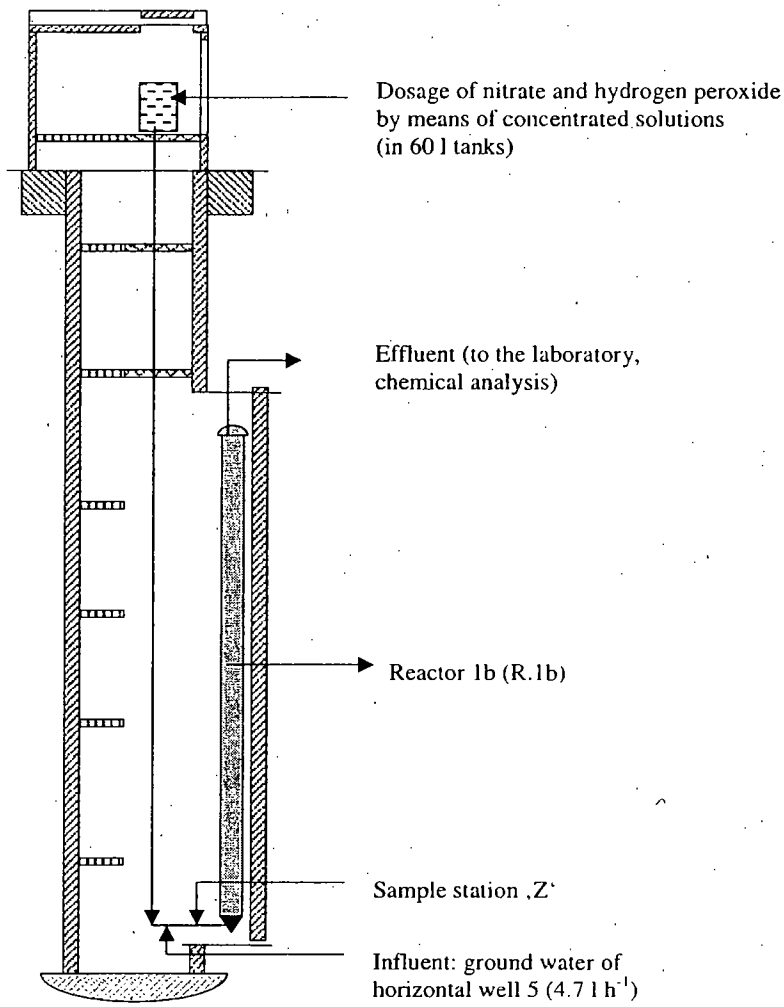

Fig. 1. Schematic diagram of shaft 5 of the SAFIRA pilot plant in Bitterfeld, which contains reactors designed for the in situ remediation of CB-contaminated ground water. For simplification, only reactor 1b is shown.

For the isolation and characterization of pure bacterial strains, liquid from grown MPN counts for CB degraders (highest grown dilution series) was spread onto plates containing modified Brunner mineral salt medium (Vogt et al., 2002a) with added agar. Plates were incubated in an air-filled, closed jar. CB was added as the sole source of energy and carbon by means of a glass plate filled with 400 μl CB (99.5%), which was placed at the top of the stacked plates so that the bacteria were supplied with the substrate via the gas phase. Plates were incubated at room temperature until the growth of colonies was visible; individual colonies were subcultured on dilution plates and fed with CB until purity was ensured microscopically. Bacterial strains were identified by primary tests (Gram staining, morphology, motility and oxidase test), by analyses of fatty acids, which were determined as methyl esters from whole-cell hydrolyzates by gas chromatography as described by Haertig et al. (1999), by the BIOLOG (BIOLOG, Hayward, USA) Automated Microbial

Identification System (Wuensche and Babel, 1996), and by 16S ribosomal DNA analyses (Alfreider et al., 2002).

Aerobic CB and benzene degradation experiments with pure cultures were performed in 116 ml serum flasks filled with 50 ml CB or benzene-amended modified Brunner medium (final concentrations of CB and benzene: 1.25 mM). Tested strains were grown on CB on agar plates at room temperature and transferred to the Brunner medium, to an initial OD_{600} of approximately 0.03. The flasks were sealed with Teflon-coated butyl rubber stoppers and aluminium crimps. These batch cultures were incubated on a rotary shaker (111 rpm) at 14 °C and sampled regularly for substrate depletion and bacterial growth. Bacterial growth was monitored as the increase in optical density (OD_{600}) compared to sterile growth medium.

Catechol 1,2-dioxygenase (types I and II) and catechol 2,3-dioxygenase activity were measured according to Farrell and Quilty (1999).

2.4. Design of the batch experiments with hydrogen peroxide

Inflowing ground water and water from the reactor bottom (reactor height 0.1 m) were collected brimful in 2-l flasks and immediately processed in the laboratory. To prepare biotic samples, the waters were purged with nitrogen to remove oxygen and CB. To prepare abiotic samples, waters were autoclaved (20 min, 121 °C) before purging with nitrogen. All the following steps were carried out in an anoxic glove-box (Coy Laboratory Products, USA; gas atmosphere: 95% nitrogen, 5% hydrogen). Abiotic and biotic waters were portioned brimful in 116 ml serum flasks. Subsequently, 7 ml was removed and replaced by 5 ml of an anoxic CB stock solution (3.4 mM). The flasks were sealed with Teflon-coated butyl rubber stoppers and aluminium crimps and incubated at 14 °C overnight. Afterwards, the flasks were reopened, spiked with hydrogen peroxide (30%; final concentration: 2.94 mM) and closed again. Two flasks were sacrificed at each point of time of a single experiment for the analysis of CB and oxygen.

2.5. Analysis methods

CB was analyzed by automated headspace gas chromatography on a CombiPal auto sampler and a Varian 3800 gas chromatograph equipped with a 0.25 mm (inner diameter) × 25 m (length) CP SIL 5 CB capillary column (DF 0.12 μm) and a flame ionization detector. The chromatographic conditions were as follows: injector temperature: 250 °C (split 1:2); detector temperature: 300 °C; oven temperature program: 35 °C (3 min), at 10 °C min^{-1} to 65 °C, at 30 °C min^{-1} to 260 °C. Liquid test samples (diluted 1:10 or 1:20 in 1.6 mM H_2SO_4, end volume: 10 ml) were prepared in 20 ml glass vials. The samples were incubated for 20 min at 35 °C in an agitator (rotation regime: 250 rpm for 5 s, no rotation for 2 s) prior to analysis. A 1 ml headspace of each sample was injected. For calibration, diluted standards of CB prepared from stock solutions were treated in the same way as the samples. Stock solutions were prepared in pure methanol.

3-Chlorocatechol (3-CC) was quantified by high-performance liquid chromatography (HPLC), using a Shimadzu LC-6A Liquid Chromatograph equipped with a Nucleosil-100 (4 mm ID) column and a Shimadzu SPD-6AV UV–VIS detector (wave lenght 283 nm).

Samples were eluted isocratically in 40% (v/v) acetonitrile/60% phosphate (pH 2.8), at a flow rate of 1 ml min^{-1}.

Chloride, sulfate, nitrate and phosphate were measured using a Dionex DX 500 ion chromatograph equipped with an AS-11 column and a CD 20 conductivity detector. Samples were eluted using a gradient of 1 to 30 mM potassium hydroxide at a flow rate of 1 ml min^{-1}.

Alternatively, nitrate was analyzed using a Dionex DX-100 ion chromatograph equipped with an IonPac AS4A Guard (4 × 50 mm) precolumn, an IonPac AS4A (2 × 250 mm) column and a conductivity detector. Samples were eluted isocratically in Na_2CO_3 (1.8 mM)/$NaHCO_3$ (1.457 mM) buffer at a flow rate of 2 ml h^{-1}.

Nitrite and ammonia was analysed photometrically using Merck test Spectroquant 1.12776.0001 and 1.14752.0001, respectively (Merck, Germany). Sulfide was measured by means of an amperometric microsensor (AMT Analysentechnik, Germany). The oxygen, pH and electrolytic conductivity in the ground water from the Bitterfeld test site were determined using a Multilab 540 measuring instrument (WTW, Germany). A CellOx 325 oxygen sensor and a pocket digital measuring instrument (WTW, Germany) were used to measure oxygen in the laboratory experiments addressing the disproportionation of hydrogen peroxide (see above). All the chemicals used throughout this study were of analytical quality.

3. Results

3.1. Reactor operation under anoxic denitrifying conditions

After approximately 210–260 days' of flushing ground water through the reactor, a *steady state* situation had emerged, since the CB concentrations in the effluent did not

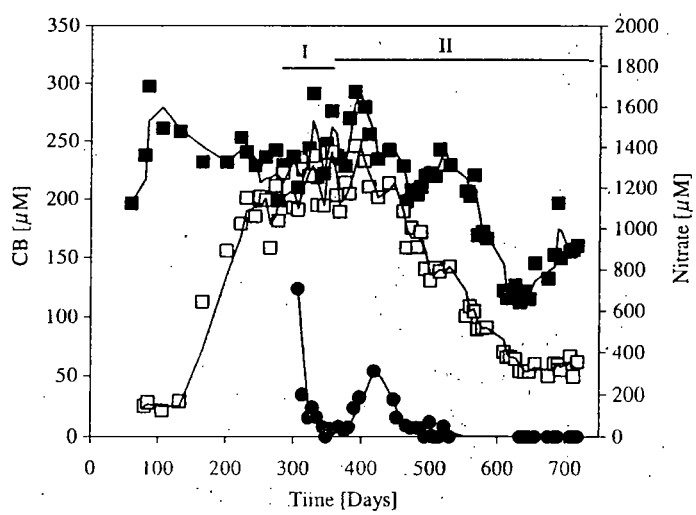

Fig. 2. Concentrations of CB (■ horizontal well 5 (influent), □ effluent) and nitrate (● effluent) during the operation of reactor 1b. Phase I: addition of nitrate (1 mM); Phase II: addition of hydrogen peroxide (2.94 mM) and nitrate (2 mM).

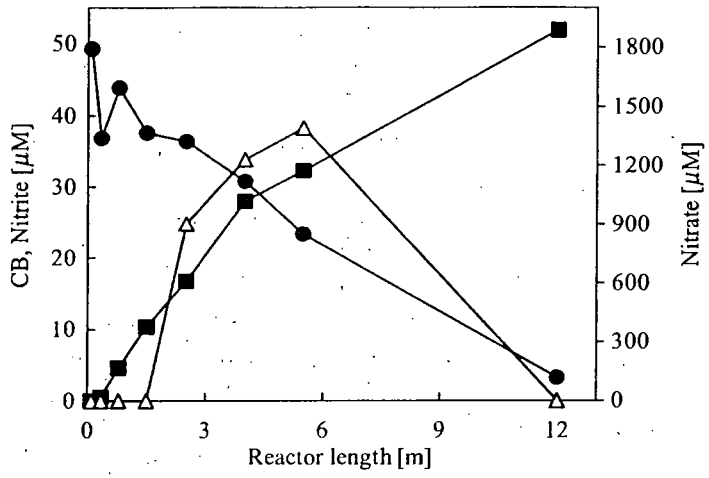

Fig. 3. Profile of CB (■), nitrate (●) and nitrite (△) concentrations in reactor 1b, operation day 709. The CB concentration of the inflowing groundwater was 128.7 μM.

further increase. The hydro-geological, chemical and microbiological characteristics of the first 286 days of reactor operation were described recently (Alfreider et al., 2002; Vogt et al., 2002a). Beginning with operating day 286, nitrate solution (1 mM) was added to the reactor. In the following 77 days, the effluent CB concentrations did not change significantly, but more than 95% of the nitrate added disappeared (Fig. 2). Nitrite was not found in the effluent. Similarly, no degradation of CB under anoxic, nitrate-reducing conditions (2 mM nitrate) was observed in anoxic batch enrichment cultures made of aquifer sediments and ground water (data not shown).

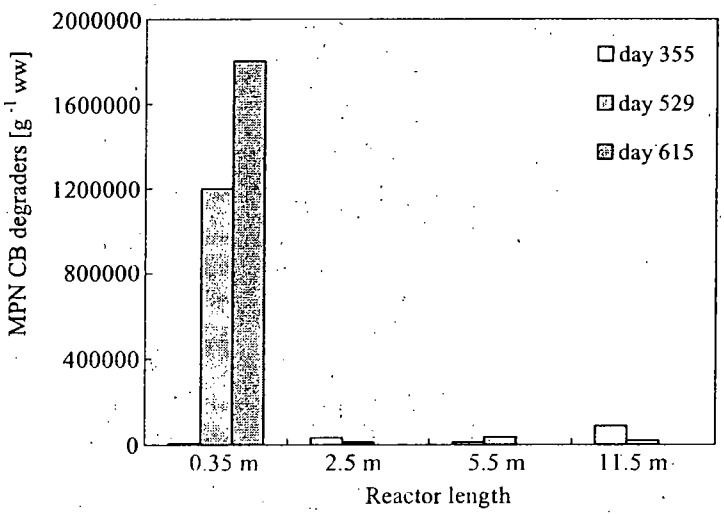

Fig. 4. Viable cell counts (MPN) of CB degrading bacteria in sediment samples from different reactor zones, reactor 1b. Data indicate that CB degrading bacteria were grown in the front part of the reactor after hydrogen peroxide was continuously added.

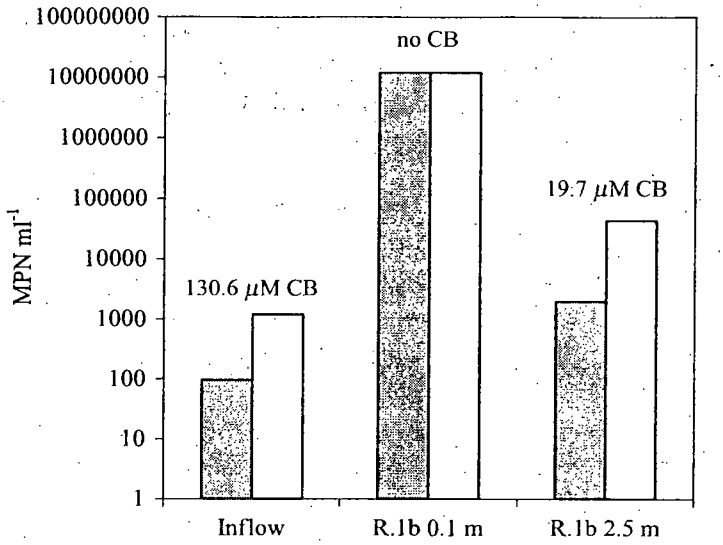

Fig. 5. Viable cell counts (MPN) of aerobic bacteria (white bars) and CB degrading bacteria (grey bars) of the inflowing groundwater and reactor water from 0.1 and 2.5 m, reactor 1b, operating day 696. The corresponding CB concentrations are indicated.

3.2. Reactor operation under conditions of hydrogen peroxide (2.94 mM) and nitrate (2 mM) dosage

Beginning with operating day 363, the reactor was amended with hydrogen peroxide (2.94 mM) and nitrate (2 mM). No nutrients were added, since the ground water contains nutrients (phosphate, ammonium, sulfate) in sufficient amounts for a productive degradation of the in situ CB concentrations (see Section 2.1); furthermore, a complete degradation of CB in the ground water under oxic conditions without addition of nutrients had been already observed in laboratory batch experiments (Lorbeer and Vogt, unpublished data; Dermietzel and Vieth, 2002). Beginning with operating day 450, CB effluent concentrations slightly decreased until operating day 630; thenceforward,

Table 1
CB-degrading strains from reactor sediments, isolated from the highest grown dilution series for viable cell counts (MPN) for aerobic CB-degrading bacteria

Genera	Number of isolated strains
Rhodococcus sp.	12
Pseudomonas sp.	11
Xanthobacter sp.	2
Acidovorax sp.	1
Paenibacillus sp.	1
Kocuria sp.	1
Stenotrophomonas sp.	1

concentrations were balanced between 49 and 67 μM CB. The CB concentrations of the influent dropped between operation days 565 and 610 from more than 200 μM to approximately 110 μM (for unknown reasons), but slightly increased in the following. Inside the reactor, on operating day 709, no CB was detectable in the lowermost sampling reactor zone (0.1 m; Fig. 3). However, CB concentrations increased linearly to around 30 μM at 4 m reactor height; from 4 m to the effluent (12 m), CB concentrations increased to a lesser extent, reaching a final concentration of 52 μM. The increase of the CB concentrations is thought to be caused by desorption from lignite (see discussion). The nitrate concentrations in the reactor decreased uniformly to final effluent concentrations lower than 120 μM nitrate; nitrite was detectable, but never exceeded concentrations of 40 μM (Fig. 3).

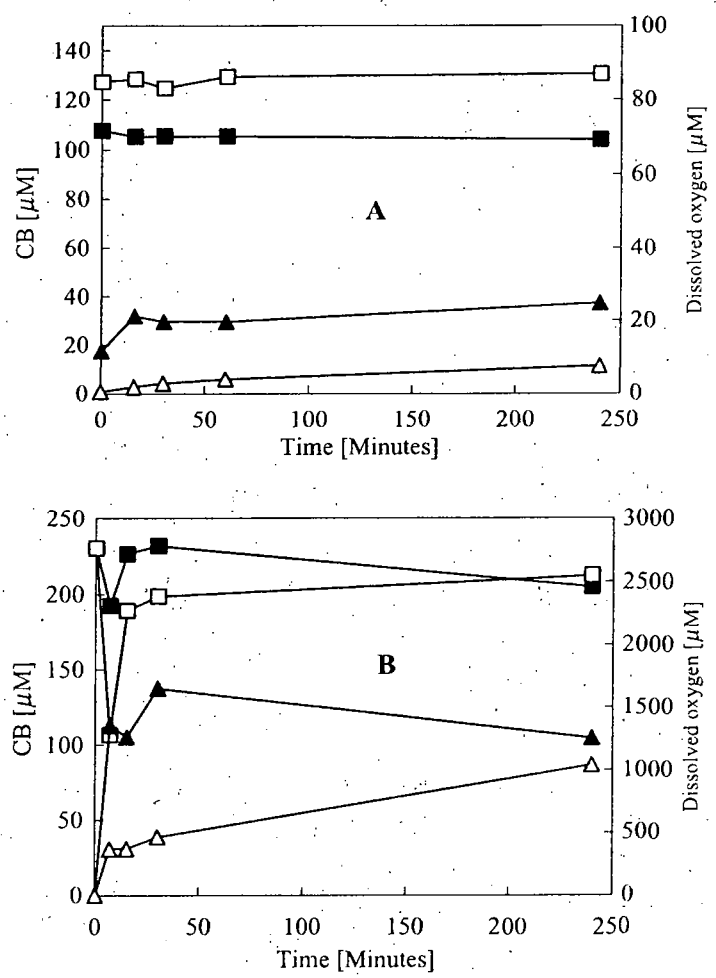

Fig. 6. Oxygen releasing rate and stability of CB after addition of hydrogen peroxide (2.94 mM) in (A) ground water of horizontal well 5 (influent of the reactors, not H_2O_2-adapted, sampled on operation day 705), and (B) reactor water from sampling point 0.1 m (reactor 1b, hydrogen peroxide-adapted, sampled on operation day 733). Note that units in (A) and (B) are different. △ oxygen, biotic; ▲ oygen, abiotic; ■ CB, biotic; □ CB, abiotic.

3.3. Evidences for aerobic microbial degradation of CB mediated by hydrogen peroxide

As shown in Fig. 4, 166 and 300 days after hydrogen peroxide (2.94 mM) and nitrate (2 mM) had been started to dose, the MPN counts of aerobic CB degraders from sediment samples from the front part of the reactor (0.35 m height) were increased by two orders of magnitude compared to the reactor operation under denitrifying conditions. In upper sediments of the reactor, MPN counts of CB degraders were rather balanced. On operating day 696, MPN counts for CB degraders in reactor water from the lowermost reactor sample port (0.1 m) accounted for 10^7 cells ml^{-1}, up to five orders of magnitude higher than in the inflowing ground water and the same value as measured for cultivable aerobic bacteria (Fig. 5). Correspondingly, no CB was detected in the water from a reactor height of 0.1 m (Fig. 5). In water samples from an upper reactor zone (2.5 m), counts for CB degraders were four orders of magnitude lower than in the water from the reactor bottom (Fig. 5). In contrast to reactor water from 0.1 m, water from a reactor height of 2.5 m contained CB (19.7 μM). Several taxonomically different bacteria were isolated from reactor sediments and ground water growing on CB as the sole source of carbon and energy. Most of the isolates belong to the genera *Rhodococcus* and *Pseudomonas* (Table 1). As determined by an enzymatic assay, all strains tested so far cleaved the aromatic ring of benzene and CB exclusively in the *ortho* position (by catechol 1,2-dioxygenases types I and II, respectively) after growing on the substrates under fully oxic conditions in batch

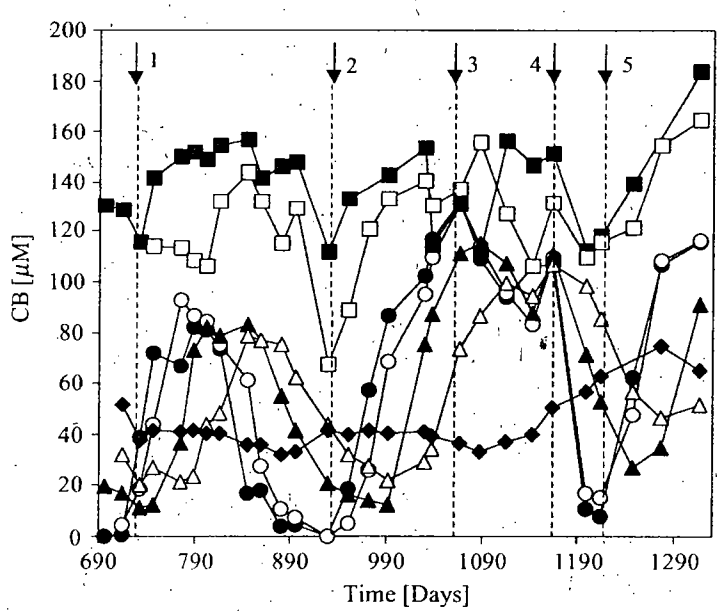

Fig. 7. Time-dependent CB concentrations at different reactor stations, operating days 714–1317. Arrows indicate start of a new H_2O_2/nitrate dosage regime, respectively. Data until operating day 924 were already published (Alfreider et al., 2003; Vogt et al., 2002b). ↓1 (day 719): 0.88 mM H_2O_2, 2 mM NO_3^-; ↓2 (day 930): 0.44 mM H_2O_2, 2 mM NO_3^-; ↓3 (day 1061): 0.88 mM H_2O_2; 2 mM NO_3^-; ↓4 (day 1165): 2.92 mM H_2O_2; 2 mM NO_3^-; ↓5 (day 1221): 0.88 mM H_2O_2; 2 mM NO_3^-. ■ horizontal well 5 (influent); □ 'Z'; ● 0.35 m; ○ 0.8 m; ▲ 2.5 m; △ 5.5 m; ♦ effluent.

cultures. To assess whether the disappearance of CB mediated by hydrogen peroxide is mainly due to biological or chemical degradation, the stability of CB under abiotic and biotic conditions was determined in the presence of hydrogen peroxide (2.94 mM), as were the quantities and rates of oxygen release from hydrogen peroxide as an end product of chemical or biological decomposition. In ground water not adapted to hydrogen peroxide, the total amounts of oxygen released were 0.5% and 0.9% of the theoretical maximum value for the complete disproportionation of hydrogen peroxide (= 1.47 mM oxygen; $H_2O_2 \rightarrow 1/2\ O_2 + H_2O$) for abiotic and biotic conditions, respectively (Fig. 6A). In contrast, in water from the lowermost sample port from reactor 1b (0.1 m), the theoretical maximum value for released oxygen exceeded 90% under biotic conditions 7 min after the addition of hydrogen peroxide (Fig. 6B). Under abiotic conditions, the rate of oxygen release was four times lower, reaching 71% of the theoretical maximum value after 240 min' incubation. The clear chemical degradation of CB mediated by hydrogen peroxide

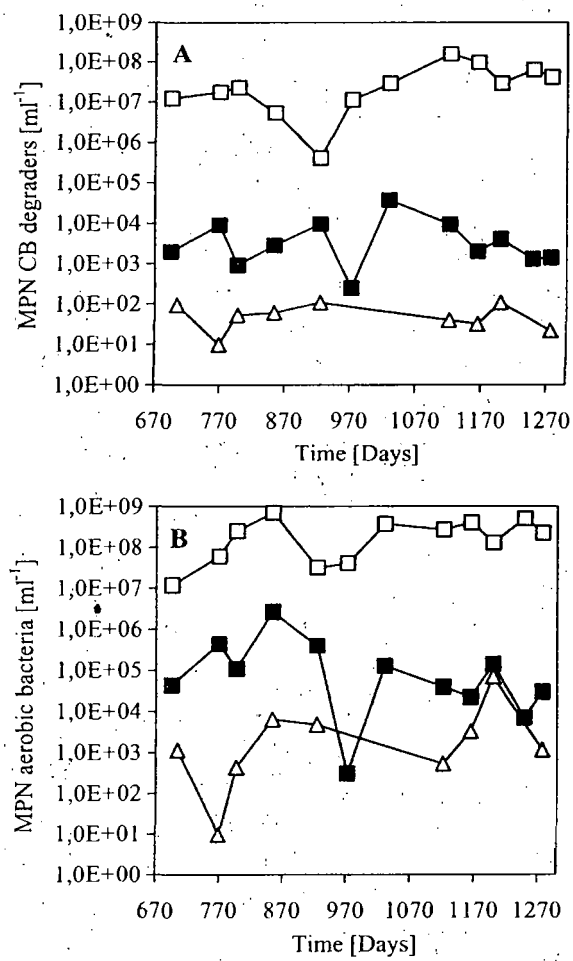

Fig. 8. Time dependent viable cell counts (MPN) of CB metabolising (A) and aerobic (B) bacteria at different reactor stations, operating days 696–1276. Data for CB metabolising bacteria until operating day 924 were already published (Vogt et al., 2002b). □ 0.1 m; ■ 2.5 m; △ horizontal well 5 (influent).

was not observed in either inflowing ground water (Fig. 6A) or reactor water (Fig. 6B), in which 88.7% and 92.2% of the CB added was recovered after 240 min' incubation in biotic and abiotic samples, respectively. Inconsistently, a decrease in CB was measured in both abiotic (>50% decrease) and biotic (17% decrease) reactor water samples shortly after adding hydrogen peroxide (Fig. 6B). This is in fact a purely methodological artefact since much more CB was recovered at the end of the experiment. A major fraction of CB might well be degraded upon catalysis by excess hydrogen peroxide and Fe(II) in the GC headspace vial.

3.4. Reactor operation under conditions of different hydrogen peroxide dosage regimes

At operating day 719, the hydrogen peroxide concentration added to the reactor was reduced to 880 μM, in order to detect how much hydrogen peroxide (and oxygen, respectively) is needed at least for complete degradation of CB in the presence of nitrate (2 mM). The CB concentrations inside the reactor increased immediately after changing the dosage regime, at first in the lowermost reactor zones (Fig. 7). At operating day 784, the CB concentration reached a peak of 82.1 μM CB at 0.35 m reactor height. Subsequently, the CB concentrations decreased. At operating day 924, no CB was detectable in the first 0.8 m of the reactor; hence, the hydrogen peroxide concentration was once more reduced to 440 μM. The CB concentrations in the lowermost reactor zones increased promptly and coincided with the influent concentrations 141 days later. At this point, the dosage regime was reconverted to 880 μM hydrogen peroxide. In the next 104 operating days, the CB concentrations decreased in the reactor at first, but slightly increased later. To test whether

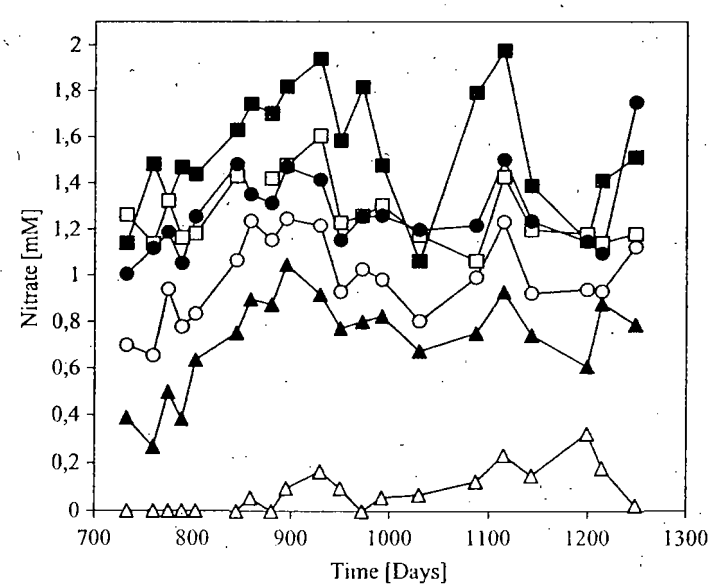

Fig. 9. Time-dependent nitrate concentrations at different reactor stations, operating days 733–1248. Data until operating day 924 were already published (Vogt et al., 2002b). ■ 'Z'; □ 0.35 m; ● 0.8 m; ○ 2.5 m; ▲ 5.5 m; △ effluent.

oxygen limitation is the reason for the incomplete degradation, the hydrogen peroxide concentration was increased to 2.94 mM at operating day 1165, which caused a strong decline of the CB concentrations inside the reactor. Subsequently, the hydrogen peroxide concentration was again reduced to 880 μM, and the CB concentrations again increased inside the reactor. 3-Chlorocatechol was never detected in reactor water samples during the whole experimental time. As can be seen in Fig. 7, the CB concentrations in the reactor pipeline shortly before reactor entrance (sampling station 'Z') were in the majority of cases lower than the CB concentrations in the horizontal well 5 (influent), indicating CB was partly degraded already inside the pipeline. Indeed, reactor water from sampling station 'Z' was enriched in cultivable CB metabolising bacteria (MPN), as determined by random sampling from operating day 972 (4×10^6 MPN ml^{-1}), operating day 1030 (3.7×10^5 MPN ml^{-1}) and operating day 1276 (5×10^5 MPN ml^{-1}). Cultivable CB metabolising bacteria and aerobic bacteria (both MPN) were continuously counted in reactor water samples from reactor stations 0.1 m and 2.5 m as well as in water samples from horizontal well 5 (influent) (Fig. 8A,B). At reactor station 0.1 m, counts for CB metabolising bacteria

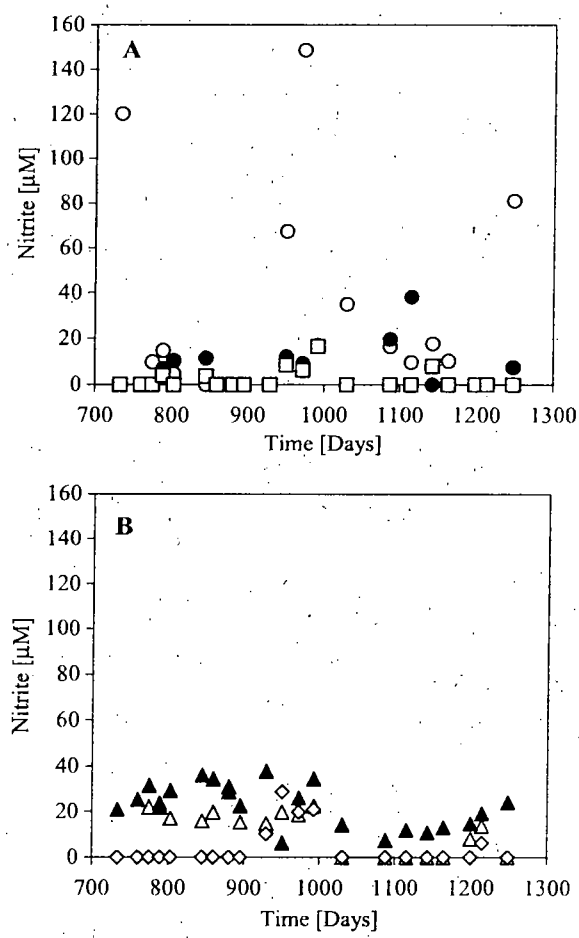

Fig. 10. Time-dependent nitrite concentrations at different reactor stations, operating days 733–1248. (A): 'Z'—0.8 m; (B): 2.5–12 m. ○ 'Z'; ● 0.35 m; □ 0.8 m; △ 2.5 m; ▲ 5.5 m; ◇ effluent.

were, with two exceptions (operating days 854 and 924), between 10^7 and 1.5×10^8 MPN ml^{-1}. These MPN counts were three to five orders of magnitude higher than the counts in reactor water samples from 2.5 m reactor height. The background concentrations of CB degraders in the influent were between 10^1 and 10^2 MPN counts ml^{-1}. The cell counts for aerobic bacteria resembled the counts for CB degraders, but were generally higher (Fig. 8B).

Nitrate was reduced in the whole reactor (Fig. 9), independent from the different hydrogen peroxide dosage regimes. A part of the nitrate seems to be reduced already in the pipeline before reactor entrance, as indicated by the sporadic nitrite accumulation in water from sampling station 'Z' (Fig. 10A). Nitrite was always detected at reactor station 5.5 m (Fig. 10B), in contrast to the samples from the other reactor stations, which contained nitrite irregularly. In general, nitrite concentrations were low, indicating that nitrite was reduced as well. Beginning with operating day 859, nitrate was frequently detected in the effluent, indicating a gradual depletion of the electron donor for nitrate reduction inside the reactor.

4. Discussion

Aerobic biodegradation can be considered an useful strategy for the removal of CB from contaminated (ground) water. Aerobic utilization and mineralization of CB by a bacterial isolate was first reported by Reineke and Knackmuss (1984), and was later demonstrated for other isolates (de Bont et al., 1986; Schraa et al., 1986; Spain and Nishino, 1987; Haigler et al., 1988; Sander et al., 1991; Stoecker et al., 1994; Zaitsev et al., 1995; Kiernicka et al., 1999). The common aerobic degradation pathway of CB is initiated by a dioxygenase attack and the subsequent *ortho* cleavage of the chlorocatechol formed, followed by further breakdown reactions and chloride elimination (Reineke and Knackmuss, 1984; de Bont et al., 1986; Schraa et al., 1986; Spain and Nishino, 1987; Haigler et al., 1988; Sander et al., 1991; Schloemann, 1994; Stoecker et al., 1994). In most cases, CB cannot be degraded by enzymes of the *meta* pathway, because catechol 2,3-dioxygenase is negatively influenced by either 3-chlorocatecol (Klĕcka and Gibson, 1981) or the product of the *meta* cleavage of 3-chlorocatechol, a reactive acylchloride (Bartels et al., 1984). As an exception, a *Pseudomonas* strain was recently described which degrades CB using the *meta* pathway without any toxic effects (Mars et al., 1997). In the pilot plant, at first 2.94 mM hydrogen peroxide was added to the ground water influent, which would lead to a maximum oxygen release of 1.47 mM oxygen, if disproportionation were the only decomposing reaction. CB concentrations in the ground water influent were between 112 and 291 μM CB (Fig. 2), making a maximum of 5–13 mol oxygen per mol CB available for aerobic CB degraders. For a complete aerobic mineralization, 7 mol oxygen per mol CB are required. Assuming that 30% carbon is assimilated, the actual oxygen demand is approximately 2 mol oxygen lower. Therefore, CB degradation should not be limited by oxygen in situ, if 2.94 mM hydrogen peroxide completely decomposes to oxygen and water. As demonstrated in Fig. 6B, oxygen was rapidly and stoichiometrically released in hydrogen peroxide-adapted water sampled from the front part of the reactor after the addition of hydrogen peroxide, proving that biotic disproportionation to oxygen

and water was the dominant hydrogen peroxide decomposition reaction, most probably caused by the enzyme catalase, as described by others previously (Spain et al., 1989; Fiorenza and Ward, 1997; Zappi et al., 2000). Abiotic disproportionation also occurred, but evidently proceeded more slowly than biotic reactions (Fig. 6B), possibly caused by iron ions, since the reactor sediments contain up to 0.65 mass% iron (Vogt et al., 2002a). On the other hand, in non-hydrogen peroxide-adapted inflowing ground water, biotic and abiotic oxygen release was irrelevant (Fig. 6A). Furthermore, CB was rather stable in the presence of 2.94 mM hydrogen peroxide (Fig. 6A,B), indicating that abiotic degradation reactions of CB caused by hydrogen peroxide could only play a minor role in the liquid phase of the reactor, if all. The rapid oxygen release observed in hydrogen peroxide-adapted reactor water is a strong indication that perhaps all the releasable oxygen is indeed available for microorganisms in the bottom of the reactor. Consequently, CB degraders ought to be enriched in the system after supplying hydrogen peroxide, and as shown in Figs. 4 and 5, this enrichment did in fact happen in the front part of the reactor. Correspondingly, no CB was detected in 0.1 m reactor height on operating days 696 and 709. This proves that oxygen was used by the bacteria for the productive degradation of CB, and also that oxygen was the only limited factor for the aerobic biodegradation of CB. MPN counts for aerobic bacteria and CB degraders were similar in reactor water on operating day 696, indicating that bacterial growth was based exclusively on the degradation of CB in 0.1 m reactor height at this stage (Fig. 5). CB concentrations increased linearly inside the reactor (Fig. 3). This behavior might be caused by the desorption of CB from lignite, because the reactor aquifer sediments contain up to 12.5 mass% lignite (Vogt et al., 2002a). CB, like other halogenated organic compounds, adsorbs easily to lignite (Dermietzel and Christoph, 2001).

Most of the CB degrading strains isolated were identified as Rhodococci and Pseudomonads (Table 1), genera which are well known for including strains with the capability to grow on CB (Spain and Nishino, 1987; Haigler et al., 1988; Stoecker et al., 1994; Zaitsev et al., 1995). Two strains were classified as *Acidovorax* species, a widespread genera and recently detected as highly abundant bacteria in the activated sludge of wastewater treatment plants (Schulze et al., 1999), but not described hitherto for CB degradation. One strain was identified as *Paenibacillus polymyxa*, also a genera not known for CB degradation to date. In all the Bitterfeld isolates tested so far, chlorocatechol 1,2-dioxygenase activity was detected after aerobic growth on CB, indicating that the cells might use the modified *ortho* pathway for CB degradation under this conditions. Reducing the hydrogen peroxide concentration to 880 μM in the reactor led to a maximal oxygen release of 440 μM oxygen. The CB concentration in the influent were between 112 and 157 μM in the following (Fig. 7), thus making a maximum of 2.8–3.9 mol oxygen per mol CB available for aerobic CB degraders. In spite of the low oxygen availability, CB was completely degraded in the reactor system (Vogt et al., 2002b), possibly in consequence of an adaptation of the bacterial population to lower oxygen availability, since the CB concentrations at first increased after reducing the hydrogen peroxide concentration (Fig. 7). Between operating days 733 and 895, several different genes coding for enzymes which are known to operate in CB degradation pathways were shown to be expressed in different reactor water and sediment samples (Alfreider et al., 2003), indicating that the CB metabolising bacterial population was rather heterogeneous, using different pathways for

CB degradation in situ. However, the bacterial population could not resist to lower oxygen availability (440 μM hydrogen peroxide, leading to a maximal oxygen release of 220 μM, thus making a maximum of 1.4–1.9 oxygen per mol CB available for CB degraders), which resulted in the complete failure of CB degradation (Fig. 7). The complete degradation of CB by dosing 880 μM hydrogen peroxide could not restored afterwards (Fig. 7), although the maximal molecules oxygen available per mol CB were in the same range as adjusted in the first phase of dosing 880 μM hydrogen peroxide. The CB degradation was limited by oxygen at this stage, since the dosage of higher hydrogen peroxide concentrations caused a rapid and strong decrease of CB concentrations in lower reactor zones (Fig. 7). As yet, the complete degradation of CB inside the reactor at a hydrogen peroxide concentration of 880 μM could not be reproduced. Although a stable and numerous consortium of bacteria including CB metabolising bacteria had enriched in the lowermost reactor zone (Fig. 8A,B), a shift of the bacterial population towards an higher oxygen demand for CB degradation seems to have occurred during the experimental phase in which the reactor was operated with inadequate amounts of hydrogen peroxide. 3-Chlorocatechol, an intermediary compound of the aerobic CB degradation pathways known to accumulate especially under oxygen-limited conditions (Fritz et al., 1992; Nishino et al., 1992), was never detected in reactor water samples. On the other hand, 3-chlorocatechol can react with oxidants like oxygen or adsorb to aquifer material, thus being fixed in the system and therefore not detectable. Currently, the CB degrading bacterial population inside the reactor is studied more closely. The reactor experiment is still proceeding; it is planned to retain the dosage regime of 880 μM hydrogen peroxide and 2 mM nitrate as long as a *steady state* situation has emerged, and to analyse how the reactor reacts if the nitrate dosage is terminated.

No definite degradation of CB was observed under anoxic denitrifying conditions, neither in the whole reactor during dosage of nitrate alone, nor in higher, anoxic reactor parts during dosage of nitrate and different hydrogen peroxide concentrations. The disappearance of CB under denitrifying conditions has been recently reported by us and others (Dijk et al., 2000; Rosenbrock et al., 2000; Wuensche et al., 2000). Since the results of our preliminary degradation experiments in microcosms and at semi-technical scale had been encouraging (Wuensche et al., 2000), an experimental approach was designed to degrade CB under anoxic, denitrifying conditions at full technical scale in the in situ reactors. However, as shown in this study, our previous encouraging results were not confirmed. We were unable to satisfactorily answer the discrepancies between the results of the different experiments. The fact that CB degradation under anoxic denitrifying conditions failed to appear in the in situ reactors could be due to (a) the lack of essential organic or inorganic factors, (b) inhibition by chemical or physical factors, or (c) the lack of microorganisms able to perform the degradation reaction(s).

The reason for the observed uniform nitrate disappearance in the reactor (Figs. 3 and 9) is rather speculative. Biological nitrate reduction apparently occurred; correspondingly, small amounts of nitrite were detected (Figs. 3 and 10A,B). In general, nitrate was rather poorly reproducible, which could be due to nitrate reduction in the reactor pipelines before reactor entrance. On the other hand, the ground water and aquifer sediments do not contain a carbon source which could be readily oxidized by microorganisms to donate electrons for a continuous nitrate reduction. A potential electron donor for nitrate reduction is

ferrous iron, because the reactor aquifer sediments contain up to 0.65 mass% iron (Vogt et al., 2002a). Autotrophic iron-oxidizing nitrate reducers that grow at neutral pH are widespread (Straub and Buchholz-Cleven, 1998) and have also been detected in ground water (Emerson and Moyer, 1997). In initial enrichments, a ferrous-iron dependent nitrate reduction has already been observed in ground water and reactor aquifer sediments (data not shown), indicating that such bacteria exist in our system. This subject will be investigated more closely in future studies. However, since nitrate reduction usually inhibits sulfate reduction (Londry and Suflita, 1999; Myhr et al., 2002; Percheron et al., 1999)—which is an undesirable respiration process in the in situ reactors, because toxic hydrogen sulfide could be released into the environment—the addition of nitrate to the ground water influent is still useful for this reason, provided that all nitrate is reduced, and toxic nitrite does not accumulate. This is indeed the case.

5. Conclusions

Addition of hydrogen peroxide (and nitrate) led to productive bacterial degradation of CB in an in situ reactor designed for the remediation of a CB-contaminated aquifer system, indicating that oxygen is the only limiting factor for an effective in situ bioremediation. The result indicate that the biochemistry of CB degradation is promising for an enhanced natural attenuation strategy based on the addition of hydrogen peroxide and nitrate, although the hydrogeological mixing issues have not been verified yet.

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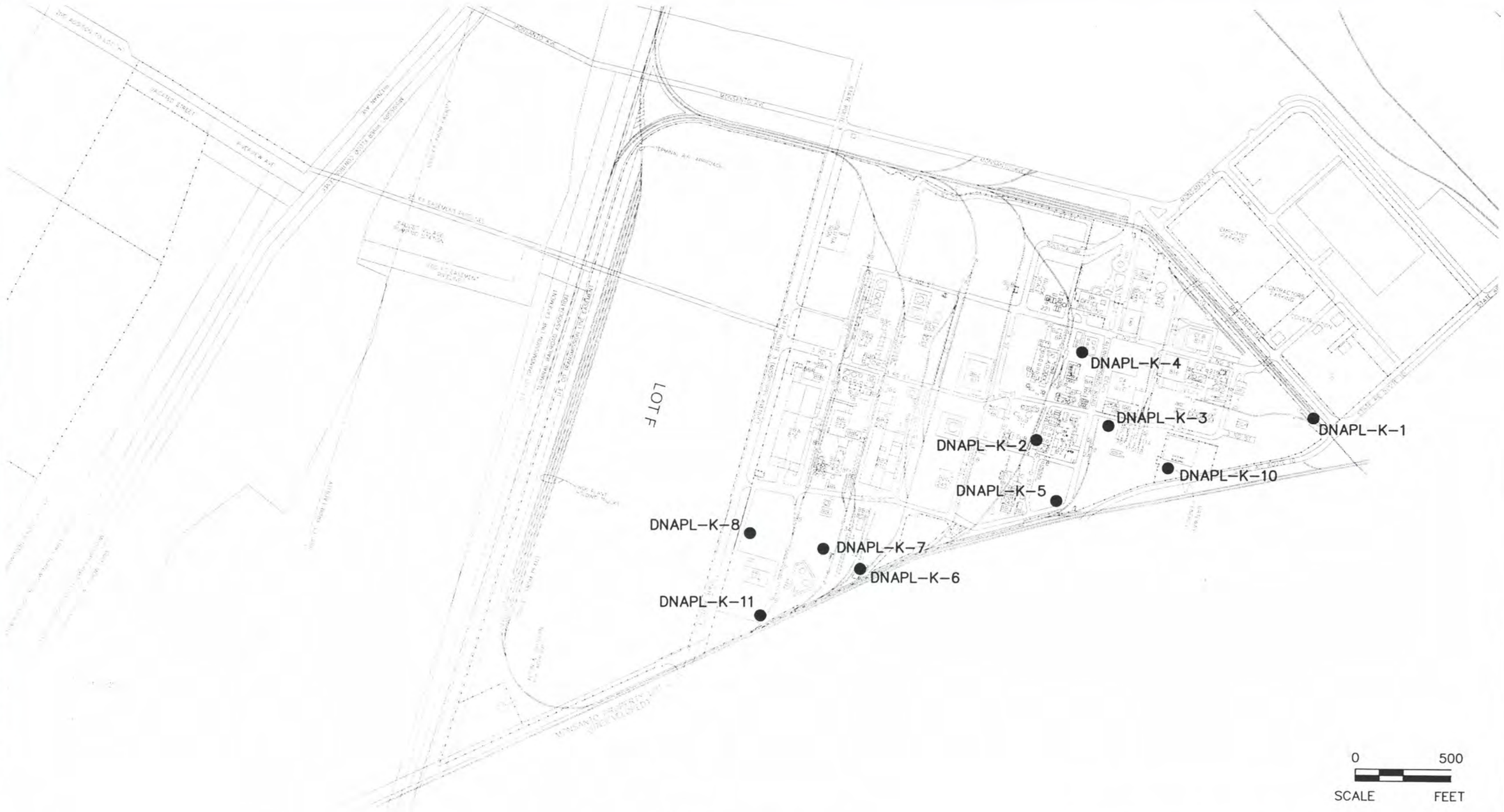
EVS MCB/DCB DATA SET



LEGEND

● SOIL BORING LOCATION

IN-SITU BIOREMEDIATION WORK PLAN MASS REMOVAL TREATABILITY TESTS W.G. KRUMMRICH FACILITY, SAUGET, ILLINOIS	PROJECT NO. 21561388.00000

URS

DRN. BY: 4/9/05 DSGN. BY: cm CHKD. BY:	DNAPL Data Soil Locations	FIG. NO. D-1

File: P:\ENVIRONMENTAL\21561388 (SOLUTIA KRUMMRICH CAS)\2005 WORK PLANS AND RELATED (3 OF THEM)\FABR\FINAL (052705)\APPENDIX D\FIGURES\FIG-D-3 DNAPL DATA SOIL.DWG Last edited: MAY 26, 05 @ 2:35 p.m. by: djdeguzo

APPENDIX D
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 2.1 THROUGH 2.8

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
DNAPL Data Soil Locations (see Figure D-1)					
K-1	2297248.7	702637.3	9	39	49
K-1	2297248.7	702637.3	16.5	0.83	1.9
K-1	2297248.7	702637.3	26.5	0.34	<1
K-1	2297248.7	702637.3	31.5	6.4	0.043
K-1	2297248.7	702637.3	56.5	<1	<1
K-1	2297248.7	702637.3	61.5	<1	<1
K-1	2297248.7	702637.3	76.5	<1	<1
K-1	2297248.7	702637.3	81.5	0.0012	<1
K-1	2297248.7	702637.3	96.5	<1	<1
K-1	2297248.7	702637.3	109	<1	<1
K-1	2297248.7	702637.3	114.5	<1	<1
K-2	2295812.7	702516.4	4	<1	<1
K-2	2295812.7	702516.4	16.5	1.9	3
K-2	2295812.7	702516.4	26.5	5.6	3.19
K-2	2295812.7	702516.4	39.5	2.4	<1
K-2	2295812.7	702516.4	46.5	2.8	<1
K-2	2295812.7	702516.4	56	2.3	<1
K-2	2295812.7	702516.4	69	12	2.09
K-2	2295812.7	702516.4	74	3.4	<1
K-2	2295812.7	702516.4	84	16	<1
K-2	2295812.7	702516.4	94	0.62	17.25
K-2	2295812.7	702516.4	106.5	3.6	5.63
K-3	2296185.9	702591.7	9	170	307
K-3	2296185.9	702591.7	14	2300	4330
K-3	2296185.9	702591.7	14	860	6280
K-3	2296185.9	702591.7	24	200	1284
K-3	2296185.9	702591.7	36.5	380	137.8
K-3	2296185.9	702591.7	46.5	570	1962
K-3	2296185.9	702591.7	58	57	43.7
K-3	2296185.9	702591.7	61.5	38	103.6
K-3	2296185.9	702591.7	61.5	50	79.7
K-3	2296185.9	702591.7	74	91	547
K-3	2296185.9	702591.7	88	0.74	23.3
K-3	2296185.9	702591.7	96.5	0.59	0.524
K-3	2296185.9	702591.7	108	0.12	0.855
K-4	2296048.7	702975.9	9	1600	13850
K-4	2296048.7	702975.9	16.5	130	3830
K-4	2296048.7	702975.9	16.5	1600	2950
K-4	2296048.7	702975.9	29	460	38.64

Notes:
1) <1 ppm indicates sample results was below the lowest concentration depicted on the figure. N.A. indicates the sample was not analyzed.
2) ft bgs = feet below ground surface

APPENDIX D
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 2.1 THROUGH 2.8

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
DNAPL Data Soil Locations (see Figure D-1)					
K-4	2296048.7	702975.9	39	27	12.1
K-4	2296048.7	702975.9	44	32	44.7
K-4	2296048.7	702975.9	59	15	7.67
K-4	2296048.7	702975.9	61.5	7.9	2.17
K-4	2296048.7	702975.9	76.5	130	51
K-4	2296048.7	702975.9	81.5	0.1	16.2
K-4	2296048.7	702975.9	91.5	1.9	12
K-4	2296048.7	702975.9	109	0.71	0.137
K-4	2296048.7	702975.9	109	1.1	0.133
K-4	2296048.7	702975.9	110.75	11	77.9
K-5	2295917.6	702200.9	4	4.9	11.05
K-5	2295917.6	702200.9	14	<1	7.24
K-5	2295917.6	702200.9	21.5	<1	41
K-5	2295917.6	702200.9	31.5	<1	0.179
K-5	2295917.6	702200.9	46.5	16	0.062
K-5	2295917.6	702200.9	56.5	0.14	<1
K-5	2295917.6	702200.9	66.5	0.16	<1
K-5	2295917.6	702200.9	74	0.18	<1
K-5	2295917.6	702200.9	84	0.06	<1
K-5	2295917.6	702200.9	91.5	0.01	<1
K-5	2295917.6	702200.9	107	N.A.	<1
K-5	2295917.6	702200.9	110	0.05	N.A.
K-5	2295917.6	702200.9	114.5	10	0.46
K-6	2294900.8	701842.4	9	4.2	0.154
K-6	2294900.8	701842.4	16.5	0.023	0.052
K-6	2294900.8	701842.4	26.5	0.0026	<1
K-6	2294900.8	701842.4	34	<1	<1
K-6	2294900.8	701842.4	41.5	0.016	<1
K-6	2294900.8	701842.4	51.5	0.0071	<1
K-6	2294900.8	701842.4	66.5	0.14	0.088
K-6	2294900.8	701842.4	74	0.032	0.24
K-6	2294900.8	701842.4	86.5	0.0038	0.048
K-6	2294900.8	701842.4	96.5	0.0025	<1
K-6	2294900.8	701842.4	109	0.0036	<1
K-6	2294900.8	701842.4	11.5	0.003	0.039
K-7	2294707.9	701947.3	1.5	0.0063	<1
K-7	2294707.9	701947.3	19	0.19	0.093
K-7	2294707.9	701947.3	29	4.7	0.037
K-7	2294707.9	701947.3	31.5	2.7	0.036

Notes:

1) <1 ppm indicates sample results was below the lowest concentration depicted on the figure. N.A. indicates the sample was not analyzed.

2) ft bgs = feet below ground surface

APPENDIX D
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 2.1 THROUGH 2.8

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
DNAPL Data Soil Locations (see Figure D-1)					
K-7	2294707.9	701947.3	41.5	0.064	0.16
K-7	2294707.9	701947.3	59	0.019	0.035
K-7	2294707.9	701947.3	69	0.028	<1
K-7	2294707.9	701947.3	74	0.025	<1
K-7	2294707.9	701947.3	84	0.0062	<1
K-7	2294707.9	701947.3	91.5	0.0076	<1
K-7	2294707.9	701947.3	109	0.037	0.071
K-7	2294707.9	701947.3	11.5	<1	0.11
K-8	2294328.4	702026.8	6.5	<1	<1
K-8	2294328.4	702026.8	16.5	<1	<1
K-8	2294328.4	702026.8	24	<1	<1
K-8	2294328.4	702026.8	24	<1	<1
K-8	2294328.4	702026.8	31.5	<1	<1
K-8	2294328.4	702026.8	46.5	7.4	<1
K-8	2294328.4	702026.8	56.5	12	<1
K-8	2294328.4	702026.8	64	6.8	0.135
K-8	2294328.4	702026.8	74	<1	<1
K-8	2294328.4	702026.8	89	0.0021	<1
K-8	2294328.4	702026.8	94	0.0022	<1
K-8	2294328.4	702026.8	106.5	0.0014	<1
K-8	2294328.4	702026.8	111.5	0.073	<1
K-10	2296495	702372.2	9.75	<1	<1
K-10	2296495	702372.2	19.75	0.0016	0.041
K-10	2296495	702372.2	22.25	0.0034	<1
K-10	2296495	702372.2	41.75	0.076	<1
K-10	2296495	702372.2	46.75	0.26	<1
K-10	2296495	702372.2	59.25	<1	<1
K-10	2296495	702372.2	67.25	<1	<1
K-10	2296495	702372.2	81.25	<1	<1
K-10	2296495	702372.2	91.75	<1	<1
K-10	2296495	702372.2	107.25	0.057	0.181
K-10	2296495	702372.2	107.25	0.056	0.647
K-10	2296495	702372.2	112.25	0.073	0.26
K-11	2294384.2	701602.1	7.25	0.009	<1
K-11	2294384.2	701602.1	14.75	0.014	<1
K-11	2294384.2	701602.1	19.75	0.0019	<1
K-11	2294384.2	701602.1	34.25	0.0058	<1
K-11	2294384.2	701602.1	46.75	0.12	0.1
K-11	2294384.2	701602.1	59.75	0.26	<1

Notes:

1) <1 ppm indicates sample results was below the lowest concentration depicted on the figure. N.A. indicates the sample was not analyzed.

2) ft bgs = feet below ground surface

APPENDIX D
ENVIRONMENTAL VISUALIZATION SYSTEM DATA SET FOR FIGURES 2.1 THROUGH 2.8

Point ID	Easting	Northing	Depth (ft bgs)	MCB Concentration (ppm)	DCB Concentration (ppm)
DNAPL Data Soil Locations (see Figure D-1)					
K-11	2294384.2	701602.1	69.25	0.097	<1
K-11	2294384.2	701602.1	74.25	<1	<1
K-11	2294384.2	701602.1	91.75	0.032	<1
K-11	2294384.2	701602.1	102.25	0.13	0.085
K-11	2294384.2	701602.1	102.25	0.39	0.18
K-11	2294384.2	701602.1	107.25	0.12	0.2

Notes:
1) <1 ppm indicates sample results was below the lowest concentration depicted on the figure. N.A. indicates the sample was not analyzed.
2) ft bgs = feet below ground surface

FIELD SAMPLING PLAN

FIELD SAMPLING PLAN/QUALITY ASSURANCE PROJECT PLAN

IN-SITU BIOREMEDIATION

MASS REMOVAL TREATABILITY TEST

Solutia, Inc.

W,G. Krummrich Facility

Sauget, Illinois

May 27, 2005

Prepared for
Solutia Inc.
575 Maryville Centre Drive
St. Louis, MO 63141

May 2005

URS

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Project #21561388

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Extractable Organic Halides - Method 9023
Moisture Content – ASTM D 2216
Particle Size ASTM D 422
Permeability ASTM D 2434 (granular soil), ASTM D 5084 (fine grain)

Appendix C Chain of Custody

SECTIONONE Project Description

1.1 INTRODUCTION

On August 27, 2004, Solutia Inc. submitted to USEPA, a Corrective Measures Study (CMS) Report for the W.G Krummrich facility in Sauget, Illinois. On November 18, 2004, USEPA issued 51 pages of comments on Volumes I, II and III of the W.G. Krummrich RCRA CMS, including 21 general comments and 71 specific comments. A "RCRA Corrective Measure Study (CMS) Response to Comments (CMS RTC)" was submitted by Solutia on February 9, 2005. On May 4, 2005 USEPA responded to the CMS .

In partial response to USEPA's November 18, 2004, and May 4, 2005 comments, Solutia will undertake bench-scale treatability tests, to assess whether or not dense non-aqueous phase liquid (DNAPL) mass removal at the Former Chlorobenzene Process Area. These bench-scale treatability tests are designed to provide a yes/no answer as to whether or not it is technically feasible to remove contaminant mass in the Former Chlorobenzene Process Area.

This Field Sampling Plan describes the sample collection and sample analysis procedures that will be used to collect and analyze the mass removal treatability test soil samples.

SECTION TWO Project Objectives and Rationale

2.1 OBJECTIVES AND RATIONALE

In-Situ Bioremediation [i.e. enhanced aerobic bioremediation (EABR)] was identified as the best technology for performing bench-scale MCB/DCB DNAPL mass removal treatability tests on saturated soil samples from the Middle and Deep Hydrogeologic Units at the Former Chlorobenzene Process Area. See **Figure 1.** Because USEPA required in-situ thermal desorption treatability testing of a sample from the saturated SHU (15 ft to 35 ft bgs), a saturated SHU soil sample was added to the EABR Bench-Scale Mass Removal Treatability Test Work Plan to allow comparison of these two in-situ treatment technologies.

Soil samples for the bench-scale EABR treatability tests will be collected from the saturated SHU unit (15 ft to 35 ft bgs), and from the MHU-DHU unit (35 to 50 ft bgs) from the Former Chlorobenzene Process Area. In addition, samples for characterization will be collected from these locations. The proposed sampling locations are shown on **Figure 2.**

This Field Sampling Plan (FSP) describes the sampling procedures for the collection of soil samples for the baseline and bench-scale treatability tests. In addition, the FSP provides objectives, organization, functional activities, and specific Quality Assurance (QA) and Quality Control (QC) activities for sampling, sample handling and storage, chain of custody, and laboratory and field analysis efforts associated with sampling of environmental media as in accordance to EPA Region 5 Model Quality Assurance Project Plan (QAPP). Field Sampling Procedures are located in **Appendix A.**

URS Corporation (URS) will perform the field activities, in accordance to the FSP, Standard Operation Procedures (SOPs), and an approved Health Safety Plan (HASP). URS will coordinate with Solutia personnel to obtain the appropriate permits and clearance to perform the subsurface activities.

Severn-Trent Laboratories (STL) Savannah, Georgia will provide analytical services for this FSP. Geotechnical testing analysis may be provided by STL out of Burlington, New Hampshire, or URS geotechnical out of Totowa, NJ. Chemical and geotechnical testing will be conducted in accordance with the Laboratory SOPs located in **Appendix B.**

After the collection of baseline samples, bench-scale treatability test samples will be collected from the same and adjacent locations from where the baseline samples were collected. The treatability samples will be properly packaged and shipped to Groundwater Services Inc. (GSI) for preparation of treatability tests.

SECTION TWO Project Objectives and Rationale

The efficacy of enhanced aerobic bioremediation will be evaluated by comparison soil phase MCB/DCB concentrations from before and after treatment. In addition, the mass flux enhancement due to bioremediation will be evaluated by comparison of mass removal rates during the equilibrium period to removal rates after oxygen addition.

Upon completion laboratory analyses and data validation, a study report that describes testing protocols, treatability test results, and includes all data collected during the study including laboratory notes and reports, will be prepared and submitted to USEPA.

SECTIONTHREE Field Procedures

3.1 SOIL DRILLING AND SAMPLING

A soil sample will be collected for baseline characterization from the saturated SHU in the Former Chlorbenzene Process Area. In addition, a baseline soil sample from the saturated MHU/DHU will be collected from the Former Chlorbenzene Process Area. The samples will be collected from approved sample locations from the estimated depths as shown in **Table 1**. The sample locations are shown on **Figure 2**. The proposed baseline sample locations were selected because these locations contained the highest concentrations detected for MCB, and DCB. The baseline samples will be collected, properly packaged and shipped to STL laboratories for analysis in accordance with the SOP guidelines included in **Appendix A**.

After collection of the baseline samples, additional samples will be collected for the EABR treatability tests. These samples are expected to be collected from same depth intervals immediately adjacent to the baseline sampling locations. Refer to **Table 1** for estimated sample depths.

For the saturated SHU location, approximately two- ½ gallon containers (approximately 10 lbs) will be collected for EABR tests. For the MHU/DHU location, approximately nine- ½ gallons containers (approximately 40 lbs) will be collected for EABR tests.

The above samples will be properly packaged and shipped in accordance to SOP guidelines to GSI in Houston, Texas for homogenization and bench-scale treatability testing.

Borings will be advanced using one or more of various methodologies in order to obtain the adequate soil volume necessary for analysis. Some of the methodologies, include:

Direct Push Technology (Geoprobe®). The Geoprobe® hydraulically drives a stainless steel, acetate-lined MacroCore® sampler (2-inch diameter by 4-foot length) to the desired subsurface sample depths. Continuous samples will be collected from the surface to the proposed sampling depths as shown on **Table 1**. Estimated depths for the saturated SHU and saturated MHU/DHU are approximately 15 to 35 ft, and 35 to 50 ft bgs, respectively. The MacroCore® sampler can retrieve up to 150 in^3 (assuming 100% recovery on a 4 ft soil core). This volume is sufficient to fill up 2 quarts, or approximately one ½ gallon sample container, (or approximately 6.5 lbs per ½ gallon). Multiple probes at each sample location will be necessary to collect the required sample volume. Should larger (large gravel to cobble) size materials be encountered, additional core

samples will be obtained and placed into additional containers. Direct push technology may be a viable option for the collection of shallow samples, and for locations where access is restricted.

Conventional Drilling Technology: 4 ¼ -inch Hollow Stem Augers (HSA) with a 3-in by 5 ft continuous tube sampler will be used to collect the soil samples from the proposed sample locations as shown on **Table 1**. Estimated depths for the saturated SHU and saturated MHU/DHU are approximately 15 to 35 ft, and 35 to 50 ft bgs, respectively. The continuous tube sampler can retrieve up to 339 in^3, (assuming 100% recovery on a 4 ft soil core), or approximately 5 quarts, or approximately 1.25 gallons. Convention drilling technology may be a viable option for collection of deeper samples, assuming there is no access restriction. However, multiple borings at each sample location will be necessary to collect the required sample volume.

Rotosonic Drilling Technology. Rotosonic technologies utilize a 6-inch by 10 ft outer casing with a 4-inch by 10 ft continuous sampler for collection of soil samples. The proposed sample depths are shown on **Table 1**. Estimated depths for the saturated SHU and saturated MHU/DHU are approximately 15 to 35 ft, and 35 to 50 ft bgs, respectively. The continuous tube sampler can retrieve up to 603 in^3, (assuming 100% recovery on a 4 ft soil core), or approximately 10.4 quarts. Rotosonic drilling technology may be the best viable option for collection of deeper samples, assuming that there is no access restriction. In addition, a limited number of borings will be necessary to collect the required sample volume.

Soil borings will be advanced using one, or a combination of the above technologies. The borings will be advanced to the estimated depth as shown in **Table 1**.

Multiple borings adjacent to the boring with the highest constituent concentration will be needed in order to collect the required soil for each EABR treatability tests (i.e., 10, and 40 lbs). The soil sample cores will be collected in four-foot lengths to help ensure that the samples are collected within the horizon of the highest known concentration. Visual observations and PID measurements of the soil core will be made to help ensure representativeness. Additional borings will be located within less than 5 ft from each other to help ensure that a representative soil sample is obtained.

At the completion of each soil boring, the boreholes will be backfilled with bentonite chips instead of bentonite grout to reduce the potential of the grout to come in contact with adjacent soil from the additional borings.

Upon completion, the soil boring locations will be surveyed to obtain X-Y coordinates.

3.2 LOGGING UNCONSOLIDATED SAMPLES

The subsurface stratigraphy will be logged during drilling operations by a qualified URS field scientist in accordance with the USCS protocols. The field scientist will note soil attributes such as color, particle size, consistency, moisture content, structure, plasticity, odor (if obvious) and organic content (if visible). Soil samples from each boring will be visually evaluated for evidence of impact and screened in the field using a Photoionization Detector (PID). Information pertaining to the subsurface soil and drilling conditions will be recorded in the field on a standard field boring log form in accordance to SOP guidelines. Scaled, color digital photographs will be taken of each soil sample to provide a record of materials present at this site.

3.3 SOIL SAMPLE ANALYSIS

The baseline soil samples will be analyzed by STL for the following parameters and methods as shown below and in **Table 2.**

Parameter	Analytical Method
Volatile Organic Compounds (VOCs)	USEPA Method 8260B
Semivolatile Organic Compounds (SVOCs)	USEPA Method 8270C
Polychlorinated Biphenyls	USEPA Method 680
Extractable Organic Halides (EOX)	USEPA Method 9023
Moisture Content	ASTM D 2216
Particle Size	ASTM D 422
Permeability	ASTM D 2434 (Granular Soil) ASTM D 5084 (Fine-Grained Soil)

The bench-scale samples, which are scheduled to be submitted to Kemron will also be analyzed for the following parameters.

Bench-Scale Treatability Tests

Parameter	Analytical Method
VOCs	USEPA Method 8260B
SVOCs	USEPA Method 8270C
PCBs	USEPA Method 680
EOX	USEPA Method 9023
Moisture Content	ASTM D 2216
Particle Size	ASTM D 422

Bench-Scale Treatability Tests

Parameter	Analytical Method
Permeability	ASTM D 2434 (Granular Soil) ASTM D 5084 (Fine-Grained Soil)

GSI will homogenize the bulk samples in accordance to the Work Plan, and SOP guidelines. Submit the necessary QA/QC samples to STL and the Rice University Civil and Environmental Engineering laboratory. It is estimated 10% of samples (one every 10 samples) will be submitted for duplicates. 5 % of samples, or (one every 20 samples) will be submitted for Matrix Spike/Matrix Spike Duplicates (MS/MSD) samples.

SECTIONFOUR Field Documentation and Quality Assurance/Quality Control

Field activities for the W.G. Krummrich site, such as documentation, QA/QC activities, equipment decontamination, and handling of investigation derived waste, and sampling procedures are presented below.

4.1 FIELD DOCUMENTATION

URS personnel will keep a bound field notebook while performing sampling and oversight activities on-site. Forms that will be used include: chain-of-custody, test boring log, and field log, and soil sampling data sheets. The field logbooks will contain tabulated results of field measurements and documentation of field instrument calibration activities. The field logbooks will also record the following:

- Personnel conducting the site activities, their arrival and departure times and their destination at the site
- Incidents and unusual activities that occur on the site such as, but not limited to, accidents, breaches of security, injuries, equipment failures, or weather related problems
- Changes to the FSP and the HASP
- Daily information such as:
  - Work accomplished and the current site status
  - Equipment calibrations, repairs and results
  - Site work zones.
- Date, time, weather conditions, equipment, and personnel on site
- Location where the work was performed
- Specific work activities conducted
  - Work zone and headspace readings.

SECTIONFOUR Field Documentation and Quality Assurance/Quality Control

In the field sampler's individual bound field logbook, samplers will note, with permanent ink, meteorological data, equipment employed for sample collection, calculations, information regarding collection of QA/QC samples, and any observations. All entries will be signed and dated, and any entry, which is to be deleted will have a single cross out which is signed and dated. The following sampling-related information will be recorded in the field logbook by the field sampling team:

- Sample number
- Project identification
- Sampling location
- Required analysis
- Date and time of sample collection
- Type and matrix of sample
- Sampling technique
- Preservative used, if applicable
- Sampling conditions
- Observations
- Initials of the sampler.
- Samples collected
- Depth of borings

Field data documentation procedures will be minimal in scope. Only direct reading instrumentation will be employed in the field. If errors are made, results will be legibly crossed out, initialed, and dated by the field member. Errors will be corrected in a space adjacent to the original entry.

Photographic records will be developed through the use of digital photographs, showing pre-sampling and post-sampling conditions at each site.

4.2 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

To verify field and laboratory procedures, quality assurance/quality control (QA/QC) samples consisting of duplicate samples, matrix spike/matrix spike duplicate (MS/MSD) samples, field blanks and trip blanks may be collected and submitted to the laboratory. It should be noted that no QA/QC sampling is anticipated for the baseline samples. However, QA/QC sampling and procedures at a frequency of 10% for duplicates and blanks and 5 % for MS/MSD will follow during the segregation of aliquots samples for treatability testing.

Samples (including QA/QC samples) will be tracked using appropriate Chain-of-Custody documentation. The Chain-of-Custody procedures are described in Section 4.7.3 of this FSP. A sample chain-of-custody form is also presented in **Appendix C.**

4.3 DECONTAMINATION

In order to reduce the potential for exposure to hazardous materials and limit the possibility of cross contamination of samples, all personnel and equipment will be subject to the decontamination program for this project. All equipment used on-site, from a small handheld PID to a large conventional drilling rig, will be decontaminated prior to beginning work, between sampling locations and/or uses, and prior to demobilizing from the site. Refer to SOP-9 in **Appendix A** of this FSP for decontamination procedures.

4.4 INVESTIGATION DERIVED WASTE

All Investigation Derived Waste (IDW) (i.e. soil cuttings and PPE) will be placed in 55-gallon drums and stored at a centralized area pending appropriate disposal.

4.5 QA/QC PROCEDURES

QA/QC procedures for the field work will consist of equipment test checks.

4.6 SAMPLE DOCUMENTATION

4.6.1. Sample Identification System

The sample identification system will involve the following nomenclature "AA-BBB-CCC-DDD-EE" where:

"AA" will denote

- BS- Baseline Sample
- BT- Bioremediation Treatability Test Sample

"BBB" will denote

- SSH- Saturated Shallow Hydrogeologic Unit
- MDU- Saturated Middle/Deep Hydrogeologic Unit

"CCC" will denote

- CPA- Former Chlorobenzene Process Area
- PMA – Former PCB Manufacturing Area

"DDD" will denote

- 001- Sample Depth

"EE" will denote QA/QC sample

- EB- equipment blank
- AD- analytical duplicate
- MS or MD – Matrix Spike or Matrix Duplicate
- TB- Trip Blank.

4.6.2 Sample Labels

For proper identification in the field and proper tracking by the analytical laboratory, samples will be labeled in a clear and consistent fashion. Sample labels will be waterproof, or sample containers will be sealed in plastic bags. Field personnel will maintain a sampling log sheet containing information sufficient to allow reconstruction of the sample collection and handling procedures at a later time.

A completed sample label will be attached to each investigative or QC sample. The following will be recorded with permanent ink on sample labels by the field sampling team:

- Project name and number
- Sample number identification
- Initials of sampler

- Sampling location (if not already encoded in the sample number)
- Required analysis
- Date and time of sample collection
- Space for laboratory sample number
- Preservative used, if applicable.

4.6.3 Chain-of-Custody Records

Chain-of-custody procedures will be instituted and followed throughout the sampling activities Samples are physical evidence and will be handled according to strict chain-of-custody protocols. The field sampler is personally responsible for the care and custody of the sample until transferred. For proper identification in the field and proper tracking by the analytical laboratory, samples will be labeled in a clear and consistent fashion.

Field personnel will record the following information with permanent ink on the chain-of-custody:

- Project identification and number
- Sample description/location
- Required analysis
- Date and time of sample collection
- Type and matrix of sample
- Number of sample containers
- Analysis requested/comments
- Sampler signature/date/time
- Air bill number.

The laboratory will assign a number for each sample upon receipt. That sample number will be placed on the sample label. The label will be attached to the sample container. A chain-of-custody document providing all information, signatures, dates, and other information, as required

on the example chain-of-custody form in **Appendix C** will be completed by the field sampler and provided for each sample cooler. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the chain-of-custody. The field sampler will sign the chain-of-custody form when relinquishing custody, make a copy to keep with the field logbook, and include the original form in an air-tight plastic bag in the sample cooler with the associated samples.

4.7 DATA MANAGEMENT RETENTION

The field data and documentation, as described in this section, will become a part of the final evidence file. The final evidence file will be the central repository for all documents, which constitute evidence relevant to sampling and analysis activities as described in this FSP and the QAPP. URS is the custodian of the evidence file and maintains the contents of evidence files for the site, including all relevant records, logs, field logbooks, pictures, subcontractor reports, data reviews, and the database management system.

Upon completion of the analyses, URS will begin assimilating the field and laboratory notes. In this way, the file for the samples will be generated. The final file for the samples will be stored at URS and will consist of the following:

- Laboratory data packages, including summary and raw data from the analysis of environmental and QC samples, chromatograms, mass spectra, calibration data, work sheets, and sample preparation notebooks
- Chain-of-custody records
- Data validation reports.

4.8 DATA VALIDATION

Data validation procedures shall be performed for both field and laboratory operations.

4.8.1 Procedures Used to Evaluate Field Data

Procedures to evaluate field data for this project primarily include checking for transcription errors on the part of field crew members and review of field notebooks. This task will be the responsibility of the URS Field Leader, who will otherwise not participate in making any of the field measurements or in adding notes, data, or other information to the notebook.

4.8.2 Procedures to Validate Laboratory Data

Data validation will be performed by the URS QA Manager in accordance with QA/QC criteria established in EPA Region 5 Model QAPP. Excursions from QA/QC criteria will be qualified based on guidance provided in the following documents or the most recent USEPA data validation guidelines:

- *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review*. USEPA 540/R-94/012 (USEPA, October 1999)
- *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*. USEPA 540/R-94/013 (USEPA, 1994d)

The analytical data from each method and matrix will be reviewed for the QC parameters as presented in the following section. Data validators will recalculate 10% of the laboratory sample calculations using raw data when verifying sample results. In addition, data validators will review 10% of the raw data to verify that compound identification was performed correctly and transcription errors are not present.

Data quality will be evaluated using method or laboratory control limits. Any control limits outside of the acceptable range shall be identified and reported. Sample data will be qualified based on excursions from method or laboratory control limits. Data not within control limits require corrective action by the laboratory. Data validators will check corrective actions and results of reanalysis and document these events in the validation report.

Minor deficiencies in the data generation process noted in the data validation will result in approximation of sample data. Approximation of a data point indicates uncertainty in the reported concentration of the chemical but not its assigned identity. Major deficiencies noted in the data, validation will result in the rejection of sample results. Rejected data would be considered unusable for quantitative or qualitative purposes. Data qualifiers may include the following:

U Indicates that the compound was analyzed for, but was not detected. The sample quantitation limit is presented and adjusted for dilution and percent moisture. This qualifier is also used to signify that the detection limit of an analyte was raised as a result of analytes detected in laboratory and/or field blank samples.

J Indicates that the detected sample result should be considered approximate based on excursions from QA/QC criteria.

UJ Indicates that the detection limit for the analyte in this sample should be considered approximate based on excursions from QA/QC criteria.

R Indicates that the previously reported detection limit or sample result has been rejected due to a major excursion from QA/QC criteria, for example percent recoveries of less than ten percent. The data should not be used for qualitative or quantitative purposes.

The following method specific QA/QC parameters will be evaluated (at a minimum) during the data validation, where applicable.

Analyses for VOCs and SVOCs (where applicable)

- Holding times, sample preservation, and percent solids
- Dilutions
- GC/MS tuning criteria
- Initial and continuing calibration
- Blank analysis
- Surrogate recovery
- MS/MSD analysis
- Field duplicate analysis
- Laboratory Control Sample (LCS) analysis
- Internal standards performance
- Compound identification and quantitation
- Reported detection limits
- System performance
- Documentation completeness
- Overall assessment.

Analyses for PCBs, (where applicable):

- Holding times, sample preservation, and percent solids
- Dilutions

- GC performance
- Analytical sequence
- Initial and continuing calibration
- Blank analysis
- Surrogate recovery
- MS/MSD analysis
- Field duplicate analysis
- LCS and MS blank analysis
- Retention time windows
- Analyte identification, quantitation, and reported detection limits
- Cleanup efficiency verification
- Confirmation analysis
- System performance
- Documentation completeness
- Overall assessment.

Analysis for Extractable Organic Halides (EOX), (where applicable):

- Holding times, sample preservation, and percent solids
- Contract required detection limit (CRDL) standard analysis criteria
- Initial and continuing calibration
- Blank analysis
- ICP interference check sample analysis
- Spike duplicate analysis
- Field duplicate analysis LCS analysis
- Laboratory duplicate analysis

- ICP serial dilution analysis
- Furnace atomic absorption analysis
- Verification of instrument parameters
- Instrument detection limits
- Linear ranges
- Analyte quantitation, and reported detection limits
- Documentation completeness
- Overall assessment.

The laboratory will be conducting analyses on samples in accordance with methods listed in Table 2 and the laboratory's SOPs. Data generated by this FSP will be computerized in a format organized to facilitate data review and evaluation. The computerized data set will include the data flags provided by Savannah Labs as well as the data validation results.

The following documentation will supplement the chain-of-custody records:

- Field logbooks and data
- Field collection report
- Photographs and drawings
- Contractor and subcontractor reports
- Correspondence.

The evidence file must be maintained in a secured, limited access area until all submittals for the project have been reviewed and approved, and for a minimum of six years past the submittal date of the final report.

A completed sample label will be attached to each investigative or QC sample and the sample placed in a shipping container. Information to be recorded on sample labels are described in Section 4.7.2 Information to be recorded on chain-of-custody forms is described in Section 4.7.3. The sample identification system used in the field is described in Section 4.7.1.

SECTIONFIVE Sample Packaging and Shipping

Sampling containers will be packed in such a way as to help prevent breakage and cross-contamination. Samples will be shipped in coolers, each containing a chain-of-custody form and ice and ice packs to maintain inside temperature at approximately 4°C. Sample coolers will then be sealed between the lid and sides of the cooler with a custody seal prior to shipment. The custody seal will be an adhesive-backed tape that easily rips if it is disturbed. Samples will be shipped to STL and/or Kemron by common overnight carrier.

Sample transportation will comply with U.S. Department of Transportation and IICAO/IATA (1999) regulations. Special sampling packing provisions will be made for samples requiring additional protection.

Samples will remain in the custody of the sampler until transfer of custody is completed. Transfer consists of:

- Delivery of samples to the laboratory sample custodian
- Signature of the laboratory sample custodian on the chain-of-custody document as receiving the samples, and signature of sampler, as relinquishing the samples.

If a carrier is used to take samples between the sampler and the laboratory; a copy of the air bill must be attached to the chain-of-custody to maintain proof of custody.

SECTIONSIX References

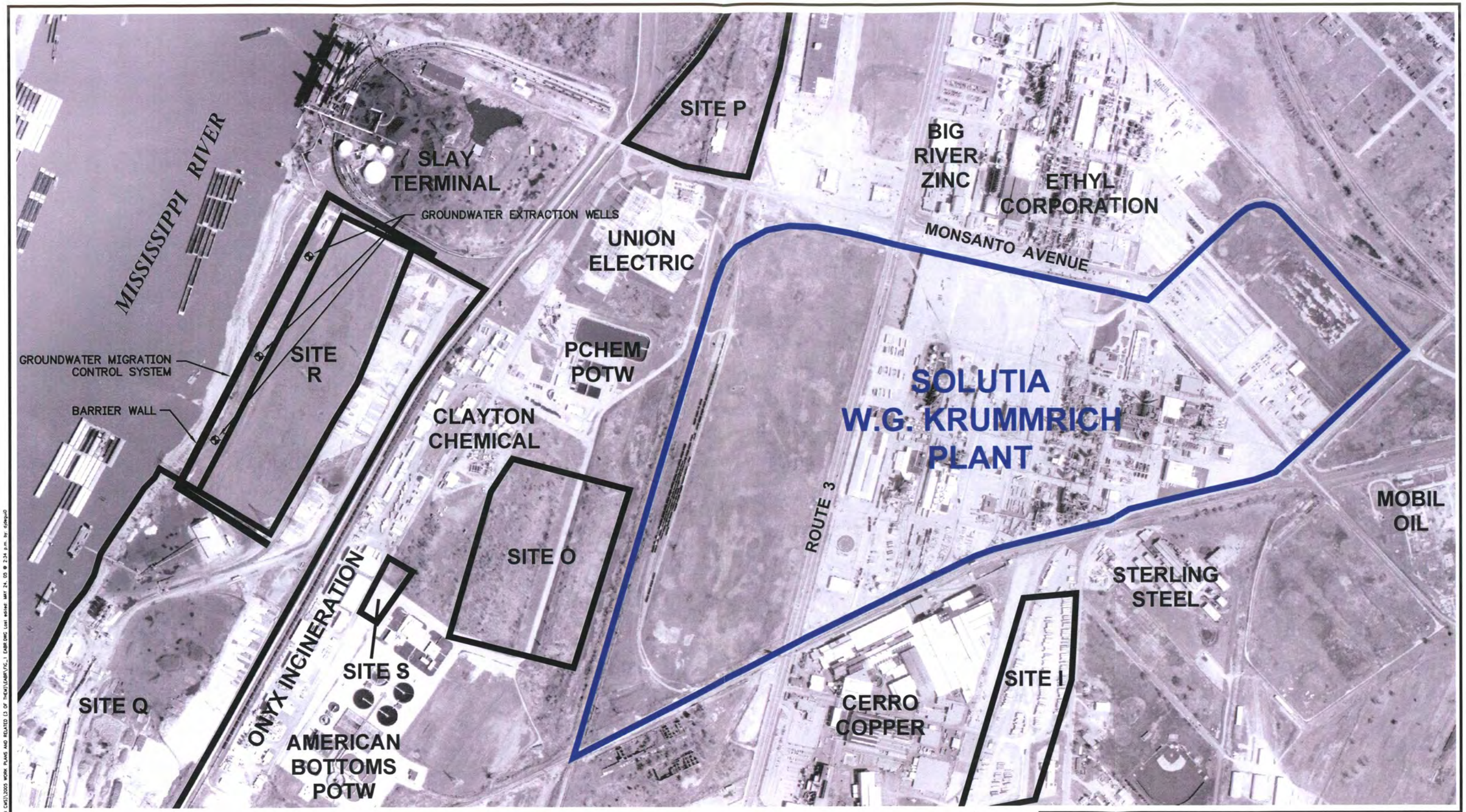
URS Corporation, 2001. *Health and Safety Plan, Sauget Area II Support Sampling Project, Sauget and Cahokia, Illinois. Volume 2C.*

URS Corporation, 2001. *Quality Assurance Project Plan, Sauget Area II Support Sampling Project, Sauget and Cahokia, Illinois, Volume 2B.*

Solutia Inc. 1999. *EFICA and RJ/FS Support Sampling Plan.*

U.S. Environmental Protection Agency (USEPA). 1988. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,* EPA/600/4-89/017, June 1988, Research Triangle Park, NC.

Figures



NOTES:
1) SITE I IS A SAUGET AREA 1 SITE (CERCLA).
2) SITES O, P, Q, R AND S ARE SAUGET AREA 2 SITES (CERCLA).

SOURCE: SURDEX AERIAL PHOTOGRAPHY DATED APRIL 2000.

0 600
SCALE FEET

IN-SITU BIOREMEDIATION SOLUTIA W.G. KRUMMRICH PLANT SAUGET, ILLINOIS	PROJECT NO. 21561388.00000
URS	
DRN. BY: djd 5/24/05 DSGN. BY: jg CHKD. BY:	Site Location Map — FIG. NO. 1

IN-SITU BIOREMEDIATION
SOLUTIA W.G. KRUMMRICH PLANT
SAUGET, ILLINOIS

SAMPLING LOCATIONS

Date:	Project Number:	Drawing Number:
5/24/05	215613888.00000	2
Drawn by: djd	Design by: tja/bbb	Checked by:

URS

File: P:\ENVIRONMENTAL\215613888 (SOLUTIA KRUMMRICH CMS)\2005 WORK PLANS AND RELATED I3 OF THEM\FABR\FIG-2 FABR.DWG Last edited: MAY 24, 05 @ 4:52 p.m. by: dideau0

Tables

Table 1
Proposed Sample Collection for In-Situ Bioremediation
W.G.Krummrich Solutia Facility
Sauget, Illinois

TEST	Area of Sample Collection	Geologic Unit	Estimated Thickness	Estimated Sample Depth	Number of Samples
Baseline	Former Chlorobenzene Process Area	Saturated SHU	15-35 ft	15 to 19 ft	1 - for Chemical Analysis
Baseline	Former Chlorobenzene Process Area	Saturated MHU/DHU	>35 ft	44.5 to 48.5 ft	1 - for Chemical Analysis
Bench-Scale	Former Chlorobenzene Process Area	Saturated SHU	15-35 ft	15 to 19 ft	1 - for Treatability Test
Bench-Scale	Former Chlorobenzene Process Area	Saturated MHU/DHU	>35 ft	44.5 to 48.5 ft	1 - for Treatability Test

Table 2
Sample Container, Preservation
In-Situ Bioremediation
W.G.Krummrich Solutia Facility
Sauget, Illinois

Parameter Group	EPA Reference Method	Sample Container and Preservative	Sample Storage
Volatile Organic Compounds (VOCs) including Chlorbenzene and Dichlorobenzene	8206B	3-5 g glass vials, headspace free 125 mL glass jar (note-1)	4+/ 2° C
Semi Volatile Organic Compounds (SVOCs)	8270C	250 or 500 mL glass jar	4+/ 2° C
Extractable Organic Halides (EOX)	9023	250 mL HDPE jar	4+/ 2° C
Moisture Content	ASTM D 2216	250 mL HDPE jar	4+/ 2° C
Particle Size	ASTM D 422	250 mL HDPE jar	4+/ 2° C
Permeability	ASTM D 2434 ASTM D 5084	250 mL HDPE jar 250 mL HDPE jar	4+/ 2° C 4+/ 2° C

Note 1:Soil samples to be preserved with 5 mL 5% sodium bisulfate, methanol, or frozen in water

APPENDIX A

Standard Operating Procedures

1.0 SCOPE

This procedure describes the methods to be used for the calibration and use of the Photoionization Detector (PID) for field headspace analysis and health and safety monitoring.

2.0 PURPOSE

The purpose of this procedure is to develop and maintain good quality control in field operations and to create uniformity between field personnel involved with PID use.

3.0 EQUIPMENT NEEDED

PID (Model P1 101, probes with 11.7 eV lamp or equivalent), log book, user's manual, calibration gas.

4.0 PROCEDURE

Calibration:

1. Prior to calibration, check the function switch on the control panel to make sure it is in the "OFF" position. The probe nozzle is stored inside the instrument cover. Remove cover plate by pulling up on the pins that fasten the cover plate.
2. Remove the nozzle from the cover. Assemble probe by screwing nozzle into casing.
3. Attach probe cable to instrument box inserting 12 pin interface connector of the probe cable into the connector on the instrument panel. Match the alignment keys and insert connector. Turn connector in clockwise direction until a distinct snap and lock is felt.
4. Turn the function switch to the Battery Check position. When the battery is charged, the needle should read within or above the green battery arc on the scale plate. If the needle is below the green arc or the red LED light comes on, the instrument should be recharged prior to making any measurements.
5. Turn the function switch to the "ON" position. In this position, the UV light source should be on. To verify, glance at the end of the probe for a purple glow. Do Not Look Directly at the Lamp Itself. If the lamp does not come on refer to the Instruction Manual.
6. To zero the instrument, turn the function switch to the standby position and rotate the zero potentiometer until the meter reads zero. Clockwise rotation of the zero potentiometer produces an upscale deflection while counter clockwise rotation yields a downscale deflection. (Note: No zero gas is needed since this is an electronic zero adjustment.) If the span adjustment is changed during instrument calibration, the zero should be rechecked and adjusted. If necessary, wait 15 to 20 seconds to ensure that the zero reading is stable. Readjust as necessary.

Instrument Daily Calibration:

1. Insert one end of T-tube into probe. Insert second end of probe into calibration gas in the 20-200 ppm range. The third end of probe should have the rotometer (bubble meter) attached.

2. Set the function switch in the 0-200 ppm range. Crack the valve on the pressured calibration gas container until a slight flow is indicated on the rotameter. The instrument will draw in the volume required for detection with the rotameter indicating excess flow.
3. Adjust the span potentiometer so that the instrument is reading the exact value of the calibration gas. (Calibration gas value is labeled on the cylinder.)
4. Turn instrument switch to the standby position and check the electronic zero. Reset zero potentiometer as necessary following step 6 above.
5. Record all original and readjusted settings in log book.
6. Set the function switch to 0-20 ppm. Remove the mid-range (20-200 ppm) calibration gas cylinder and attach the low-range (0-20 ppm) calibration gas cylinder as described above.
7. Do not adjust the span potentiometer. The observed reading should be ±3 ppm of the concentration specified for the low-range calibration gas. If this is not the case, recalibrate the mid-range scale repeating Steps 1 through 6 above. If the low-range reading consistently falls outside the recommended tolerance range, the probe light source window likely needs cleaning. Clean window according to instruction manual. When the observed reading is within the required tolerances, the instrument is fully calibrated.

Instrument Calibration Check:

1. Exit the exclusion zone and turn meter to "ON" position. Check that the meter is reading a value of zero.
2. Insert one end of T-tube into probe and other end into calibration gas. The third end of the T-tube should be attached to a flow meter.
3. Crack the valve on the calibration gas and read the value shown by the instrument. Record the value and calibration gas concentration on a field-data sheet.
4. If the value shown by the instrument is greater than ±20% of the calibration gas concentration, take meter outside of exclusion zone and recalibrate as outlined above.

Sample Measurement:

1. Place function switch in 0-20 ppm range for field monitoring. This will allow for most sensitive, quick response in detecting airborne contaminants.
2. Before entering a contaminated area, determine background concentration. This concentration should be used as a reference to readings made in the contaminated area. <u>Under no circumstance should one attempt to adjust the zero or span adjustments while the instrument is being operated in the field.</u>
3. Take measurements in contaminated area, recording readings and locations. Should readings exceed the 0-20 scale, switch the function switch to the 0-200 or 0-2,000 range as appropriate to receive a direct reading. Return the instrument switch to the 0-20 range when readings are reduced to that level. Record measurements on field-data sheet.

Note: The instrument will not function properly in high humidity or when the window to the light housing is dirty. If the instrument response is erratic or lower than expected, recalibrate or obtain a different meter and calibrate as outlined above.

4. When finished, reverse Steps 1 through 6 in Instrument Setup section to shut down the instrument.

1.0 SCOPE

This procedure describes the methods to be used in measuring organic vapors emitted from soils collected with a mechanical device or hand augering device. Results will be used as a field screening for volatile organic vapors.

2.0 PURPOSE

The purpose of this procedure is to maintain uniformity between field personnel performing the measurements and to provide representativeness of readings obtained.

3.0 EQUIPMENT NEEDED

Personal protective equipment, PID, wide-mouth sample jars and aluminum foil or polyethylene bags (Ziploc type), rubber bands, field data forms.

4.0 PROCEDURES

1. Samples are collected and placed in wide-mouth sample jars or polyethylene bags (zip-loc type) so that the jars or bags are approximately half full. The jars or bags are labeled to document sample location and depth, time, date, and field personnel collecting the sample.
2. The glass jar is capped with aluminum foil, a rubber band, and the lid, if it will fit or the bag is zipped shut.
3. The air-tight sample container is then allowed to warm for at least one hour to allow the liberation of soil gases into the headspace.
4. Calibrate and prepare PID for use as per SOP-1.
5. Puncture the aluminum foil or polyethylene bag with the calibrated monitor probe and allow headspace gases to be drawn through the PID unit.
6. Record the highest response obtained on an appropriate sampling log.
7. Remove the punctured foil and seal jar with the proper lid.
8. Allow instrument to return to zero and repeat procedure for next sample.

1.0 OBJECTIVE

To obtain representative subsurface soil samples for geologic logging and physical and chemical laboratory testing.

2.0 EQUIPMENT

The following equipment is typically required:

- Hydraulic percussion hammer Geoprobe
- 1 inch diameter by 3 foot length steel probe rods
- Barrel sampler - 2 1/4 in diameter by 4 ft length
- Acetate liners
- Disposable sample retainers
- Photoionization detector (OVM, PID)
- Surveyor's stakes
- Stainless steel pans, knives and plastic Zip-loc bags
- Sample containers
- Decontamination equipment.

3.0 PROCEDURE

The general procedure for using the Geoprobe equipment for sampling is as follows:

1. Locate boring using facility drawings to check utilities
2. Log boring location on site base map
3. Hydraulically push or drive 1 in. diameter probe rods with barrel sampler attached to the first sample depth
4. Remove barrel sampler and retrieve acetate liner. Visually log and classify the soil, select specimen for physical and/or chemical testing. Record information on field data sheets
5. Decontaminate barrel sampler and install new acetate liner
6. Measure VOC concentrations with PID at top of probe hole prior to sampling the next depth interval (if VOCs are a concern)
7. Insert barrel sampler in exiting probe hole and push or drive sampler to the next sample depth, repeat sampling procedure
8. Repeat Geoprobe sampling until the target depth is reached
9. Record total depth
10. Retrieve probe rods
11. Backfill probe hole with bentonite

12. Place survey stake at boring location
13. Record data collected on boring log and log book
14. Decontaminate equipment.

4.0 DECONTAMINATION

Refer to the HSP for personnel decontamination procedures; refer to Operating Procedure No. 9 (SOP-9) for equipment decontamination procedures.

1.0 SCOPE

The operating procedure describes the ways and means of obtaining a soil sample from a boring via a split-spoon sampler, continuous tube sampler, and/or rotosonic continuous sampler for the purpose of visual description, organic vapor screening, and laboratory analysis.

2.0 PURPOSE

The purpose of this procedure is to assure good quality control in field operations and create uniformity of technique among field personnel.

3.0 EQUIPMENT NEEDED

Split-spoon sampler, continuous tube sampler, rotosonic continuous sampler, tape measure, hand lens, sample/core log, log book, sample containers with labels, chain-of-custody record, knife or trowel, disposable gloves, and plastic sheeting.

4.0 PROCEDURES

1. Place sheeting in a designated area where the split-spoon sampler will be opened.
2. Position sampler over point to be sampled.
3. Drive the sampler by pushing or percussion driven, or rotosonic vibrated down.
4. Remove the sampler, open and extract the sample, and place the sample in the appropriate sample jar or bag for headspace screening as described in SOP-2. Fill out sample label.
6. Proceed to fill sample containers designated for laboratory analysis in the following order per analytical method (as appropriate): VOCs (see SOP-5 regarding the En Core® sampling system for soil VOCs), SVOCs, PCBs, EOX, particle size, Moisture content, and permeability.
7. Examine and record sample description on sample/core log sheet. Make special note of any obviously affected zones.
8. Clean sampler by dry brushing, followed by a detergent wash using Alconox® or equivalent detergent solution, followed by potable water rinse.

1.0 OBJECTIVE

Collection of soil samples for low level VOC analysis that will minimize the loss of contaminants due to volatilization and biodegradation

2.0 EQUIPMENT

The following equipment is required for each sample point.

- Stainless steel T-Handle
- Two or three 5 g EnCore™ samplers (or equivalent)
- One 125 ml jar or one 25 g EnCore™ sampler for screening and/or high level analysis, and dry weight conversions (or as specified by laboratory)
- Paper towels
- Indelible pen
- Clear Tape and Labels.

3.0 PROCEDURE

1. The following general procedures are followed for collection of soil samples with the EnCore™ sampler
2. Remove sampler and cap from package and attach T-handle to sampler body
3. Inspect sampler piston to ensure it can be pushed up to accommodate soil core
4. Push the T-handle and sampler straight down into a freshly exposed surface of soil until the sampler is full
5. Slowly remove sampler and T-handle and inspect bottom of sampler. If sampler is not full, repeat step 3
6. Remove excess soil from the sampler rim lip
7. Place cap on sampler and push down evenly until the end cap clicks on the sampler body
8. Turn the sampler piston until it locks to prevent the sample core from being extruded
9. Repeat procedures 1 through 7 for the other EnCore™ samplers
10. Place EnCore™ samplers in EnCore™ packages and attach sample label
11. Secure label with clear tape and place in cooler, keep sample at 4 degrees Celsius
12. Collect additional soil and place in glass jar or 25 mg sampler to be used for dry weight conversion.

1.0 PURPOSE AND SCOPE

This document defines the standard protocols for sample handling, documentation, and tracking. This SOP serves as a supplement to the Work Plan Addendum and Sampling and Analysis Plan.

2.0 PROCEDURES FOR SAMPLE IDENTIFICATION, HANDLING, AND DOCUMENTATION

Sample Identification

Samples collected during site activities shall have discrete sample identification numbers. These numbers are necessary to identify and track each of the many samples collected for analysis during the life of this project. In addition, the sample identification numbers will be used in the data base to identify and retrieve the analytical results received from the laboratory.

Each sample is identified by a unique code which indicates the site identification number, sample location number, sample matrix identifier, and sample depth. The sample locations will be numbered sequentially starting at location number 0001.
Sample matrix identifiers include the following:

SB - Subsurface Soil Sample
SW - Surface Water Sample
SD - Sediment Sample
TB - Trip Blank
RN - Rinsate (Deionized Water)

An example of the sample identification number codes for a soil sample collected for analysis will be: SB-0A2B-004-05.

Where AUS indicates Additional Uncharacterized Sites, 0A2B indicates the site location, 004 indicates the sample location, SL indicates the sample media, and 05 indicates the sampling interval.

Sample Labeling

Sample labels will be filled out as completely as possible by a designated member of the sampling team prior to beginning field sampling activities each day. The date, time, sampler's signature, and the last field of the sample identification number should not be completed until the time of sample collection. All sample labels shall be filled out using waterproof ink. At a minimum, each label shall contain the following information:

- Sampler's company affiliation
- Site location
- Sample identification code
- Date and time of sample collection
- Analyses required
- Method of preservation (if any) used
- Sample matrix (i.e., soil, groundwater, surface water)
- Sampler's signature

Sample Handling

This section discusses proper sample containers, preservatives, and handling and shipping procedures.

Sample Handling and Shipping

After sample collection, each container will be labeled as described above, and then stored on ice at 4°C in an insulated cooler until packed for shipment to the laboratory. The ice will be double bagged in Ziploc-type storage bags.

The sample containers will be placed in reclosable Ziploc plastic storage bags and wrapped in protective packing material (bubble wrap). Samples will then be placed right side up in a cooler with ice (double bagged using plastic bags), and taped with a custody seal for delivery to the laboratory. Samples will be hand delivered or shipped by overnight express carrier for delivery to the analytical laboratory. All samples must be shipped for laboratory receipt and analyses within specific holding times. This may require daily shipment of samples with short holding times. A chain-of-custody (COC) form will accompany each cooler. The temperature of all coolers will be measured upon receipt at the laboratory. A temperature blank will be included in each cooler for temperature measurement purposes.

Sample Documentation and Tracking

This section describes documentation required in the field notes and on the sample Chain-of-Custody forms.

Field Notes

Documentation of observations and data acquired in the field will provide information on the acquisition of samples and also provide a permanent record of field activities. The observations and data will be recorded using pens with permanent waterproof ink in a permanently bound weatherproof field log book containing consecutively numbered pages.

The information in the field book will include the following as a minimum. Additional information is included in the specific SOPs regarding the field books.

- Project name
- Location of sample
- Sampler's printed name and signature
- Date and time of sample collection
- Sample identification code including QC and QA identification
- Description of samples (matrix sampled)
- Sample depth (if applicable)
- Number and volume of samples
- Sampling methods or reference to the appropriate SOP
- Sample handling, including filtration and preservation, as appropriate for separate sample aliquots
- Analytes of interest
- Field observations
- Results of any field measurements, such as depth to water, pH, temperature, and conductivity
- Personnel present
- Level of PPE used during sampling

Changes or deletions in the field book should be lined out with a single strike mark, initialed, and remain legible. Sufficient information should be recorded to allow the sampling event to be reconstructed without relying on the sampler's memory.

Each page in the field books will be signed by the person making the entry at the end of the day, as well as on the bottom of each page. Anyone making entries in another person's field book will sign and date those entries.

Sample Chain-of-Custody

During field sampling activities, traceability of the sample must be maintained from the time the samples are collected until laboratory data are issued. Initial information concerning collection of the samples will be recorded in the field log book as described above. Information on the custody, transfer, handling, and shipping of samples will be recorded on a COC form.

The sampler will be responsible for initiating and filling out the COC form. The COC will be signed by the sampler when the sampler relinquishes the samples to anyone else. One COC form will be completed for each cooler of samples collected daily. The COC will contain the following information:

- Sampler's signature and affiliation
- Project number
- Date and time of collection
- Sample identification number
- Sample type
- Analyses requested
- Number of containers
- Signature of persons relinquishing custody, dates, and times
- Signature of persons accepting custody, dates, and times
- Method of shipment
- Shipping air bill number (if appropriate).

The person responsible for delivery of the samples to the laboratory will sign the COC form, retain the last copy of the three-part COC form, document the method of shipment, and send the original and the second copy of the COC form with the samples. Upon receipt at the laboratory, the person receiving the samples will sign the COC form and return the second copy to the Project Manager. Copies of the COC forms documenting custody changes and all custody documentation will be received and kept in the central files. The original COC forms will remain with the samples until final disposition of the samples by the laboratory. The analytical laboratory will dispose of the samples in an appropriate manner 60 to 90 days after data reporting. After sample disposal, a copy of the original COC will be sent to the Project Manager by the analytical laboratory to be incorporated into the central files.

DAILY QUALITY CONTROL REPORT

Date _____

Day	S	M	T	W	TH	F	S

Weather	Bright Sun	Clear	Overcast	Rain	Snow
Temp	To 32	32-50	50-70	70-85	85 up
Wind	Still	Moderate	High	Report No.	
Humidity	Dry	Moderate	Humid		

COE Project Manager _____
Project _____
Project No. _____
Contract No. _____

Subcontractors on Site:
Equipment on Site:
Visitors on Site:
W-C Personnel on Site:
Work Performed (including sampling):

Quality Control Activities (including field calibrations):
Health and Safety Levels and Activities:
Problems Encountered/Corrective Actions Taken:
Downtime/Standby:
Special Notes:

By _____ Title _____

1.0 OBJECTIVE

This document defines the standard protocols for sample handling, documentation, and tracking. This SOP serves as a supplement to the Work Plan Addendum and Sampling and Analysis Plan.

2.0 EQUIPMENT

The following equipment will be required for this SOP:

- Waterproof coolers (hard plastic or metal)
- Custody Seals
- Field forms such as COC or sample collection sheet
- Field Notebook
- Ice
- Bubble Wrap
- Clear Tape
- Duct Tape
- Zip Loc Bags
- Sample Containers
- Waterproof Pen
- Permanent Marker.

3.0 SAMPLE CONTAINERS

Certified commercially clean sample containers will be obtained from the contract analytical laboratory. The lab will indicate the type of sample to be collected in each bottle type. The work plan will list the appropriate sample containers for the specific analyses require for each project.

4.0 SAMPLE PRESERVATION

Samples will be preserved at the time of the sample collection. Chemical preservatives, if necessary, will be added to the sample containers either by the laboratory prior to shipment to the field, or in the field by sampling personnel.

After sample collection, each container will be labeled and stored on ice at 4°C in an insulated cooler until packed for shipment until packed for shipment to the laboratory. The ice will be double bagged in Zip Loc storage bags. Freezing samples will not be permitted. Any breakable sample bottles need to be wrapped in protective packing material (bubble wrap) to prevent breakage during shipping.

5.0 SAMPLE HOLD TIMES

Samples will be hand delivered or shipped by overnight express carrier for delivery to the analytical laboratory. All samples must be shipped for laboratory receipt and analyses within specific holding times. This may require daily shipment of samples with short holding times. The hold time varies for each type of analysis. It will be necessary to check with the lab to verify the hold times to determine how frequently samples need to be sent to the lab.

Documentation of observations and data acquired in the field will provide information on the acquisition of samples and also provide a permanent record of field activities. The observations and data will be recorded using pens with permanent waterproof ink in a permanently bound weatherproof field log book containing consecutively numbered pages.

1.0 OBJECTIVE

This document defines the standard procedure for the control and custody of environmental samples.

2.0 EQUIPMENT

The following equipment will be needed for sample control and custody procedures:

- Waterproof coolers (hard plastic or metal)
- Custody Seals
- Field forms such as a Chain of Custody (COC) or sample collection sheet
- Field Notebook
- Ice
- Sample Log-in Book
- Clear Tape
- Duct Tape
- Zip-Loc Bags
- Waterproof pens
- Permanent Markers.

3.0 SAMPLE CONTROL AND CUSTODY PROCEDURES

Once the samples are collected, they must remain in the custody of the sampler or another worker from the site. The samples can also remain unattended in a locked vehicle so tampering with the samples will not be possible. Right before shipment, a custody seal should be placed over the opening of the cooler and then the cooler should be taped all the way around with clear packing tape to prevent tampering with the samples. Samples will be hand delivered or shipped by overnight express carrier for delivery to the analytical laboratory. All samples must be shipped for laboratory receipt and analyses within specific holding times. This may require daily shipment of samples with short holding times. Each cooler will contain a chain of custody (COC) form.

During field sampling activities, traceability of the samples must be maintained from the time the samples are collected until the laboratory data is issued. Initial information concerning the collection of the samples will be recorded in the field log book as outlined in SOP 6 – Sample Handling, Documentation, and Tracking. Information on the custody, transfer, handling, and shipping of samples will be recorded on a COC form.

The sampler will be responsible for initiating and filling out the COC form. The COC will be signed by the sampler or the field person responsible for sample handling when the sampler relinquishes the samples to anyone else. One COC form will be completed for each cooler of samples collected daily and if samples are not hand delivered, the COC will be placed in a Zip-Loc bag and shipped inside the cooler. COC forms will be used to document the transport and

receipt of samples from the field to the lab. Information required on a COC includes the following:

- Samplers signature and affiliation
- Project Number
- Date and time of collection
- Sample identification number
- Sample Type
- Analyses requested
- The total number of containers being sent to the lab for each sample
- The appropriate preservative used
- If any samples are to be placed on hold at the laboratory, this should be clearly indicated on the COC in the comments section
- Signature of person(s) relinquishing custody, dates, and times
- Signature of person(s) accepting custody, dates, and times
- Method of shipment
- Shipping air bill number (if appropriate).

The person responsible for delivery of the samples to the laboratory will sign the COC form, retain the last copy of the three-part COC form, document the method of shipment, and send the original and the second copy of the COC form with the samples. Upon receipt at the laboratory, the person receiving the samples will sign the COC form. The original COC will remain with the samples until final disposition of the samples by the laboratory.

3.2 Drilling and Heavy Equipment

Drilling rigs will be decontaminated at a decontamination station located near a staging area. The decontamination station may be a temporary structure, or mobile trailer, capable of collecting all decontamination fluids. The following steps will be used to decontaminate drilling and heavy equipment.

- Personnel will suit up in proper PPE to reduce the potential for exposure as required by the HASP.
- Equipment showing gross impacted soil materials will be scrapped with a flat-bladed scrapper, and material containerized.
- Equipment that cannot be damaged by water, such as a drill rig, augers, drill bits, sampling equipment, shovels, etc, will be washed with a hot water, high-pressure sprayer, the rinsed with potable water.
- Following decontamination, drilling equipment will be placed on the clean drill rig and moved to the next sampling location. If equipment is not immediately used, it should be stored in a clean designated area.

Equipment rinsante samples of the decontaminated sampling equipment may be collected to verify the effectiveness of the decontamination procedures.

1.0 OBJECTIVE

This document defines the standard procedure for decontamination of equipment used in environmental sites.

2.0 EQUIPMENT

The following equipment will be needed for decontamination procedures:

- Brushes
- Wash Tubs
- Buckets
- Scrapers, flat bladed
- Hot water – high pressure washer
- Paper towels
- Alconox detergent (or equivalent)
- Potable tap water
- Laboratory-grade deionized or distilled water
- Garden-type water sprayers

3.0 DECONTAMINATION PROCEDURES

31. Sampling Equipment

Sampling equipment will be decontaminated at the sampling location under the following procedures:

- Personnel will wear the proper PPE to reduce the potential for exposure as required by the HASP.
- Partially fill two buckets with potable tap water, and add Alconox detergent to one of the buckets
- Use brushes to wash the sampling equipment (i.e. stainless steel bowls, stainless steel spoons, sampling utility knife, etc)
- Rinse sampling equipment in bucket containing potable tap water
- Rinse clean equipment with water sprayers containing distilled water (or equivalent)
- Place decontaminated equipment in clean area and allow to air dry.

APPENDIX B Laboratory Standard Operating Procedures

PREPARATION, SCREENING, AND STORAGE OF VOLATILES SAMPLES

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Approved by:

R. Wayne Robbins — 30 Aug 2002
R. Wayne Robbins — Date

Title: Technical Manager

STL X Savannah __ Tallahassee __ Mobile __ Tampa

1.0 SCOPE AND APPLICATION

This SOP describes the procedures that are used to prepare and screen samples for volatile organic compounds (VOC) in water and soils by GC and GC/MS.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Aqueous samples are checked for sample integrity and pH and are screened by GC/FID. The pH of the sample is documented at log-in. If the sample integrity or hold time has been compromised, the project manager must be notified.

2.2 Soils are routinely collected in Encore devices. Three Encore devices and a bulk container are routinely received for each sample. The bulk sample is used to determine the type of preservation required, the percent solids, and to perform the screening analysis. Samples collected in Encore devices are transferred to vials and preserved within 48 hours of collection. Two of the vials are routinely used for low-level analysis and the third preserved in methanol for high level analysis, if required. If the sample integrity or hold time has been compromised, the project manager must be notified.

2.3 Definitions

VOC – volatile organic compound(s)
VOA – volatile organic analytes (analysis)

2.4 This method is based on the guidance in SW-846 Methods 5021, 5030, 5035.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or that will put yourself or others in a potentially hazardous situation.

3.2 Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, eye protection, or other equipment should be used. Standards and highly contaminated samples should be handled in a hood.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst. These sheets specify the type of hazard that each chemical poses and the procedures that are used to safely handle these materials.

4.0 INTERFERENCES

4.1 VOCs commonly used in the laboratory are potential sources of contamination. Methylene chloride, acetone, Freon-113, MEK, hexane, toluene, and isopropanol are used in the laboratory and tend to present the most problems.

4.2 The volatiles lab must be kept as free from contamination as possible. Highly contaminated samples must be segregated from routine samples. Contact with sections of the laboratory where solvents are used should be minimized. Refrigerator blanks should be prepared, stored, and analyzed to evaluate the sample storage areas for possible contamination. Guidance is provided in SOP AN70: *Compositing and Homogenization of Field Samples and Segregation of Low and High Concentration Volatile and Semivolatile Samples.*

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

5.1 Liquids: Aqueous samples are routinely collected with no headspace in 40mL vials equipped with Teflon-lined caps. The samples are acidified at the time of collection with about 0.30mL of concentrated HCl per 40mL of sample. The acid prevents the biological degradation of the aromatic compounds and prevents the dehydrohalogenation of some of the chlorinated alkanes. The sample must be iced at the time of collection and refrigerated at 4C (less than 6C with no frozen samples) in the lab until analysis.

The holding time for samples preserved with HCl is 14 days for all target compounds. The holding time for unpreserved samples is 7 days.

5.2 Soils: Soils are routinely collected in triplicate in Encore samplers. A "bulk" sample is also routinely collected in a 125-mL jar fitted with a Teflon-lined cap. The bulk sample is used for determining the percent solids and can be used for the methanol extraction if the concentration of the sample collected in the Encore exceeds the working range of the analytical system.

Soils collected in Encore samplers must be analyzed within 48 hours of collection or must be preserved using sodium bisulfate solution within 48 hours of collection. If the sample contains high levels of carbonates, the sample is preserved with water and frozen until the time of analysis. The procedure for preparing soil samples is given in Section 9.2.

The hold time for the preserved sample is 14 days from the date of collection. The hold time for frozen samples is 14 days from the date of collection.

5.3 Field Preserved Soils
Soil samples may be collected in pre-weighed vials containing either sodium bisulfate or methanol preservative. The vials with preservative are routinely weighed in the lab, the tare weight is recorded, and the containers sent to the field. The samples are collected and returned to the lab where the container is weighed and the weight of the sample determined by the difference. The hold time for field preserved samples is 14 days from the date of collection.

5.4 High level soil and waste samples are collected in glass containers (usually 125-mL clear glass) equipped with Teflon-lined caps. Soil samples may also be submitted as core samples contained in Encore samplers, in metal or plastic "tubes", or in 40-mL VOA vials. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples). The holding time for soil and waste samples subjected to methanol extraction is 14 days from date of collection. Extraction and analysis must be completed within 14 days of collection.

5.5 TCLP leachate samples are collected with no headspace in Tedlar bags or syringes. The leachate samples are acidified after the leaching procedure with about 0.10mL of concentrated HCl per 40mL of sample and stored at 4C (less than 6C with no frozen samples) from the time leaching is completed until the analysis. The acidified leachate sample must be analyzed within 14 days of the leaching procedure. If the sample is not acidified, the leachate must be analyzed within 7 days of the leaching procedure.

NOTE: Samples that are suspected of having very high concentrations of VOC should be segregated from the "routine" samples and stored in a manner that will minimize sample and laboratory contamination. See SOP AN70: *Compositing and Homogenization of Field Samples and Segregation of Low and High Concentration Volatile and Semivolatile Samples* for guidance. If possible, keep the field QC in the same storage refrigerator as the samples.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph with flame ionization detector (FID)

6.2 Headspace device: Tekmar 7000 or equivalent

6.3 Data System compatible with the analytical system

6.4 Microsyringes: 100uL

6.5 Gastight syringe: 5mL, 25mL

6.6 Volumetric flasks: various sizes

6.7 Recommended Column: J&W DB-624, 30m x 0.53mmID x 3.0um or equivalent

6.8 Headspace vials with crimp-top septum caps

6.9 40-mL VOA vial with methanol preservative: weigh and record vial before sending to the field

6.10 40-mL VOA vial with sodium sulfate preservative: weigh and record vial before sending to the field

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability*.

7.1 Reagent water - free of volatile contaminants (obtained by purging with inert gas or carbon filtration)

7.2 Methanol - Purge and Trap grade

7.3 Sodium bisulfate - reagent grade. This salt is hydroscopic and should be stored in a dessicator.

7.4 Sodium bisulfate soil preservation solution - Slowly add, while stirring, 200g of sodium bisulfate to a 1.0-L volumetric flask containing about 700mL of reagent water. After the salt has dissolved, dilute to volume with reagent water, transfer to a storage container, and store the solution in an area free from VOC - especially water-soluble solvents such as acetone. The reagent should be tested prior to use by the analysis of a blank containing 5mL of the solution. The reagent is acceptable if it meets the same criteria as a method blank.

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions purchased from vendors or from stock standards prepared from neat materials. Certificates of analysis or purity must be received with all stock solutions or neat compounds. All preparation steps must be in accordance with SOP AN41: *Standard Material Traceability*.

Prepare calibration standards containing the following compounds at 50, 100, 200, 400, 800, and 1600ug/L in reagent water: methlyene chloride, 1,1-dichloroethene, cis-1,2-dichoroethene, chloroform, benzene, trichloroethene, toluene, tetrachloroethene, ethylbenzene, m/p-xylene, o-xylene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2-dichlorobenzene.

Transfer 4mL of the calibration standard to a labeled headspace vial and add 1mL of reagent water. Analyze according to Section 10.

9.0 SAMPLE PREPARATION

Composite samples can be prepared using the guidance in SOP AN70: *Compositing and Homogenization of Field Samples and Segregation of Low and High Concentration Volatile and Semivolatile Samples.*

9.1 Preparation of Aqueous Samples

Aqueous samples are analyzed directly by purge and trap GC and GC/MS. No sample preparation is necessary except to homogenize the sample prior to subsampling. The pH of liquid samples is checked and recorded prior to analysis and recorded on the appropriate log.

9.1.1 Samples are logged into the Volatiles' Liquid Logbook. Three vials are routinely received and the vials are designated A, B, and C. If more than three vials are received, then letter accordingly. Use the last vial for the screening and pH determination.

9.1.2 Check each sample vial at the time of receipt for the presence of "bubbles". If the bubbles are less than 3mm in diameter, the vial is acceptable. If all vials contain bubbles greater than 3mm, notify the department supervisor or project manager that there are no acceptable vials for analysis.

9.1.3 Use the "C" vial (or last vial) for screening and pH check. (If a vial contains air bubbles, then sacrifice this vial for screening and pH determination, since the sample is already compromised. Save acceptable vials for analyis.)

Determine the pH of the sample using narrow range pH paper and record in the Volatiles' Liquid Logbook.

If the sample pH is greater than 2, fill out a 7-Day Hold Sheet and notify the department supervisor. All samples with pH greater than 2 must be analyzed within 7 days of collection. All samples with pH less than 2 must be analyzed within 14 days of collection.

Transfer 4mL from the C vial to a labeled headspace vial and add 1mL of reagent water. Analyze this screening vial according to Section 10. Evaluate the results according to Section 11.

9.1.4 Transfer the A and B vials to the storage racks. Store the screening C vial separately from the A and B vials.

9.2 Preparation of Soil Samples (5035)

The preparation of soil samples must be performed within 48 hours of collection. Three Encore devices and one bulk container are routinely received for each sample. Two of the Encores are prepared for low level analysis, and one is extracted in methanol. The bulk container is used for determining the type of preservation for the low level samples and, if required, for screening. The Encores are labeled as the A, B, and C samples.

NOTE: If soil samples are received in 25-g Encore devices, contact the supervisor immediately to confirm the preparation steps. The procedures given below are to be used as the default.

9.2.1 Low Level Preparation (A and B Vials)

9.2.1.1 Carbonate Test

Transfer a small aliquot (~0.5g) of sample from the bulk container to a 20-mL scintillation vial.

Add approximately 5mL of the sodium bisulfate preservation solution.

If the sample fizzes (effervesces), preserve with volatile-free water and place in a freezer at –10C. If no fizzing is noted, preserve with 5mL of the soil preservation solution (sodium bisulfate) and store at 4C in the soil storage refrigerator.

9.2.1.2 Add a stir bar to a 40-mL vial. Attach the bar code label and ID label to the 40-mL vial. Write the sample ID and vial designation (A or B) on the ID label. Place the vial on the balance and tare the vial and stir bar weight by pressing the autotare button.

9.2.1.3 Transfer the sample from the Encore device to the labeled, tared vial and record the weight of the sample to the nearest 0.01g in the Volatile Soil Sample logbook.

NOTE: If the sample is received in a 25-g Encore device, transfer two 5-g (5.0-5.5g) aliquots from the device to the tared vials (A and B). Transfer a third 5-g aliquot to the C-vial for methanol preservation (Section 9.2.2). A plastic syringe may be used to remove an aliquot of the sample from the 25-g sampler. On average, a 3mL plug of soil will be approximately 5g.

If the sample fizzed during the carbonate test (9.2.1.1), add 5mL of reagent water and freeze at –10C. If the sample did not fizz, add 5mL of the soil preservation solution and store the sample at 4C until the time of analysis. The preserved samples must be analyzed within 14 days of collection.

Place samples from the same log number with the same preservation in a plastic bag and seal. Write the log number and type of preservation on the outside of the bag. For example, put all of the sodium bisulfate preserved samples together, all of the water preserved samples together, and all of the methanol preserved samples together. Do not put samples from different log numbers in the same bag.

9.2.2 Methanol Preservation (C Vial)
A methanol extraction is prepared from the third Encore device or from the bulk container when an Encore is unavailable. Carry out the preparation quickly to minimize the loss of volatiles.

9.2.2.1 Attach the bar code label and ID label to a 40-mL vial. Write the sample ID and vial designation (C) on the ID label. Place the vial on the balance and tare the vial and stir bar weight by pressing the autotare button.

9.2.2.2 Transfer the sample from the Encore to a 40-mL VOA vial.

NOTE: If the sample is received in a 25-g Encore device, transfer 5-g aliquot to the C-vial for methanol preservation after taking the two 5-g aliquots for low level analysis (Section 9.2.1.2).

Add 5mL of methanol and shake vigorously for approximately 10 seconds.

Put in bag and seal. Samples preserved in methanol from the same log number may be put in same bag. Do not put samples from different log numbers in the same bag.

Store in refrigerator at 4C.

9.2.2.3 Transfer 100uL (0.1mL) of the methanol extract (Vial C) to 5mL of reagent water contained in a labeled headspace vial. Analyze this screening vial according to Section 10. Evaluate the results according to Section 11.

9.3 Pre-Weighed Vials with Methanol or Sodium Bisulfate Preservative

9.3.1 Pre-sampling

9.3.1.1 Select number of vials for sampling. Attach label if not already attached but do not obscure the vial identification number. Inspect each vial to ensure that there is preservative at the correct volume, that the cap is secure, and that there is no extraneous material or moisture adhering to the outside of the vial.

9.3.1.2 Weigh the vial and record the weight and vial identification in the appropriate logbook. Record the weight to the nearest 0.01g.

9.3.1.3 Pack the vials and transfer to the shipping and receiving department. Include at least one trip blank with each set of vials.

9.3.2 Post-sampling

9.3.2.1 Remove vials from storage and allow them to come to room temperature.

9.3.2.2 Wipe off any extraneous moisture or material adhering to the outside of the vial.

9.3.2.3 Weigh and record the weight of the vial, sample, and preservative to the nearest 0.01g. Calculate the weight of the sample as:

$$W_{sample}(g) = W_2 - W_1$$

where:
W_2 = weight of sample, vial, and preservative (g)
W_1 = weight of vial and preservative (g)

9.3.2.4 Shake the vial for approximately two minutes.

9.3.2.5 Screening
Remove 100uL (o.10mL) of the extract through the septum and transfer to 5.0mL of water. Screen sample as in Section 10.

9.3.2.6 Store the remaining extract at 4C until the time of analysis.

10.0 PROCEDURE

10.1 Screening Instrument Conditions

The instrument parameters are provided as examples. The actual operating parameters and conditions must be documented in the appropriate log.

Gas Chromatograph Program for DB-624 column:

Initial temperature:	50 C for 2.0 minutes
Temperature Ramp:	16 C per minute
Final Temperature:	200 C for 1.0 minute

Set column flow to provide adequate separation of analytes. Set makeup and detector gases according to manufacturer's instructions.

Tekmar 7000 Headspace Analyzer Parameters:

Temperature to heat vials:	85C
Equilibration time:	10 minutes
Mixing time:	1 minute
Volume of headspace analyzed:	1mL
Heated line temperatures:	100C

10.2 Screening Calibration

Analyze the six calibration standards outlined in Section 8.0. Prepare a calibration curve in accordance with SOP AN67: *Evaluation of Calibration Curves*. An external calibration curve is prepared with nanograms (ng) of compound plotted on the x-axis.

ICAL Criterion: Use professional judgement
CCV Criterion: +/-50% of true value

10.3 Screening Analysis

An ICAL should be analyzed initially and when the percent difference of the CCV exceeds 50%. The CCV and a method blank should be analyzed daily prior to sample screening.

10.3.1 Liquid Samples

Transfer the screening vial from Section 9.1.3 to the autosampler and analyze. Evaluate data according to Section 11.

10.3.2 Soil Samples

Transfer the screening vial from Section 9.2.2.3 to the autosampler and analyze. Evaluate data according to Section 11.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Identify the compounds based on the retention time and compare the nanograms (ng) of compound to the upper level of the liquid or soil calibration curve.

11.2 Liquids: Calculate the dilution (as dilution factor, DF) to run on the instrument as follows:

$$DF = \frac{ng(screen)}{ng(cal)}$$

where:
ng(screen) = nanograms of compound from screening run
ng(cal) = nanograms of upper level of calibration curve

If the ratio is<=1, run at DF=1. If the ratio is >1, run at next highest whole number DF. For example, if ratio is 1.5, run at DF=2.

11.3 Soils: Calculate the dilution (as dilution factor, DF) to run on the instrument as follows:

$$DF = \frac{ng(screen)}{ng(cal)} \otimes 50$$

where:
ng(screen) = nanograms of compound from screening run
ng(cal) = nanograms of upper level of calibration curve

If the ratio is<=5, run at DF=1. If the ratio is >5, run methanol extraction.

NOTE: the factor of 50 is the ratio of the low level soil weight (5g) divided by the weight of sample (0.1g) analyzed in the screening analysis.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

There are no formal QC or QA requirements for this SOP since the results are used to estimate the dilution used for the definitive analysis of the samples. The analyst must use good professional judgement in evaluating the data. A method blank should be analyzed each day screening takes place.

13.0 TROUBLE-SHOOTING AND PREVENTIVE MAINTENANCE

See instrument manufacturer's manual and SOP AN53: *Maintenance Procedures for Laboratory Instruments* for preventive maintenance and troubleshooting guidance.

14.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Excess samples, extracts, reagents, and standards must be disposed in accordance with SOP CA70: *Waste Management.*

15.0 REFERENCES

Test Methods for Evaluating Solid Wastes, Third Edition, SW-846.including Update III U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

VOLATILE COMPOUNDS BY GC/MS (EPA 8260B)

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Approved by: R Wayne Robb — 3 April 2001 (Date)

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STL X Savannah ___ Tallahassee ___ Mobile ___ Tampa West

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedures that can be used to determine the concentration of volatile organic compounds (VOC) in water, wastewater, soils/sediments, wastes, oils, sludges, and solids. The attached quantitation report lists the target compounds, an example of the retention time order of each target compound, the quantitation and confirmation ions of the target compounds, and internal standard assignments.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria for each target compound are listed in Section 5 of the current revisions of the STL Laboratories' *Comprehensive Quality Assurance Plan* and *Corporate Quality Assurance Plan.*

2.0 SUMMARY OF METHOD

2.1 Volatile organic compounds (VOC) are purged from the sample matrix with helium. The VOC are transferred from the sample matrix to the vapor phase. The vapor is swept through a sorbent tube where the VOC are trapped. After the purging is completed, the trap is heated and backflushed with helium to desorb the VOCs onto a GC column. The GC is temperature-programmed to separate the VOC, which are then detected by a mass spectrometer. Qualitative identification of the target compounds in the sample is based on the relative retention time and the mass spectra of the characteristic masses (ions) determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

2.2 Aqueous samples may be purged at ambient conditions (recommended) or at 40C (optional). Five to twenty-five milliliter aliquots of the sample may be purged. The calibration standards and the associated QC must be analyzed under the same conditions and volume.

2.3 Low-level (nominally <1mg/kg) soil samples are purged at 40C in a purge and trap instrument designed to add water and internal standards to the vial containing the sample without breaking the seal. The sample is stirred during purging to thoroughly mix the soil and water. The calibration standards are purged under the same conditions.

2.4 High level soils (nominally >1mg/kg) and waste samples are extracted with methanol-1mL of methanol per gram of sample. An aliquot of the methanol extract is injected into reagent water. The methanol extract/reagent water is purged at ambient temperature using the same instrument conditions and calibration used for aqueous samples.

2.5 This method is based on the guidance in SW-846 Methods 8260B and 5035.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or that will put yourself or others in a potentially hazardous situation.

3.2 Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, eye protection, or other equipment should be used. Standards and highly contaminated samples should be handled in a hood.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst at each lab division. These sheets specify the type of hazard that each chemical poses and the procedures that are used to safely handle these materials.

3.4 The exit vent of the split injector must have a carbon trap in-line to collect the volatile compounds that are vented during the injection of the sample. The traps should be changed a minimum of every three months and disposed of in accordance with STL-SL SOP CA70: *Waste Management.*

4.0 INTERFERENCES

4.1 VOCs commonly used in the laboratory are potential sources of contamination. Methylene chloride, acetone, Freon-113, MEK, hexane, toluene, and isopropanol are used in the laboratory and tend to present the most problems.

4.2 The volatiles lab must be kept as free from contamination as possible. Highly contaminated samples must be segregated from routine samples. Contact with sections of the laboratory where solvents are used should be minimized. Refrigerator blanks should be prepared, stored, and analyzed to evaluate the sample storage areas for possible contamination. Guidance is provided in STL-SL SOP AN70: *Segregation of Low and High Concentration Volatile and Semivolatile Samples.*

4.3 Matrix interferences may be overcome by the use of the secondary ions for quantitation. An example of this is the use of mass 82 for quantitation with chlorobenzene-d5 internal standard when a potential co-eluter, 1,1,1,2-terachloroethane, is a target compound. One of the mass fragments of 1,1,1,2-tetrachloroethane is mass 117, which is the recommended quantitation ion for chlorobenzene-d5. The use of the secondary ions should be used for quantitation in such cases when the lab can clearly demonstrate matrix problems. Mass 58 is recommended for quantitation of acetone due to the elution of a hydrocarbon at the same retention time.

4.4 The analysis of highly contaminated samples (>1mg/L or >1mg/kg) can affect succeeding analyses. Carry-over can occur when low concentration samples are analyzed after high concentration samples. Trap replacement and purging of the entire purging system may be necessary when carry-over is suspected. Reagent blanks must be analyzed when carryover is suspected to demonstrate that the system is free from contamination.

4.5 The Teflon seals of the purge and trap device can absorb and outgas many of the compounds that are included in this method. These Teflon fittings should be periodically checked for integrity. If contamination of the fittings is suspected, the fittings may be heated at 105 C for one hour or replaced.

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

5.1 Liquid samples are collected with no headspace in 40mL vials equipped with Teflon-lined caps. The samples are acidified at the time of collection with about 0.10mL of concentrated HCl per 40mL of sample. The acid prevents the biological degradation of the aromatic compounds and prevents the dehydrohalogenation of some of the chlorinated alkanes. The sample must be iced at the time of collection and refrigerated at 4C (less than 6C with no frozen samples) in the lab until analysis.

Check each sample vial at the time of receipt for the presence of "bubbles". If the bubbles are less than 3mm in diameter, the vial is acceptable. If the bubble is greater than 3mm, use another vial. Notify the department supervisor or project manager if there are no acceptable vials for analysis.

A "sacrificial" vial or the vial used for screening analysis is used to check the sample pH. If the sample pH is greater than 2, notify the department supervisor or project manager. If directed by supervisor or project manager, hydrochloric acid may be added through the septum to bring the pH <2. Do not add more than 400uL (0.40mL) of 1:1 HCl to a VOC vial. If pH cannot be adjusted to <=2 without destroying the integrity of the sample, the sample must be analyzed within 7 days of collection.

The holding time for samples preserved with HCl is 14 days for all target compounds. The holding time for un-preserved samples is 7 days.

5.2 Soils: Soils are routinely collected in duplicate in Encore samplers. A "bulk" sample is also routinely collected in a 125-mL jar fitted with a Teflon-lined cap. The bulk sample can be used for the methanol extraction if the concentration of the sample collected in the Encore exceeds the working range of the analytical system.

Soils collected in Encore samplers must be analyzed within 48 hours of collection or must be transferred within 48 hours of collection to sealed vials containing sodium bisulfate solution or methanol. If the sample contains high levels of carbonates, the sample is preserved with water and frozen until the time of analysis. The procedure for preparing soil samples is given in Section 9.2.

The hold time of the preserved sample is 14 days from the date of collection. The hold time for frozen samples is 14 days from the date of collection.

5.3 High level soil and waste samples are collected in glass containers (usually 125-mL clear glass) equipped with Teflon-lined caps. Soil samples may also be submitted as core samples contained in Encore samplers, metal or plastic "tubes", or in 40-mL VOA vials. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples). The holding time for soil and waste samples subjected to methanol extraction is14 days from date of collection; that is, the extraction and analysis must be completed within 14 days of collection.

5.4 TCLP leachate samples are collected with no headspace in Tedlar bags or syringes. The leachate samples are acidified at the time of collection (after the leaching procedure) with about 0.10mL of concentrated HCl per 40mL of sample and stored at 4C (less than 6C with no frozen samples) from the time leaching is completed until the analysis. The acidified leachate sample must be analyzed within 14 days of the leaching procedure. If the sample is not acidified, the leachate must be analyzed within 7 days of the leaching procedure.

NOTE: Samples that are suspected of having very high concentrations of VOC should be segregated from the "routine" samples and stored in a manner that will minimize sample and laboratory contamination. See STL-SL SOP AN70. If possible, keep the field QC in the same storage refrigerator as the samples.

6.0 APPARATUS AND MATERIALS

The apparatus and materials listed in this section may vary from lab to lab. The items listed are to give guidance and to provide a general overview of the equipment employed in this analysis.

6.1 Mass spectrometer: equipped with a capillary direct interface and a split/splitless injector or molecular jet separator

6.2 Gas chromatograph, compatible with the MS and purge and trap systems. If the GC is equipped with an injector that is operated in the split mode, the exit vent must have a carbon trap in-line to collect the volatile compounds that are vented during the transfer from the purge and trap device. The carbon traps should be changed a minimum of every three months.

6.3 Purge and trap device Tekmar 3000 Liquid Concentrator or equivalent

6.4 Supelco Vocarb 3000 trap or equivalent, Other traps may be used as long as the target compounds can be detected at the required quantitation limit.

6.5 Archon soil analyzer for low level soils, compatible with Tekmar purge and trap instruments. The instrument must be capable of automatically adding water and internal standard to the container while maintaining the septum seal, heating the sample to 40C, and spinning the stir bar to mix the sample during the purging step.

6.5 Data System compatible with the analytical system

6.6 Microsyringes: 10ul, 25ul, 50ul, 100ul, 250ul, 500ul, 2.5mL

6.7 Gastight syringe: 5mL, 25mL with luerlock tip

6.8 Volumetric flasks: 1.0mL, 10mL, 100mL

6.9 Recommended Columns

J&W DB-624: 60m x 0.32mm ID, 1.8um film
J&W DB-624: 20m x 0.18mm ID, 1.8um film

7.0 REAGENTS

Reagents must be tracked in accordance with STL-SL SOP AN44: *Reagent Traceability.*

7.1 Reagent water-free of volatile contaminants (obtained by purging with inert gas or carbon filtration)

7.2 Methanol-Burdich and Jackson, Purge and Trap grade

7.3 Sodium bisulfate-reagent grade. This salt is hydroscopic and should be stored in a dessicator.

7.4 Soil preservation solution- Slowly add, while stirring, 200g of sodium bisulfate to a 1.0-L volumetric containing about 700mL of reagent water. After the salt has dissolved, dilute to volume with reagent water, transfer to a storage container, and store the solution in an area free from VOC-especially water-soluble solvents such as acetone. The reagent should be tested prior to use by the analysis of a blank containing 5mL of the solution. The reagent is acceptable if it meets the same criteria as a method blank.

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions purchased from vendors or from stock standards prepared from neat materials. Certificates of analysis or purity must be received with all stock solutions or neat compounds. All preparation steps must be in accordance with STL-SL SOP AN41: *Standard Material Traceability.*

8.1 Preparation of **Stock Standards** from Neat Compounds

The lab should attempt to obtain a certified primary standard or secondary standard before preparing stock standards from neat materials. If primary stock standards must be prepared in-house, the target concentration range is from 2000ug/mL to 10000ug/mL. SL-SOP AN43: *Standard Preparation* gives the general instructions for the preparation of the stock solutions from neat materials.

8.2 Preparation of the **Working Standard** from Stock Standards

The working standard is prepared from the primary stock standards that are either prepared from neat compounds or purchased as certified solutions. The working standard contains one or more of the target compounds at a concentration suitable for preparing the calibration standards, generally 10-200ug/mL. A known volume of the working standard is then added to a known volume of reagent water to make the calibration standard.

The standards and standard concentrations listed in Table 1 are the suggested for routine use. If other "recipes" are used, the lab must document the standard preparation procedures in the standard traceability log.

8.3 Preparation of the **Calibration Standards** from the Working Standards

The calibration standards are the standards that are analyzed on the instrument. The calibration standard is made by adding a known volume of the working standard to a known volume of reagent water. The instrument must be calibrated using a minimum of five calibration standards. The lowest level standard must be at the reporting limit and the rest of the standards will define the working range of the analytical system.

8.3.1 Add 5.0mL of reagent water to a 5mL-glass syringe or 25ml of reagent water to a 25-ml glass syringe.

8.3.2 Add a known volume of the working standard to 5.0mL or 25ml of reagent water.

NOTE: The calibration standards for the low level soils are prepared using the same procedures as for the 5mL water purge except that the standards are purged at 40C. The lab has the option of using blank sand in the calibration standards.

The calibration standards listed in Table 1 are the suggested for routine use. If other "recipes" are used, the lab must document these standard preparation procedures in the standard traceablity log. A 5mL-purge volume may be used for low level (nominal RL of 1ug/L) if the instrument has sufficient sensitivity to detect the targets and the calibration criteria is met.

9.0 SAMPLE PREPARATION

Composite samples can be prepared using the guidance provided in STL-SL-SOP AN70.

9.1 **Aqueous samples** are analyzed directly by purge and trap/GC-MS. No sample preparation is necessary except to homogenize the sample prior to subsampling. The pH of liquid samples is checked and recorded prior to analysis to determine if the sample has been properly preserved.

9.2 Preparation of Soil Samples (5035)

9.2.1 Remove the Encore samples and the bulk sample from the storage area.

9.2.2 Test an aliquot of the bulk sample for the presence of carbonates.

- Transfer 5g of sample from the bulk sample to a 40mL vial..
- Add 5ml of the sodium bisulfate solution and shake the vial .
- If the sample exhibits effervescence, the Encore samples should be preserved as described above using 5mL of volatile-free water in place of the sodium bisulfate solution and placed in a freezer at –10C. The analytical hold time for frozen samples is 14 days from collection.
- If no effervescence is noted, the Encore samples may be preserved with 5mL soil preservation solution.

9.2.3 Add a stir bar to a vial and weigh the vial and record its tare weight(or tare the vial and stir bar weight by pressing the autotare button).

9.2.4 Transfer the sample from the Encore sampler to the tared vial and record the weight of the sample log.

If the sample effervesced during the carbonate test (9.2.2), add 5.0mL of reagent water and freeze at –10C. The hold time is 14 days from collection.

If not, add 5.0mL of the soil preservation solution, seal the vial, and store the sample at 4C until the time of analysis. The preserved sample must be analyzed within 14 days of collection.

NOTE: A preparation blank is prepared when Encore samples are transferred. The preparation blank contains the same reagents as the samples-either 5mL of reagent water or 5mL of soil preservation solution.

9.3 A methanol extraction is prepared when the concentration of the target compounds (by direct purge) exceeds the working range of the calibration curve. The bulk sample, collected in the 125-mL sample container, can be used to prepare the methanol extraction. Carry out the preparation quickly to minimize the loss of volatiles.

-Mix the sample with a stainless steel spatula and transfer 10g (+/- 0.5g) to a glass vial.

-Add 8uL of the surrogate spiking solution (2500ug/mL) to the sample and quickly add 10mL of purge and trap grade methanol. The theoretical concentration of the surrogates in the sample, assuming a sample weight of 10g and 100% percent solids, is calculated:

$$Ct(ug/kg,dw) = \frac{0.008mL \otimes 2500ug/mL}{0.010g \otimes solids} = 2000ug/kg,dw$$

-Shake the sample for two minutes. Allow the solvent to separate from the solids portion of the sample and transfer a 1-2mL aliquot of the extract to a storage vial. The vial should be sealed with no headspace. Store the methanol extract at 4C until the time of analysis. The extract must be analyzed within 14 days of sample collection.

-For each batch of twenty or fewer samples, prepare a method blank and a lab control standard. Prepare a matrix spike and matrix spike duplicate at a frequency of 5% of all samples.

The method blank is prepared by adding 8uL of the surrogate spiking solution to 10mL of purge and trap grade methanol. Assume a sample weight of 10g. Analyze 125uL of the extract.

The lab control standard is prepared by adding 8uL of the surrogate spiking solution and 8uL of the matrix spiking solution to 10mL of purge and trap grade methanol. Assume a sample weight of 10g. Analyze 125uL of the extract.

The matrix spikes are prepared by adding 8uL of the surrogate spiking solution (2500ug/mL) and 8uL of the matrix spiking solution (2500ug/mL) to 10-g aliquots of the sample selected for the MS/MSD. Quickly add 10mL of purge and trap grade methanol to each sample and shake for two minutes. Analyze 125uL of the extract or a smaller volume if the VOC concentration is high.

-Add 125uL of the extract (or a smaller volume if the VOC concentration exceeds the linear range of the system with 125uL) to 5.0mL of water (or to 25mL if the calibration is based on 25mL). Add the internal standard solution and analyze the sample using the ambient water calibration.

9.4 Methanol Extraction for Wastes

Carry out the preparation quickly to minimize the loss of volatiles.

9.4.1 Mix the sample with a stainless steel spatula and transfer 1g (+/- 0.2g) to a glass vial.

9.4.2 Add 10uL of the surrogate spiking solution (2500ug/mL) to the sample and quickly add 10mL of purge and trap grade methanol. If the sample is completely soluble in the methanol, dilute to a final volume of 10mL. The theoretical concentration of the surrogates in the sample, assuming a sample weight of 1.0g , is calculated:

$$Ct(ug/kg) = \frac{0.010mL \otimes 2500ug/mL}{0.0010g \otimes solids} = 25000ug/kg$$

9.4.2 Shake the sample for one minute. Allow the solvent to separate from the solids portion of the sample and transfer 1mL to 2mL of the extract to a storage vial. The vial should be sealed with no headspace. Store the methanol extract at 4C until the time of analysis. The extract must be analyzed within 14 days of sample collection.

For each batch of twenty or fewer samples, prepare a method blank and a lab control standard. Prepare a matrix spike and matrix spike duplicate at a frequency of 5% of all samples.

The method blank is prepared by adding 8uL of the surrogate spiking solution (2500ug/mL) to 10mL of purge and trap grade methanol. Assume a sample weight of 1.0g. Analyze 100uL of the extract.

The lab control standard is prepared by adding 10uL of the surrogate spiking solution (2500ug/mL) and 10uL of the matrix spiking solution (2500ug/mL) to 5.0mL of purge and trap grade methanol. Assume a sample weight of 5.0g. Analyze 100uL of the extract.

The matrix spikes are prepared by adding 10uL of the surrogate spiking solution (2500ug/mL) and 10uL of the matrix spiking solution (2500ug/mL) to 1g aliquots of the sample selected for the MS/MSD. Quickly add 10mL of purge and trap grade methanol to each sample and shake for one minute.

Add 100uL of the extract (or a smaller volume) to 5.0mL of water (or to 25mL if the calibration is based on 25mL). Add the internal standard solution and analyze the sample using the ambient water calibration.

NOTE: Waste samples may require significant dilution prior to analysis.

10.0 PROCEDURE

The following instrument conditions are recommended. The actual conditions may vary due to differences in instrumentation. The lab must document the instrument conditions in the maintenance log, the data system, or on the analysis log.

10.1 Instrument Conditions

10.1.1 GC Conditions
GC conditions may vary according to the environment and condition of each instrument. The lab must document the instrument conditions to assure consistent results and to aid in trouble-shooting the analytical system. Each lab is responsible for assuring that the conditions necessary to achieve adequate separation and sensitivity of the target analytes are maintained.

10.1.1.1 Example GC temperature program

Initial column temperature: 35 C for 3 minutes
Column temperature program 1: 20C per minute
Intermediate column temperature: 70C for 4 minutes
Column temperature program 2: 10C per minute
Final column temperature: 200C for 5.25 minutes

10.1.1.2 Column flow: Approximately 5-10mL/minute helium with a make-up of 20-25mL/minute helium. Total flow into the jet separator should be about 30mL/minute. The vacuum gauge on the jet separator will read about 0.5Torr.

If no jet separator is used and the column is plumbed directly into the source, the column flow should be adjusted to 0.5-1.0ml/min and a split ratio (desorb to column flow) of about 40:1 established. Smaller bore capillary columns (0.18 to 0.32mm) are required if the column is plumbed directly into the source

10.1.1.3 Mass Spectrometer and interface parameters

Jet separator temperature: 240C
Mass spectrometer interface: 240C
Mass spectrometer source temperature: factory set at 300C
range: 35-300amu, with a minimum scan cycle of 1 scan per second

10.1.2 Purge and Trap Conditions
The purge and trap conditions listed in this section are for guidance. The lab must document the actual conditions used. The purge time must be 11 minutes. Other parameters may be varied to optimize the detection of the target compounds.

10.1.2.1 "Three ring trap"-charcoal, Tenax, silica gel
Purge Time: 11 minutes
Purge temperature: aqueous-ambient; soils-heated 40C
Desorb time: 4 minutes
Desorb temperature: 180C
Bake time: 8 minutes at 225C
Purge flow: Approximately 20-30mL/minute
Valve temperature: 100C
Transfer line: 100C

10.1.2.1 VOCARB 3000 trap
Purge Time: 11 minutes
Purge temperature: aqueous-ambient; soils-heated 40C
Desorb time: 4 minutes
Desorb temperature: 225C
Bake time: 8 minutes at 250C
Purge flow: Approximately 20-30mL/minute
Valve temperature: 100C
Transfer line: 100C

The purge flow must be balanced for adequate sensitivity of the target compounds. If the purge flow is too high, the response of the gases will be low and not reproducible. The SPCC criteria for chloromethane may not be achieved if the purge flow is too high. If the purge flow is too low, the response of the more water-soluble targets-ketones, ethers, bromoform-may be low and the reporting limit may not be achieved on a routine basis.

10.2 BFB Tune Check

10.2.1 Fifty nanograms of 4-BFB must be analyzed at the beginning of each 12-hour clock as a check on the "**tune**" of the mass spectrometer. Meeting the tuning criteria ensures that the instrument is measuring the proper masses in the proper ratios. The 4-BFB analysis takes place under the same instrument conditions as the calibration standards and samples except that a different temperature program can be used to allow for the timely elution of 4-BFB. All other instrument conditions must be identical-the mass range, scan rate, and multiplier voltage. If the instrument is configured for direct injection, 50ng of 4-BFB may be injected directly on to the column. If the purge and trap is used to analyze the 4-BFB, the purge and trap conditions must be the same as for the calibration standards and samples.

10.2.2 Evaluation of the 4-BFB peak.

10.2.2.1 The chromatogram should exhibit acceptable baseline behavior and the 4-BFB peak should be symmetrical. A spectrum of the baseline that shows high abundances of mass 40 (Argon) and mass 44 (carbon dioxide) may indicate a leak or contaminated carrier gas.

10.2.2.2 The spectrum of the 4-BFB must meet the criteria listed in the attached SOP Summary. Background subtraction must be straightforward and designed only to eliminate column bleed or instrumental background. Scans +/- 5 scans from the apex can be evaluated for the 4-BFB criteria. Consecutive scans within this range can be averaged to meet the criteria.

10.2.2.3 The following records must be kept for each 4-BFB analysis that meets the criteria:
- the date, time, and data file of the analysis
- a spectrum of the scan or averaged scans
- a tabulation of the ion abundances of the scan

10.2.2.4 The 4-BFB analysis should be evaluated as to the relative size of the 4-BFB peak under the m/z 95 profile. A benchmark area window should be established for each instrument. Response outside of this window suggests instrumental problems such as a poor purge, clogged jet separator, leak in the Tekmar purging device, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open , or other anomalies.

10.2.2.5 If the 4-BFB fails to meet the acceptance criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the 4-BFB analysis, other corrective measures may include remaking the 4-BFB standard and/or cleaning the mass spectrometer source.

10.3 Initial Calibration

After the 4-BFB criteria has been met, the initial calibration standards are analyzed. Prepare the initial calibration standards according to the example recipes in the SOP appendices or lab-specific recipe. The lab must document the "recipe" used to prepare the calibration standards. The lowest level calibration standard must be at or below the routine RL and the other calibration standards will define the working range of the system.

10.3.1 Remove the plunger from the syringe and fill the barrel to overflowing with reagent water (syringe valve in the "red" position).

10.3.2 Replace the plunger, switch the syringe valve to "green", and force any airspace out of the syringe. Adjust the volume to the syringe volume(5mL or 25mL)

10.3.3 Briefly remove the syringe valve and inject the standards and internal standards into the syringe.

NOTE: Use the internal standard (IST) mix when preparing the calibration standards for analysis. The surrogates are already included in the standard mixes.

10.3.4 Load the standard(s) onto the purge and trap device and begin the analysis. All pertinent information concerning the standards must be recorded on the analysis log. The standards must be clearly identified and traceable to the preparation steps.

NOTE: The standards for low-level soil samples are prepared in the same manner as the 5mL standards. The standards for the low-level soils are purged at 40C. The lab has the option of using blank sand or soil in the calibration standards and the blank in the low level soil analysis.

10.3.5 After the acquisition has taken place, evaluate the calibration standards to ensure that each target compound, surrogate, and internal standard has been correctly identified. The analyst must be careful to complete this step before proceeding.

10.3.6 After each target compound, surrogate, and internal standard has been correctly identified, the relative response factor for each target compound and surrogate is calculated using the data system or using a PC spreadsheet as follows:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where
Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (see the attached quantitation report for a list of the compounds that are associated with the various internal standards)
Cx = concentration or mass on-column of the target compound being measured (ug/L or ug/kg OR ng or ug on-column)
Cis = concentration or mass on-column of the internal standard (ug/L or ug/kg OR ng or ug on-column)

The average relative response factor (RRFavg) is calculated for each target compound and each surrogate compound:

$$RRFavg = \frac{RRF1 + RRF2 + ... + RRFn}{n}$$

where n = number of calibration levels

Calculate the standard deviation (SD) for the target compounds and surrogates at all calibration levels:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RFi - RFavg)^2}{n-1}}$$

where
Rfi = response factor of a target compound in the individual calibration level
Rfavg = average response factor
n= number of calibration levels

10.3.7 Calculate the relative standard deviation (% RSD) of the calibration levels for each target:

$$\%RSD = \frac{standard\ deviation}{RRFavg} \otimes 100$$

10.3.8 The results of the initial calibration are evaluated against the Calibration Check Compound (CCC) criteria and the System Performance Check Compound (SPCC) criteria, which are listed below. The CCC and SPCC criteria must be met before samples can be analyzed.

Calibration Check Compounds – CCC Vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene

Initial Calibration	Continuing Calibration
<=30% RSD	<=20% difference from initial calibration

System Performance Check Compounds-SPCC

SPCC	Minimum RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Chlorobenzene	0.30
Bromoform	>0.10
1,1,2,2-Tetrachloroethane	0.30 (0.10 for 25mL purge volume)

NOTE: The CCC and SPCC criteria must be met even if the calibration curve option is used for quantitation. If the CCC and SPCC criteria do not pass, a new calibration curve must be prepared and analyzed.

10.3.9 After the initial calibration criteria (CCC and SPCC) have been met, each target is evaluated for linearity.

If the %RSD of the target compound is less than or equal to 15%, the average response factor can be used for quantitation of samples.

If the %RSD of the target compound is greater than 15%, a regression curve (linear, quadratic, etc) must be used for the quantitation of samples. A regression curve may also be used for the compounds that have %RSD less than 15%. The results can be used to plot a calibration curve of response ratios-Ax/Ais is plotted on the y-axis; Cx/Cis is plotted on the x-axis where

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (See attached quantitation report for a list of the compounds that are associated with the correct internal standard)
Cx = concentration or mass on-column of the target compound being measured (ug/L or ug/kg OR ng or ug)
Cis = concentration of the internal standard (ug/L or ug/kg OR ng or ug)

If the correlation coefficient of the regression curve is greater than 0.99, the curve can be used to quantify samples.. Regression curves may be forced through zero but it is recommended that the curve be evaluated without forcing through zero first and then with the curve forced through the origin. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire calibration range

When more calibration levels are analyzed than required, individual compounds may be eliminated from the lowest or highest calibration levels(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of the calibration curve be eliminated without eliminating the entire level.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPPs for other exceptions to using non-linear curve fitting.

8000B exception: evaluation of the "grand mean": If the average %RSD of ALL (all targets including CCC and SPCC) compounds in the initial calibration is less than 15%, the average response factor can be used for quantitation of all target compounds. The recommended course is to use regression curves, as described above, to quantify targets where the %RSD criterion (<=15%) is exceeded.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

10.3.10 After the initial calibration criteria has been met, the method blank is analyzed. 5.0mL or 25mL of reagent water is spiked with the internal standard/surrogate and analyzed. The concentrations of the target compounds in the method blank are calculated and the results are compared to the reporting limits (RL) in Table 5 of the STL-SL CQAP or other specified QAP.

If the concentrations of all target compounds are below the RL, analysis of client samples can take place. Note that all target compounds must meet the criteria.

If the concentration of any target compound is above the RL in Table 5 of the STL-SL CQAP, the method blank must be reanalyzed. The analytical system must be demonstrated to be free from contamination before the analysis of samples can take place.

If the method blank repeatedly fails to meet the criteria, contact the immediate supervisor to determine the cause of the problem and to determine a course of action. This action may include re-cleaning the sparging tubes (with soap, hot water, and methanol), purging the effected autosampler ports with heated methanol, flushing the purge and trap ALS concentrator with methanol, replacing the trap, changing the transfer line, and changing the column. A method blank is then analyzed after taking the corrective action to demonstrate that the contamination has been eliminated. Once the system is determined to be free from contamination, sample analysis may begin. Method blanks may be required after the analysis of samples that contain very high levels of VOC.

10.4 Continuing Calibration Verification

At the beginning of each 12-hour clock, the tune of the instrument must be checked by the analysis of 50ng of 4-BFB. This criteria must be met before the analysis of the calibration check standards can take place.

10.4.1 After the tune criteria has been met, a continuing calibration check standard(s) is analyzed. The continuing calibration standard should be at a nominal concentration of 50ug/L-kg for 5ml/5g samples and 10ug/L for 25mL with ketones and poor purgeables at higher concentrations. The CCC and SPCC criteria (Section 10.3.8) must be met before the analysis of the method blank and samples can take place. The percent difference (%D) is calculated as follows:

$$\%D = \frac{RRFavg - RRFccv}{RRFavg} \otimes 100$$

where
RRFavg = average response factor from initial calibration
RRFccv = response factor from the check (12-hour) standard-calibration verification

The percent drift (%Drift) may also be used to evaluate the change/deviation of the curve:

$$\%Drift = \frac{Ci - Cccv}{Ci} \otimes 100$$

where
Ci = Calibration Check Compound standard concentration
Cccv = measured concentration using the selected quantitation method

NOTE: The SPCC criteria (10.3.8) must be met even if the regression curve option is used for quantitation. If this criteria is not met, corrective action must be taken. The corrective action may include reanalysis of the calibration check standard or preparation of a new secondary stock standard and reanalysis of the calibration check standard. If subsequent analysis of the standard is still out of criteria, a new initial calibration curve must be analyzed and evaluated.

10.4.2 The calibration standard (CCV) must also be evaluated for internal standard retention time and response.

If the retention time of any internal standard changes by more than 30 seconds from the retention times of the internal standards in the initial calibration, the analytical system must be inspected for problems and corrective action instituted.

If the extracted ion current profile (EICP) area for any of the internal standards changes by more than a factor of two (-50% to +100%) from the last calibration check standard, the analytical system must be inspected for problems and corrective action instituted. If the CCV is the first one after the initial calibration, compare the ISTD response to the corresponding level in the ICAL.

10.4.3 After the continuing calibration criteria has been met, the method blank is analyzed. 5.0mL or 25mL of reagent water is spiked with the internal standard/surrogate and analyzed. The concentrations of the target compounds in the method blank are calculated and the results are compared to the reporting limits (RL) in Table 5 of the STL-SL CQAP.

If the concentrations of all target compounds are below the RL, analysis of client samples can take place. Note that all target compound must meet the criteria.

If the concentration of any target compound is above the RL in Table 5 of the STL-SL CQAP, the method blank must be reanalyzed. The analytical system must be demonstrated to be free from contamination before the analysis of client samples can take place.

10.5 Aqueous Sample Analysis-5.0mL to 25mL

The analyst must use the same volume as was used for the calibration standards-if a 5mL sample is used, it must be quanted off of the 5mL calibration curve; if a 25ml sample is used, it must be quanted off of the 25mL calibration curve. Samples are analyzed only after the tune criteria, the calibration (initial or continuing) criteria has been met, and the method blank criteria has been met. See the SOP Summary for the analytical sequence.

10.5.1 Remove the samples to be analyzed from the refrigerator and allow the samples to come to ambient temperature.

10.5.2 Put on a pair of gloves before transferring the sample from the vial to the syringe. The sample is most likely preserved with acid or may contain toxic or hazardous chemicals or biologically active components that may cause skin irritations. ***Gloves must be worn when handling samples.***

10.5.3 Mix the contents of the vial by inverting the vial several times. Check to see if there are air bubbles present in the sample. If air bubbles are present, use another vial if available. Make a note on the analysis log if the sample used contained bubbles and notify the supervisor and/or the project manager.

10.5.5 Remove the plunger from the glass syringe. Attach a syringe valve to the syringe Luer-tip to prevent sample from spilling out of the syringe when sample is added.

10.5.5 Open the vial of the well-mixed sample and gently pour the sample into the syringe barrel. The sample should fill the barrel of the syringe and overflow to allow trapped air bubbles to escape.

10.5.6 Replace the plunger into the syringe barrel. Try not to let air bubbles get into the barrel. If air bubbles are present, turn the syringe up, open the syringe valve , and expel the air while adjusting the volume to 5.0mL or 25mL. If no air bubbles were trapped, adjust the syringe to volume.

NOTE: For TCLP leachate samples, use 1.25mL of sample (1:4 dilution).

10.5.7 Open the syringe valve and inject the internal standard/surrogate (ISSU) mix into the sample.

10.5.8 Transfer the sample from the syringe to the purge and trap device. Record all of the sample identification information on the analysis log. Check the pH of the sample with pH paper and record the pH on the instrument log or other appropriate log.

10.5.9 Analyze the samples using the purge and trap and GC/MS conditions used for the initial and continuing calibration standards.

10.5.10 Determine the concentration of the samples and QC items. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

NOTE: Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client. For TCLP analyses, every reasonable effort should be made to achieve the regulatory level with out instrument overload.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with t the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower RLs.

A dilution is made when a volume of the sample is mixed with the reagent water to a final volume of 5.0mL or 25ml,depending on which curve is being used. The dilution factor is calculated by dividing the volume of sample into the volume used for the calibration curve.

$$DF = \frac{final\ volume\ of\ dilution(mL)}{volume\ of\ sample\ used(mL)}$$

For example, if 1.0mL of sample is diluted to final volume of 5.0mL, the dilution factor is 5. (5.0/1.0 = 5). If 1.0mL of sample is diluted to a final volume of 25mL, the dilution factor is 25 (25/1=25).

The following table gives some dilution factors:

Volume of Sample (mL)	Volume of Reagent Water (mL)	Final Volume (mL)	Dilution factor
5.0	0	5.0	1
2.5	2.5	5.0	2
1.0	4.0	5.0	5
0.5	4.5	5.0	10
0.10	4.9	5.0	50
25.0	0	25.0	1
5.0	20.0	25.0	5
2.5	22.5	25.0	10
1.0	24.0	25.0	25
0.50	24.5	25.0	50
0.10	24.9	25.0	250

NOTE: The same volume of internal standard/surrogate mix (ISSU) is added to the dilution as was added to the undiluted sample.

10.6 Low Level Soil Samples by Heated Purge and Trap (Method 5035)

The soil analytical system is calibrated using the same concentrations as the 5mL purge. The tune, initial and continuing calibration criteria, and the method blank criteria must be met before samples are analyzed. Standards and QC items must be analyzed under the same heated purge and trap conditions.

Remove the samples to be analyzed (Section 9.2) from the refrigerator or freezer and allow the sample to come to ambient temperature. Inspect the vial for cracks or obvious breaches in the septum. Load the samples on to the soil-purging unit and analyze according to the sequence described in Appendix B.

Liquid field QC for soils (trip blank, field blank, etc.) should be analyzed with the associated soil samples, using the same preparation and analytical procedures, including the heated purge. Report the results for liquid trip blanks as ug/L.

10.7 Analysis of Methanol Extracts of Soils and Wastes

The methanol extraction is used when the concentration of one or more target compounds exceeds the linear range of the low-level purge technique (>1000ug/kg). or if the concentration of VOC in the soil or waste samples is high. Samples are analyzed only after the 4-BFB criteria, the calibration criteria (initial and continuing), and the method blank criteria has been met. Medium level soil extracts are quanted using the ambient purge calibration curve. Sample preparation steps are included in Section 9.

10.7.1 Remove the plunger from the 5.0-mL syringe and fill the barrel to overflowing with reagent water(syringe valve in the "red" position). Replace the plunger, switch the syringe valve to "green", and force any airspace out of the syringe. Adjust the volume to the syringe volume(5mL)

10.7.2 Briefly remove the syringe valve and inject the sample extract and 5uL of the internal standard (IST) solution into the syringe. Use 125ul of the extract for soils and 100uL of the extract for wastes. Smaller aliquots are used if the concentration of target analytes exceed the working range of the system.

NOTE: Use the internal standard (IST) mix when preparing the medium level samples. Recall that the surrogates have already been added to the sample during the methanol extraction step (Section 9).

10.7.3 Load the sample on to the purge and trap device and begin the analysis. All pertinent information concerning the samples must be recorded on the analysis log. The samples must be clearly identified and traceable to the extraction log. These conditions must be the same as was used for the initial and continuing calibration standards-ambient purge for aqueous samples.

10.7.4 Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, a smaller aliquot of the methanol extract is reanalyzed to bring the highest target within the upper half of the calibration curve. Follow the guidelines in Section 10.4.10 for reporting dilutions.

NOTE: It is possible to dilute the surrogates in the sample extract below the linear range of the calibration curve. The minimum extract aliquot that can be used to provide a quantifiable result for the surrogates and matrix spikes is 0.0025mL (2.5uL).

SOIL: 10g to 10mL MeOH	WASTES: 1g to 10mL MeOH	Surrogates- Theoretical ng on-column
125uL(0.125mL)	100uL (0.100mL)	250
62.5uL(0.0625mL)	50uL(0.050mL)	125
25uL(0.025mL)	25uL(0.020mL)	50
12.5uL(0.0125mL)	10ul(0.010mL)	25
2.5uL(0.0025mL)	2.0uL(0.0020mL)	5.0-quantiation limit
<2.5uL(0.025mL)	<2.0uL(0.0020mL)	<5.0ng- below the quantitation limit-diluted out

NOTE: Some instrument quantitation limits may be higher than the limit listed in the table. The volume of extract should be adjusted accordingly.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Qualitative Analysis of Target Compounds

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from a reference spectrum of the target compound stored in a library generated on the same instrument or a standard spectral library such as the NIST/NBS.

11.1.1 Two criteria must be met in order to identify a target compound.

1) elution of the sample component within +/-0.06 RRT (relative retention time) units of the daily standard containing that compound.

$$RRT = \frac{\textit{retention time of the target compound}}{\textit{retention time of the associated internal standard}}$$

2) correspondence of the target compound spectrum and the standard component mass spectrum

11.1.2 All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion = 100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound will make the identification of the target compound more difficult. These ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

11.1.3 The relative intensities of the ions present in the sample component spectrum should agree within +/- 30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum.

11.1.4 If the above criteria are not met exactly, the analyst should seek help from a senior analyst or supervisor. If there is sufficient evidence to support the identification of the component, then the component is identified, quantified, and reported.

11.2 Tentatively Identified Compounds

For samples containing components not associated with the calibration standards, a library search on a reference library, such as the NIST/NBS, may be conducted in order to identify the non-target compounds. Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification. Tentative identifications of non-targets will be made only by analysts having completed the training specified in the training schedule.

11.2.1 Relative intensities of the major ions (masses) in the reference spectra (ions >10% of the most abundant ion) should be present in the sample spectrum.

11.2.2 The relative intensities of the major ions should agree within +/-30%.

11.2.3 Molecular ions present in the spectrum should be present in the sample spectrum.

11.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible subtraction from the sample spectrum because of over-lapping or co-eluting peaks.

11.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of coeluting peaks.

11.2.6 If, in the opinion of the analyst, there is enough evidence to support the tentative identification of a compound even though the above criteria is not met exactly, the peak may be considered tentatively identified. The analyst should consult other analysts or the mass spectral interpretation specialist if there are any questions concerning an interpretation of spectra.

11.2.7 The estimated concentration of the tentatively identified compound (TIC) is calculated using the total ion area of the tentatively identified peak and total ion area of the nearest internal standard that has no interferences. The calculation is

Aqueous

$$TIC(ug/L) = \frac{Cis}{AREAis} \otimes AREAtic \otimes DF$$

where
Cis = concentration of the internal standard, ug/L
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
DF = dilution factor

Soils by Heated P/T

$$TIC\ (ug/kg,dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{5.0g}{(W)(solids)}$$

where
Cis = concentration of the internal standard, ug/kg
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
W = weight of sample analyzed, g
solids = decimal equivalent of percent solids

Soils by Methanol Extraction

$$TIC\ (ug/kg,dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{Vcal}{(W)(solids)}$$

where
Cis = concentration of the internal standard, ug/kg
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
Vcal = volume that calibration curve is based on (5mL or 25mL)
solids = decimal equivalent of the percent solids(percent solids/100)
W = weight of sample added to the reagent water (g)

This weight is determined using the following equation:

$$W = \frac{Wext(g)}{Vf(mL)} \otimes Vext(mL)$$

where
Wext = weight of sample extracted (g)
Vf = final volume of the extract (mL)
Vext = volume of extract added to the water (mL)

11.3 Calculations for Samples-Internal Standard Technique

Aqueous Samples- relative response factor :

$$concentration(ug/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes DF$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/L)
RRFavg = average response factor of the compound being measured
DF = dilution factor

Aqueous Samples: regression curve

$$concentration(ug/L) = concentration(curve) \otimes DF$$

where
DF = dilution factor

The reporting limit (RL) is calculated:

$$RL(ug/L) = RLqap \otimes DF$$

where
DF = dilution factor. The SL CQAP Table 5 RL(RLqap) assumes a DF of 1.

Soils by Heated P/T- relative response factor :

$$concentration(ug/kg, dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{5.0g}{(W)(solids)}$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/kg)
RRFavg = average response factor of the compound being measured
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

Soils by Heated P/T: regression curve

$$conc(ug/kg, dw) = Ccurve(ug/kg) \otimes \frac{5.0g}{(W)(solids)}$$

where
Ccurve = concentration from curve(ug/kg)
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

The reporting limit (RL) is calculated:

$$RL = RLqap \otimes \frac{5.0g}{(W)(solids)}$$

where
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

The STL-SL CQAP assumes W= 5.0g and solids = 1.

Methanol Extraction Soils and Wastes- relative response factor

$$concentration(ug/kg,dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{Vcal}{(W)(solids)}$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/L)
RRFavg = average response factor of the compound being measured
Vcal = volume that calibration curve is based on (5mL or 25mL)
solids = (percent solids)/100)
W = weight of sample added to the reagent water (g)

This weight is determined using the following equation:

$$W = \frac{Wext(g)}{Vf(mL)} \otimes Vext(mL)$$

Wext = weight of sample extracted (g)
Vf = final volume of the extract (mL)
Vext = volume of extract added to the water (mL)

Methanol Extraction of Soils and Solids- regression curve:

$$conc(ug,kg,dw) = Ccurve(ug/L) \otimes \frac{Vcal}{(W)(solids)}$$

where
Vcal = volume that calibration curve is based on (0.005L or 0.025L)
W = weight of sample added to the reagent water (g)-defined above

The reporting limit (RL)is calculated:

$$RL = RLqap \otimes \frac{5.0g}{(W)(solids)}$$

where
W = weight of sample added to the reagent water (g)
solids = (percent solids)/100)

The STL-SL CQAP assumes W= 5.0g and solids = 1.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items that are analyzed together. The matrix spike and LCS frequency is defined in Section 3.1.3 of STL-SL SOP AN02: *Analytical Batching*. Note that the method blank for liquid samples and low-level soils is clock-specific and that the method blank for medium level soil samples is extraction batch-specific.

STL-SLSOP AN02: *Analytical Batching* describes the procedure for evaluating batch-specific QC. This criteria is summarized in the attached 8260 SOP Summary.

STL-SL SOP AN02 also contains the calculations for accuracy and precision and the calculations for the theoretical concentrations of surrogates, lab spikes, and matrix spikes.

12.2 Initial Demonstration of Capability (IDOC) to Generate Acceptable Accuracy and Precision

Each analyst must demonstrate competence in the analysis of samples by this procedure. The minimum criteria for this demonstration is the preparation and analysis of spiked reagent water. Section 8.3 of EPA Method 8260A gives the general procedure for the performance of the IDOC and Table 6 of EPA Method 8260A gives the acceptance criteria for the accuracy and precision.

12.3 Method Detection Limit

The method detection limit is determined in accordance with STL-SL SOP CA90.

13.0 PREVENTIVE MAINTENANCE

Preventive maintenance items will be added at a later date. Section 10 of the STL-SL QAPs provide guidance on preventive maintenance.

14.0 TROUBLE-SHOOTING

Trouble-shooting items will be added at a later time. See instrument manufacturers' manuals for guidance on locating and repairing instrument problems.

15.0 REFERENCES

1. *Savannah Laboratories' Comprehensive Quality Assurance Plan* and *Savannah Laboratories' Corporate Quality Assurance Plan*, current revisions.
2. Method s 5035, 8000B, and 8260B. *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846.including Update III* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

Appendix A

VOLATILES BY GC/MS WORKING STANDARDS -EXAMPLE

These standards can be used to prepare the working standards for EPA Method 8260 to report the TCL (target compound list) compounds and the extended list of target compounds generally associated with EPA 8260. The standards are prepared in purge and trap grade methanol and are stored at 4C with minimum headspace.

Working Standard 1 (TCL WS-1)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA Cal #2	2000	12.5	25
VOA Cal #3	2000	12.5	25
VOA Cal #4	2000	12.5	25
1,2,-DCB	5000	5.0	25
1,3-DCB	5000	5.0	25
1,4-DCB	5000	5.0	25
2-CEVE	1000	125	125

Working Standard 2 (TCL WS-2)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA Cal #1	5000	25	125
8260 Surrogates	2500	10	25

Working Standard for GASES (TCL GASES)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
502.2 Cal 1	2000	12.5	25

Appendix A

Working Standard 3 (8260 WS-3)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
8260 Custom Mix #1	200	125	25
8260 Custom Mix #2	200	125	25
1,1,2,2-Tetrachloroethane	2000	12.5	25

Appendix A

Internal Standard (8260 ISTD)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
VOA ISTD	2500	20	50
1,2-DCE-d4	2000	25	50

Internal Standard/Surrogate (8260 ISSU)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA ISTD	2500	20	50
1,2-DCE-d4	2000	25	50
8260 Surrogate	2500	20	50

Tune Evaluation Standard (4-BFB)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
4-BFB	5000	10	50

Matrix Spike Standard (5-component subset)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
Matrix Spiking Solution	2500	20	50

TCLP matrix Spike Standard (5-component subset)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
TCLP Spiking Solution	2000	16	125

Appendix A

VOLATILES BY GC/MS CALIBRATION STANDARDS - EXAMPLES

The following calibration standards are prepared to define the working range of the EPA 8260 analysis for the target compound list (TCL) and the extended list of compounds generally associated with EPA 8260. The lowest level standard is at the reporting limit and the other standards define the working range. Samples with target analytes above the concentration of the highest calibration standard must be diluted and reanalyzed.

TARGET COMPOUND LIST

Working Level standards	Conc (ug/mL)	TCL-1 *	TCL-2 *	TCL-3 *	TCL-4 *	TCL-5 *	TCL-6 *
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 5.0mL of reagent water or to 5.0g of blank sand.

8260 EXTENDED LIST (TCL+ADDITIONAL COMPOUNDS)

Working Level standards	Conc (ug/mL)	8260-1 *	8260-2 *	8260-3 *	8260-4 *	8260-5 *	8260-6 *
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
8260 WS-3	25	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 5.0mL of reagent water or to 5.0g of blank sand.

CONCENTRATIONS OF THE CALIBRATION STANDARDS-5.0mL OR 5.0g

Cal Std	all targets except ketones, 2-CEVE	ketones, 2-CEVE
TCL-1,8260-1	5ug/l-kg	25ug/l-kg
TCL-2,8260-2	10ug/l-kg	50ug/l-kg
TCL-3,8260-3	25ug/l-kg	125ug/l-kg
TCL-4,8260-4	50ug/l-kg	250ug/l-kg
TCL-5,8260-5	100ug/l-kg	500ug/l-kg
TCL-6,8260-6	200ug/l-kg	1000ug/l-kg

Appendix A

VOLATILES BY GC/MS CALIBRATION STANDARDS-25mL Purge Volume-EXAMPLES

These calibration standards are prepared to define the working range of the EPA 8260 analysis for the target compound list (TCL) and the extended list of compounds generally associated with EPA 8260. The standards are based on a volume of 25mL to achieve lower quantitation limits for the target compounds. The lowest level standard is at the reporting limit and the other standards define the working range. Samples with target analytes above the concentration of the highest calibration standard must be diluted and reanalyzed.

TARGET COMPOUND LIST

Working Level standards	Conc (ug/mL)	25TCL -1*	25TCL-2*	25TCL-3*	25TCL-4*	25TCL-5*	25TCL-6*
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 25mL of reagent water.

8260 EXTENDED LIST (TCL+ADDITIONAL COMPOUNDS)

Working Level standards	Conc (ug/mL)	258260-1*	258260 -2*	258260-3*	258260-4*	258260-5*	258260-6*
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
8260 WS-3	25	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 25mL of reagent water.

CONCENTRATIONS OF THE CALIBRATION STANDARDS

Cal Std	all targets except ketones, 2-CEVE	ketones, 2-CEVE
25TCL-1,25-8260-1	1.0ug/l	5.0ug/l
25TCL-2,25-8260-2	2.0ug/l	10ug/l
25TCL-3,25-8260-3	5.0ug/l	25ug/l
25TCL-4,25-8260-4	10ug/l	50ug/l
25TCL-5,25-8260-5	20ug/l	100ug/l
25TCL-6,25-8260-6	40ug/l	200ug/l

Appendix B
8260 SOP SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage*	Container	Hold Time
Aqueous	None; 4C	40mL no headspace	7 days
	HCl pH<2; 4C	40mL-no headspace	14 days
Soil/solid(low level)	Iced at collection; 5mL sodium bisulfate added upon arrival in lab; store at 4C	5-g Encore Sampler	14 days
Soil/solid(low level) -high carbonates	Iced at collection; 5mL water added upon arrival in lab; store at –10C	5-g Encore Sampler	14 days
Soil/solid(high level)	None; 4C	Glass 125mL	14 days
TCLP	HCl pH<2; 4C	Tedlar bag or syringe	14 days

*storage temperature is 4C with a control criteria of less than 6C with no frozen samples

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
4-BFB 50ng on column Clock starts at injection	4-BFB 50ng on column Clock starts at injection
Calibration standards- minimum of five cal levels	Mid point calibration verification (50ug/L or 50ug/kg)) RL Standard-low point on cal curve (if necessary)
Method blank	Method blank
Samples analyzed until the 12-hour clock expires	Samples analyzed until 12-hour clock expires

See SL SOP AN02, Section 3.1.3, for the batch/clock options for LCS and MS/MSD.

Recommended Internal Standards:
1,2-dichloroethane-d4; 1,4-difluorobenzene; chlorobenzene-d5; 1,4-dichlorobenzene-d4

Surrogates/System Monitoring Compounds:
dibromofluoromethane; toluene-d8; 4-bromofluorobenzene

LCS/MS: CQAP Subset:
1,1-dichloroethene; benzene; trichloroethene; toluene; chlorobenzene

Appendix B
8260 SOP SUMMARY

VOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION BROMOFLUOROBENZENE (BFB)	
m/e	**Abundance Criteria**
50	8.0-40.0% of mass 95
75	30.0-66.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0-9.0% of mass 95
173	< 2.0% of mass 174
174	50-120%% of mass 95
175	4.0-9.0% of mass 174
176	93.0-101.0% of mass 174
177	5.0-9.0% of mass 176

(1) *8260 criteria taken from CLP OLMO4.0 (January 1998)

CALIBRATION ACCEPTANCE CRITERIA

Calibration Check Compounds - CCC
Vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene

Initial Calibration	**Continuing Calibration**
Less than or equal to 30% RSD	Less than or equal to 20% difference or drift from initial calibration

System Performance Check Compounds-SPCC

SPCC	Minimum RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Chlorobenzene	0.30
Bromoform	>0.10
1,1,2,2-Tetrachloroethane	0.30 (0.10 for 25mL purge volume)

See Sections 10.3 and 10.4 for ICAL and CCV linearity checks and criteria.

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
MS Tune Check - 50ng 4-BFB	Before initial and continuing calibration standards - every 12 hours	Mass abundances within method acceptance criteria	-Evaluate chromatogram and spectrum - Reanalyze - Retune MS and reanalyze - Remake standard and reanalyze - Perform instrument maintenance and reanalyze
Initial Calibration – minimum five point curve with lowest point at or below the Reporting Limit (RL)	Initially; after major instrument maintenance; whenever continuing calibration check fails. Prior to analysis of method blank and samples	Method criteria for CCC/SPCC (see -Calibration Acceptance Criteria – Table presented earlier in this document)	- Evaluate chromatograms, spectra, and integrations - Reanalyze standard(s) - Remake and reanalyze standard(s) - Perform instrument maintenance and recalibrate
Continuing Calibration check - midpoint standard	Every 12 hours before analysis of method blank and samples	Method criteria for CCC/SPCC (see Calibration Acceptance Criteria - Table presented earlier in this document)	- Evaluate chromatogram, spectra, integrations - Reanalyze standard - Remake and reanalyze standard - Recalibrate - Perform instrument maintenance and recalibrate
Method Blank	Every 12 hours (per clock) before sample analyses	All reported targets <RL	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
Lab Control Sample (LCS) -subset of target compounds unless full target spike specified by client	Each batch	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Matrix Spike/Matrix Spike Duplicate (MS/MSD) -subset of target compounds unless full target spike specified by client	Each batch	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Surrogates	All samples, blanks, LCS, MS	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Internal Standard Area	Evaluate all standards and samples	-Areas in continuing calibration verification must be 50% to +200% of previous initial calibration sequence -Retention time of internal standard must be +/-30 seconds from internal standard in initial calibration -Areas in samples should be evaluated for gross error . Consult supervisor.	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
Reporting Limit Standard -1x to 2x the RL	(Optional) Daily. Required for Florida DEP	Detected with reasonable response	-Evaluate chromatogram, spectra, and integrations -Reanalyze -Remake standard and reanalyze -Retune and recalibrate -Perform instrument maintenance and recalibrate
Initial Demonstration of Capability	Per analyst	Method criteria	-Reanalyze targets that do not meet criteria
Method Detection Limit (MDL)	See STL-SL SOP CA90	See STL-SL SOP CA90	-Reanalyze and re-evaluate

Appendix C
EXAMPLE QUANTITATION REPORT

-quantitation ions
-internal standard and target compound association

SEMI-VOLATILE COMPOUNDS BY GC/MS
Method: 8270C

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Approved by:

R. Wayne Robbins — 30 Aug 2002
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1.0 SCOPE AND APPLICATION

1.1 This method can be used to determine the concentration of various semi-volatile organic compounds (SVOC) in groundwater, TCLP and SPLP leachates, soils, sediments, wastes, and solid sample extracts. The attached quantitation report (Appendix B) lists the routine target compounds, the retention times of the target compounds, the characteristic ions of the target compounds, and the internal standard associated with each target compound.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision limits for the target compounds are given in Section 5 of the current revision of the Laboratory Quality Manual (LQM).

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample is extracted using an appropriate extraction procedure. The extract is dried, concentrated to a volume of 1.0mL, and analyzed by GC/MS. Qualitative identification of the target compounds in the extract is based on the retention time and the mass spectra determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

2.2 This procedure is based on the guidance provided in SW-846 Method 8270C.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The toxicity or carcinogenicity of each chemical used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, and lab glasses or face shield should be worn while handling extracts and standards. Standard preparation, addition of the internal standard solution, and sample extract dilution should be performed in a hood or well ventilated area.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst. These sheets specify the type of hazard that each chemical poses and the procedures that are used to handle these materials safely.

3.4 The exit vent of the splitless injector must have a carbon trap in-line to collect the semivolatile compounds that are vented during the injection of the extract. The traps should be changed every six months and disposed of in accordance with SOP CA70: *Waste Management.*

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, or glassware. Glassware and/or extraction vessels that have not been properly cleaned may contribute artifacts that make identification and quantification of the target compounds difficult. Elevated baselines may be due to oils, greases, or other hydrocarbons that may be extracted from improperly cleaned glassware or extraction vessels.

4.2 Matrix interferences may be caused by contaminants that are extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. Sample extracts that contain high concentrations of non-volatile material such as lipids and high molecular weight resins and polymers may require the optional GPC cleanup prior to analysis. The GPC cleanup is generally not effective in removing non-target material that is associated with common petroleum products like diesel.

4.3 Secondary ions may be used for quantification if there is interference with the primary quantitation ion. If a secondary ion is used for quantification, the concentration/response relationship of the secondary ion must be established. The secondary ion must meet the same calibration criteria as the primary ion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	none; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Waste	none; 4C	Glass	14 days	40 days
TCLP	none; 4C	1-L amber	7 days from TCLP leaching procedure	40 days

Refrigerator temperature acceptance criterion is less than 6C with no frozen samples.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph- Hewlett-Packard (HP) 5890 or equivalent with compatible autosampler, splitless injector, and direct capillary interface. The exit vent of the splitless injector must have a carbon trap in-line to collect the semivolatile compounds that are vented during the injection of extracts. The carbon traps should be changed every six months.

6.2 Mass spectrometer- HP5971, HP5972, HP5973 or equivalent

6.3 Recommended Capillary column-HP-5MS, 30m x 0.25mm ID x 0.25um film thickness or equivalent column

6.4 Data system- compatible with GC/MS system

6.5 Microsyringes- appropriate volumes

6.6 Volumetric flasks- Class A, appropriate volumes

6.7 Autosampler vials and crimper- compatible with autosampler

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability.*

7.1 Methylene chloride- pesticide residue grade, for preparation of standards

7.2 Acetone- pesticide residue grade, for preparation of standards

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with SOP AN41: *Standard Material Traceability*. General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation.*

The lab should purchase certified solutions from STL approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation from neat materials.

8.1 Preparation of the Stocks from Neat Standards

The steps for the preparation of primary stock standards from neat materials are given in SOP *AN43: Standard Preparation.* The standards should be prepared in methylene chloride but may require other solvents to dissolve the material.

8.2 Preparation the calibration standards from the stock standards

A minimum of five calibration standards are prepared. The concentrations of the stock standards are in the 1000-10000ug/mL range. The recommended standards are listed in Section 10.2. The lowest level standard should be at the equivalent of the reporting limit and the rest of the standards should define the working range of the detector. Note that six calibration levels are required for a second order regression curve. Internal standards should be added to each standard to give a final concentration of 40ug/mL.

Each lab should develop controlled recipes that can be posted or maintained in appropriate logbooks.

9.0 SAMPLE PREPARATION

9.1 The sample extraction procedures are given in the following SOPs:

Matrix	SOP	Extraction Technique
Aqueous, TCLP leachates	EX30	Continuous Liquid-liquid Extraction
Aqueous, TCLP leachates	EX35	Separatory Funnel
Soils/Sediments	EX40	Sonication
Wastes	EX42	Waste dilution

9.2 The sample concentration procedures are given in SOP EX 50: Zymark Nitrogen Concentration.

9.3 Gel permeation chromatography (SOP EX61) may help to eliminate or minimize matrix interferences in a limited number of samples. The GPC cleanup is generally not effective on samples containing petroleum products.

10.0 PROCEDURE

10.1 Instrument Conditions

Instrument conditions may vary according to the sensitivity of each instrument. The following conditions are provided for guidance. The lab must optimize and document the conditions used for the analysis of SVOC by GC/MS.

Recommended Column:

HP-5MS 30m x 0.25mm ID x 0.25um film thickness or equivalent

Column flow: Approximately 1mL/min helium

GC Oven temperatures:

Initial column temperature: 45 C for 3 minutes
Column temperature program: 10C per minute
Final column temperature: 300C (until at least one minute past the elution time of Benzo (g,h,i) perylene).

GC injector parameters

Injector temperature: 250-270EC
Injection type: split, approximately 1:10 or splitless injection
Injector liner: 4mm ID quartz or 4mm glass, deactivated (single "Gooseneck")
Sample injection volume: 1-2uL

Mass Spectrometer and interface parameters

Mass spectrometer interface: 300C
Mass spectrometer source temperature: Factory Set
Mass range: 35-500amu, with a scan time of 1.0 scans per second or greater

10.2 Calibration

A minimum of five calibration standards are prepared and analyzed. The recommended standards are 10, 20, 50, 80, 100, 200ug/mL. The lowest level standard should be at or below the equivalent of the reporting limit and the rest of the standards should define the working range of the detector. Note that six calibration levels are required for a second order regression curve.

10.2.1 Fifty nanograms of DFTPP must be analyzed at the beginning of each 12-hour clock as a check on the "tune" of the mass spectrometer. Meeting the tuning criteria demonstrates that the instrument is measuring the proper masses in the proper ratios. The DFTPP analysis takes place under the same instrument conditions as the calibration standards and samples except that a different temperature program can be used to allow for the timely elution of DFTPP. All other instrument conditions must be identical-the mass range, scan rate, and multiplier voltage.

10.2.1.1 Prepare a 50ng/uL solution of tune/column evaluation standard containing each of the following compounds at 50ug/mL in methylene chloride: DFTPP, pentachlorophenol, p,p'-DDT, and benzidine.

10.2.1.2 Analyze a 1uL aliquot of the tune/column evaluation solution.

10.2.1.3Evaluate the DFTPP peak.

-The chromatogram should exhibit acceptable baseline behavior and the DFTPP peak should be symmetrical.

-The spectrum of the DFTPP must meet the criteria listed in the SOP Summary (Appendix A). Background subtraction must be straightforward, that is, no scan within the elution window of DFTPP may be subtracted from another scan within the elution window, and designed only to eliminate column bleed or instrumental background. Scans +/- 2 scans from the apex can be evaluated for the DFTPP criteria. Consecutive scans within this range may be averaged to meet the criteria.

NOTE: The DFTPP analysis should be evaluated as to the relative size of the DFTPP peak under the m/z 198 profile. A benchmark area window should be established for each instrument and data system. Area outside of this window suggests instrumental problems such as a bad injection, clogged autosampler syringe, leaking injector, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open, etc.

If the DFTPP fails to meet the criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the DFTPP analysis, other corrective measures may include remaking the DFTPP standard, cleaning the mass spectrometer source, etc.

10.2.1.4Benzidine and pentachlorophenol should be present at their normal responses with minimal peak tailing visible. Peak tailing guidance is taken from EPA Method 625 which allows pentachlorophenol to be less than or equal to five and benzidine less than or equal to three. Refer to Figure 1for an example of [eak tailing factor calculation.

This is a good check on the system: if pentachlorophenol (a CCC) does not respond well, the calibration standard should not be analyzed. Injector port and column maintenance should be performed and the tune/column evaluation standard reanalyzed.

The percent breakdown of p,p'- DDT is calculated using the following equation. The percent breakdown should not exceed 20%.

$$\%Breakdown = \frac{(areaDDE + areaDDD)}{(areaDDT + areaDDE + areaDDD)} x\ 100$$

Areas from the total ion chromatogram are used to calculate DDT breakdown.

10.2.2 After the DFTPP criteria and column evaluation criteria have been met, the initial calibration standards are analyzed.

10.2.2.1Prepare the initial calibration standards. The lowest calibration standard should be at the RL and the rest of the standards will define the working range. See section 10.2 for guidance regarding calibration levels.

10.2.2.2Set up a sequence and analyze the calibration standards. The injection volume must be the same for the calibration standards and all sample extracts.

10.2.3 Identify the internal standards, surrogates, and the target compounds. The data system must be updated with the proper retention times and ion data.

10.2.4 Calculate the relative response factor for each compound as follows:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured
(See the attached quantitation report for a list of the compounds that are associated with the correct internal standard)
Cx = concentration of the compound being measured (ug/mL)
Cis = concentration of the internal standard (40ug/mL)

Secondary ions may be used for quantification if there is interference with the primary quantitation ion. If a secondary ion is used for quantification, the concentration/response relationship of the secondary ion must be established. The secondary ion must meet the same calibration criteria as the primary ion.

10.2.5 Calculate the average relative response factor (RRF_{avg}) for each target compound and each surrogate compound:

$$RRF_{avg} = \frac{RRF1 + RRF2 + RRF3.... + RRFn}{n}$$

RRF1 = relative response factor of the first standard
RRFn = relative response factor of the last standard
n = number of calibration standards

10.2.6 Calculate the standard deviation (SD) for the initial calibration standards:

$$SD = \sqrt{\frac{\sum_{i-1}^{n_1} (RRF_i - RRF_{avg})^2}{n-1}}$$

10.2.7 Calculate the relative standard deviation (%RSD) of the target compounds in the calibration standards.

$$\%RSD = \frac{SD}{RRF_{avg}} x\ 100$$

10.2.8 Evaluation of the Initial Calibration

The initial calibration is evaluated specifically for the calibration check compounds (CCC) and the system performance check compounds (SPCC). The CCC and SPCC criteria are given in the SOP Summary (Appendix A). The %RSD criteria for CCC and minimum RRF for SPCC must be met before the analysis of sample extracts can begin.

If the CCC and SPCC criteria are not met, action must be taken to bring the analytical system into compliance with the criteria. This action may include injection port maintenance, source cleaning, changing the column, or replacement of injection port lines and assembly. In any case, if the criteria are not met, the initial calibration must be repeated. The analyst must be aware of the 12-hour clock for the DFTPP analysis. The DFTPP criteria must be met prior to the analysis of the calibration standards.

10.2.9 After the initial calibration criteria (CCC/SPCC) have been met, each target is evaluated for linearity. Refer to SOP AN67: *Evaluation of Calibration Curves* for guidance.

If the %RSD of the target compound is less than or equal to 15%, the average response factor can be used for quantitation of samples.

If the %RSD of the target compound is greater than 15%, a regression curve (linear, quadratic, etc) must be used for the quantitation of samples. A regression curve may also be used for the compounds that have %RSD less than 15%. The results can be used to plot a calibration curve of response ratios-Ax/Ais is plotted on the y-axis; Cx/Cis is plotted on the x-axis where:

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (See attached quantitation report for a list of the compounds and their associated internal standard)
Cx = concentration of the target compound being measured (ug/mL)
Cis = concentration of the internal standard (ug/mL)

A linear or quadratic curve may be used to define the concentration/response relationship. If r^2 is greater than 0.99, the curve can be used to quantify samples. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire concentration range.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPPs for other exceptions to using non-linear curve fitting.

When more calibration levels are analyzed than required, individual compounds may be eliminated from the lowest or highest calibration levels(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of the calibration curve be eliminated without eliminating the entire level.

8000B exception: evaluation of the "grand mean": If the average %RSD of ALL (all targets including CCC and SPCC) compounds in the initial calibration is less than 15%, the average response factor can be used for quantitation of all target compounds. The recommended course is to use regression curves, as described above, to quantify targets where the %RSD criterion (<=15%) is exceeded.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

10.3 Continuing Calibration Verification

At the beginning of each 12-hour clock, the tune of the instrument must be checked by the analysis of the tune/column evaluation solution (10.2.1.1). The tune and column evaluation criteria (10.2.1.3 and 10.2.1.4) must be met before the analysis of the calibration check standards can take place.

10.3.1 After the tune and column evaluation criteria have been met, a continuing calibration check standard(s) is analyzed. The continuing calibration standard should be at a mid-level concentration. The CCC and SPCC criteria (SOP Summary, Appendix A) must be met before the analysis of samples can take place. The percent difference (%D) is calculated as follows:

$$\%D = \frac{RRFavg - RRFccv}{RRFavg} \otimes 100$$

where
RRFavg = average response factor from initial calibration
RRFccv = response factor from the check (12-hour) standard-calibration verification

The percent drift (%Drift) may also be used to evaluate the change/deviation of the curve:

$$\%Drift = \frac{Ci - Cccv}{Ci} \otimes 100$$

where
Ci = Calibration Check Compound standard concentration (ug/mL)
Cccv = measured concentration using the selected quantitation method (ug/mL)

NOTE: The SPCC criteria (10.3.8) must be met even if the regression curve option is used for quantitation. If these criteria are not met, corrective action must be taken. The corrective action may include reanalysis of the calibration check standard or preparation of a new secondary stock standard and reanalysis of the calibration check standard. If subsequent analysis of the standard is still out of criteria, a new initial calibration curve must be analyzed and evaluated.

10.3.2 The continuing calibration verification standard (CCV) must also be evaluated for internal standard response.

If the extracted ion current profile (EICP) area for any of the internal standards in the CCV changes by more than a factor of two (-50% to +100%) from the last initial calibration sequence, the analytical system must be inspected for problems and corrective action instituted.

10.4 Samples are analyzed only after the DFTPP criteria, column evaluation criteria and the calibration verification criteria have been met. The analytical system must be evaluated every 12 hours by the analysis and evaluation of the tune/column evaluation standard and a mid-level calibration standard.

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
Tune/Column Evaluation Standard Clock starts at injection	Tune/Column Evaluation Standard Clock starts at injection
Calibration standards- Minimum of five cal levels	Mid point calibration verification Optional RL: Standard-low point on cal curve
Samples analyzed until 12-hour clock expires	Samples analyzed until 12-hour clock expires

10.4.1 Remove the sample extracts to be analyzed from the refrigerator and allow the sample to come to ambient temperature.

10.4.2 Add 20-uL of the internal standard mix (2000 ug/mL) to each 1.0mL aliquot of the sample extract. The concentration of the internal standard in the extract is 40 g/mL.

10.4.3 Mix the contents of the autosampler vial by inverting several times.

10.4.4 Analyze the samples using the same analytical conditions used for the initial and continuing calibration standard. Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

NOTE: Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client. For TCLP analyses, every reasonable effort should be made to achieve the regulatory level with out instrument overload.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with t the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower RLs.

10.4.5 The dilution factor is calculated by dividing the volume of sample extract in microliters into 1000. For example, if 100uL of a sample extract are diluted to final volume of 1.0mL, the dilution factor is 10. (1000/100 = 10). The following table gives some dilution factors:

Dilution Preparation

uL extract-Vext	uL MeCl2	volume of dilution (Vdil-uL)	uL ISTD (2000ug/mL)-Vistd	DF
1000	0	1000	20	1
500	500	1000	10*	2
200	800	1000	16*	5
100	900	1000	18*	10
50	950	1000	19*	20
20	980	1000	20*	50

*assumes dilution of a 1mL extract or 1mL aliquot of an extract that has been spiked with the internal standard at 40ug/mL using 20ul of a 2000ug/mL internal standard solution

The concentration of internal standards must remain constant for all extracts and extract dilutions at 40ug/mL. The following equation can be used to determine the volume of the 2000ug/mL internal standard solution to add to an extract when a dilution is prepared from an extract that has already been spiked with the internal standard solution:

$$Vistd(uL) = 20uL - \left(\frac{Vext}{Vdil} \otimes 20ul\right)$$

Vistd = volume of 2000ug/mL internal standard to add to the diluted extract (uL)
Vext = volume of extract used to prepare the dilution (uL)
Vdil = final volume of the dilution (uL)-1000uL (1.0mL)

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Qualitative Analysis

11.1.1 Target Compounds

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from the daily calibration standard or a reference spectrum of the target compound stored in a library generated on the same instrument or a standard spectral library such as the NIST/NBS.

11.1.1.1 Two criteria must be met in order to positively identify a compound.

1) elution of the sample component within +/-0.06 RRT (relative retention time) units of the daily standard containing that compound.

$$RRT = \frac{\textit{retention time of the target compound}}{\textit{retention time of the associated internal standard}}$$

2) correspondence of the target compound spectrum and the standard component mass spectrum.

11.1.1.2 All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion = 100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound will make the identification of the target compound more difficult. Ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

11.1.1.3 The relative intensities of the ions present in the sample component spectrum should agree within +/- 30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum.

11.1.1.4 If the above criteria are not met exactly, the analyst should seek help from a senior analyst or supervisor. If there is sufficient evidence to support the identification of the component, then the component is identified, quantified, and reported.

11.1.2 Tentatively Identified Compounds (TICs)

For samples containing components not associated with the calibration standards, a library search on a reference library, such as the NIST/NBS, may be conducted in order to identify the non-target compounds. Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification.

The default procedure is to evaluate up to 20 compounds of greatest apparent concentration that are not included as target compounds or routinely reported volatile compounds. The unknown compounds are tentatively identified using a forward search of the reference library.

If the library search produces a match at or above 85%, report that compound. If the library search produces more than one compound at or above 85%, report the first compound (the highest match quality). If the library search produces no matches at or above 85%, report the compound as unknown. If possible, provide a general classification of the unknown – for example, unknown aromatic, unknown hydrocarbon, etc.

TICs should be evaluated within the retention time range from the first eluting target or surrogate (whichever is first in the target list) to three minutes after the elution of the last target compound.

11.1.2.1 Relative intensities of the major ions (masses) in the reference spectra (ions >10% of the most abundant ion) should be present in the sample spectrum.

11.1.2.2 The relative intensities of the major ions should agree within +/-20%.

11.1.2.3 Molecular ions present in the spectrum should be present in the sample spectrum.

11.1.2.4 Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible subtraction from the sample spectrum because of over-lapping or co-eluting peaks.

11.1.2.5 Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of coeluting peaks.

11.1.2.6 If, in the opinion of the analyst, there is enough evidence to support the tentative identification of a compound even though the above criteria is not met exactly, the peak may be considered tentatively identified. The analyst should consult senior analysts or the mass spectral interpretation specialist if there are any questions concerning an interpretation of spectra.

11.1.2.7 The estimated concentration of the tentatively identified compound (TIC) is calculated using the total ion area of the tentatively identified peak and total ion area of the nearest internal standard that has no interferences. The calculations assume that the same volume is injected for standards and samples.

Aqueous

$$TIC(ug/L) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{F}{V} \otimes DF$$

where:

Cis =	concentration of the internal standard (ug/mL)
AREAis =	total ion peak area of the internal standard
AREAtic=	total ion peak area of the TIC
F =	final volume of extract (mL)
V =	volume of sample extract (L)
DF =	dilution factor

Soils

$$TIC\ (ug/kg,dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{F}{(W)(solids)} \otimes DF$$

where:

Cis =	concentration of the internal standard, ug/mL
AREAis =	total ion peak area of the internal standard
AREAtic=	total ion peak area of the TIC
F =	final volume of extract mL
W =	weight of sample analyzed (kg)
solids =	decimal equivalent of percent solids

11.2 Calculations for Samples-Internal Standard Technique
These calculations assume that the same volume is injected for standards and samples and that the standards and samples have the same concentration of internal standard.

11.2.1 Aqueous Samples

11.2.1.1 If the relative response factor is used, the calculation for samples is :

$$concentration(ug/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{V} \otimes DF$$

where:

Ax =	area of the characteristic ion of the compound being measured
Ais =	area of the characteristic ion of the internal standard
Cis =	concentration of the internal standard (ug/mL)
RRFavg =	average response factor of the compound being measured
F =	final volume of extract (mL)
V =	volume of sample extracted (L)
DF =	dilution factor

11.2.1.2 If a regression curve is used, the concentration is given:

$$concentration(ug/L) = Ccurve \otimes \frac{F}{V} \otimes DF$$

where:

C_{curve} =	concentration from curve (ug/mL)
F =	final volume of extract (mL)
V =	volume of sample extracted (L)
DF =	dilution factor

11.2.1.3 The reporting limit (RL) for each sample is given:

$$RL(ug/L) = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Vqap}{V} \otimes DF$$

where:

F = final volume of extract (mL)
Fqap = 1.0mL
Vqap = 1.0L
V = volume of sample extracted
DF = dilution factor. The LQM RL assumes a DF of 1.

NOTE: If V = 800mL to 1200mL, assume that Vqap/ V = 1 in the calculation of the reporting limit.

11.2.2 Soils

11.2.2.1 If the relative response factor is used, the calculation for samples is :

$$concentration(ug/kg,dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/mL)
RRFavg = average response factor of the compound being measured
F = final volume of extract (mL)
W = weight of sample extracted (kg)
solids = (percent solids)/100
DF = dilution factor

11.2.2.2 If the regression curve is used, the concentration is given:

$$conc(ug/kg,dw) = Ccurve \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Ccurve = concentration from curve(ug/mL)
W = weight of sample extracted (kg)
F = final volume of extract (mL)
solids = (percent solids)/100)
DF = dilution factor

11.2.2.3 The reporting limit (RL) for each sample is given:

$$RL = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Wqap}{(W)(solids)} \otimes DF$$

where

F = final volume of extract (mL)
W = weight of sample extracted (kg)
solids = (percent solids)/100

The LQM assumes Wqap = 30g, solids = 1, Fqap = 1.0mL, and DF = 1.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items that are analyzed together. The matrix spike and LCS frequency is defined in AN02: *Analytical Batching.* SOP AN02 also describes the procedure for evaluating batch-specific QC. The QA/QC criteria are summarized in the SOP Summary (Appendix A).

12.2 Initial Demonstration of Capability (IDOC) to Generate Acceptable Accuracy and Precision

Each analyst must participate in the analysis of samples by this procedure in accordance with SOP CA92: *Evaluation of IDOCs.*

12.3 Method Detection Limit

The method detection limit is determined in accordance with SOP CA90: *Procedure for the Determination of the Method Detection Limit.*

13.0 PREVENTIVE MAINTENANCE & TROUBLESHOOTING

Refer to SOP AN53: *Preventive Maintenance Procedures for Laboratory Instruments* for guidance.

14.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Refer to SOP CA70: *Waste Management* for proper waste handling procedures.

15.0 REFERENCES

15.1 *STL Savannah Laboratory Quality Manual* current revision.

15.2 Method 8270C:*Test Methods for Evaluating Solid Wastes, Third Edition, SW-846;* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

APPENDIX A
8270C SOP SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	none; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Waste	none; 4C	Glass	14 days	40 days
TCLP	none; 4C	1-L amber	7 days	40 days

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
Tune/Column Evaluation Standard Clock starts at injection	Tune/Column Evaluation Standard Clock starts at injection
Calibration standards- minimum of five cal levels	Mid point calibration verification standard RL Standard (lowest point on calibration curve if required by client or state-specific QAP)
Samples analyzed until the 12-hour clock expires	Samples analyzed until 12-hour clock expires

SEMIVOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION (DFTPP)	
m/e	**Ion Abundance Criteria (1)**
51	30-80% of mass 442
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	25-75% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of mass 198
275	10-30% of mass 198
365	Greater than 0.75% of mass 198
441	Present but less than mass 443
442	40-110% of mass 198
443	15.0-24.0% of mass 442

(1) 8270 criteria taken from CLP OLMO4.0 (January 1998). The use of alternate criteria is expressly allowed in SW-846 Method 8270C.

APPENDIX A
8270C SOP SUMMARY

CALIBRATION ACCEPTANCE CRITERIA

Calibration Check Compounds - CCC
Phenol, 1,4-Dichlorobenzene, 2-Nitrophenol, 2,4-Dichlorophenol, Hexachlorobutadiene, 4-Chloro-3-methylphenol, 2,4,6-Trichlorophenol, Acenapthene, N-Nitrosodiphenylamine, Pentachlorophenol, Fluoranthene, Di-n-octylphthalate, Benzo(a) pyrene

System Performance Check Compounds-SPCC
N-Nitrosodi-n-propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol, 4-Nitrophenol

Initial Calibration	Continuing Calibration*
CCC: <= 30% RSD	CCC: <= 20% difference from initial calibration
SPCC: RRFavg >= 0.050	SPCC: RRF>= 0.050

*If CCC and/or SPCC do not meet the stated criteria, all targets that are reported must meet the CCC criteria.

NOTE: The CCC and SPCC criteria must be met even if the calibration curve option is used for quantitation. If the CCC and SPCC criteria do not pass, a new calibration curve must be prepared and analyzed.

The results for all target compounds are evaluated for linearity. If the %RSD is less than 15%, the calibration is assumed linear through the origin and the average response factor can be used for quantitation. If the average response factor for the target exceeds 15% (including any CCC), the analyst must use the calibration curve option.

NOTE: The lab has the option of using a regression curve for all analytes.

A linear, quadratic, or higher order regression fit may be used to define the concentration/response relationship. If r^2 is greater than 0.99, the curve can be used to quantify samples. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire calibration range. The minimum number of calibration standards required for a regression curve are given in the following table:

Type of curve	Minimum Number of Calibration Points
Linear (first order)	5
Quadratic (second order)	6

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tune/Column Evaluation Standard DFTPP 50ng Pentachlorophenol - 50ng Benzidine – 50ng p,p'-DDT 50ng	Prior to analysis of calibration standards every 12 hours	DFTPP - within criteria	-Evaluate alternative scans -Reanalyze and evaluate -Retune and reanalyze -Clean source, retune, reanalyze
		Pentachlorophenol and benzidine - present at usual response with no peak tailing visible p,p'-DDT - %breakdown <20%	-Reanalyze -Perform injector port maintenance and reanalyze -Cut more than usual length of column and reanalyze -Replace column
Initial Calibration	After Tune Check and when calibration verification standard fails acceptance criteria. All initial calibration standards	CCC: %RSD < 30% SPCC: RRFavg > 0.050 Use regression curve for quantitation if %RSD for any target compound exceeds 15%	-Reanalyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standards -Retune and reanalyze standards -Replace column and reanalyze standards -Clean source and reanalyze standards
Continuing Calibration Verification	After tune check; every 12 hours prior to analysis of samples	CCC: %Difference <= 20% Or %Drift <= 20% SPCC: RRF >= 0.050	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate
Internal Standard Areas	Evaluate all standards and samples	Areas in continuing calibration verification must be 50% to +200% of previous initial calibration sequence Areas in samples should be evaluated for gross error. Consult supervisor Retention time of internal standard must be +/-30 seconds from internal standard in previous CCV.	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available -Recalibrate

QC Item	Frequency	Acceptance Criteria	Corrective Action
Surrogate recovery	Evaluate for all samples and QC items if extract is not diluted OR If diluted, where >RL	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract(s) -Re-extract and reanalyze if sufficient sample available
Method Blank	Per batch	All targets < RL in LQM	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL-SL SOP AN02
Lab Control Standard (LCS) - QAP subset	Per batch See SOP AN02	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL-SL SOP AN02
Matrix spike (MS) Matrix spike duplicate (MSD)	Per batch if sufficient sample volume/weight supplied See SOP AN02	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL-SL SOP AN02
RL Standard (reporting limit)	Daily (optional)-lowest point on calibration curve if required by client or state-specific QAP	Detected at reasonable sensitivity	-Evaluate integrations and spectra; -Reanalyze -Prepare new standard and reanalyze
Initial Demonstration of Capability (IDOC)	Each work group	Accuracy and precision within method specified criteria	-Evaluate data -Reanalyze extracts if warranted -Re-extract and reanalyze for targets that fail criteria
Method Detection Limit (MDL)	Annually for each routine matrix See SOP CA90	Evaluate according to SOP CA90	Evaluate according to SOP CA90

APPENDIX B- TARGET COMPOUNDS

ROUTINE TARGET LIST

PARAMETER	RT	Quant Ion	Secondary Ions		ISTD
1,4-Dioxane	1.894	88	58	45	1
Pyridine	2.123	79	52	51	1
N-Nitrosodimethylamine	2.102	42	74		1
Aniline	3.812	93	66		1
Phenol	3.796	94	66	65	1
Bis(2-chloroethyl)ether	3.854	63	93	95	1
2-Chlorophenol	3.908	128	130	64	1
1,3-Dichlorobenzene	4.025	146	148	111	1
1,4-Dichlorobenzene	4.073	146	148	111	1
Benzyl Alcohol	4.202	108	79	77	1
1,2-Dichlorobenzene	4.239	146	148		1
2-Methylphenol	4.314	107	108	77	1
bis(2-Chloroisopropyl)ether	4.335	45	121		1
N-Nitroso-di-n-propylamine	4.469	70	42	101	1
3&4-Methylphenol	4.447	107	108		1
Hexachloroethane	4.522	117	201	199	1
Nitrobenzene	4.602	77	123	65	2
Isophorone	4.837	82	95	138	2
2-Nitrophenol	4.923	139	109	65	2
2,4-Dimethylphenol	4.965	107	122	121	2
Bis(2-chloroethoxy)methane	5.067	93	123	95	2
Benzoic acid	5.115	105	122		2
2,4-Dichlorophenol	5.169	162	164	98	2
1,2,4-Trichlorobenzene	5.259	180	182	145	2
Naphthalene	5.323	128	129		2
4-Chloroaniline	5.409	127	129	65	2
Hexachlorobutadiene	5.532	225	223	227	2
4-Chloro-3-methylphenol	5.991	107	144	142	2
2-Methylnaphthalene	6.135	142	141		2
1-Methylnaphthalene	6.269	142	141		2
Hexachlorocyclopentadiene	6.429	237	235	272	3
2,4,6-Trichlorophenol	6.541	196	198	200	3
2,4,5-Trichlorophenol	6.590	196	198	200	3
2-Chloronaphthalene	6.760	162	164	127	3
2-Nitroaniline	6.958	65	92	138	3
Dimethylphthalate	7.268	163	194	164	3
2,6-Dinitrotoluene	7.353	165	89	63	3
Acenaphthylene	7.337	152	151	153	3
3-Nitroaniline	7.540	138	108	92	3
Acenaphthene	7.599	154	153	152	3
2,4-Dinitrophenol	7.685	184	63	154	3
4-Nitrophenol	7.824	65	109	139	3
Dibenzofuran	7.829	168	139		3
2,4-Dinitrotoluene	7.914	165	89	63	3
2,3,4,5-Tetrachlorophenol	8.064	232	230	131	3
2,3,4,6-Tetrachlorophenol	8.091	232	230	131	3
Diethylphthalate	8.310	149	177	150	3

Fluorene	8.336	166	165	167	3
4-Chlorophenyl-phenylether	8.363	204	141	206	3
4-Nitroaniline	8.454	138	108	92	3
4,6-Dinitro-2-methylphenol	8.513	198	105	121	4
N-Nitrosodiphenylamine	8.555	169	168	167	4
1,2-Diphenylhydrazine	8.593	77	105	182	4
4-Bromophenyl-phenylether	9.090	248	250	141	4
Hexachlorobenzene	9.293	284	142	249	4
Pentachlorophenol	9.581	266	264	268	4
Phenanthrene	9.784	178	176	179	4
Anthracene	9.854	178	176	179	4
Carbazole	10.137	167			4
Di-n-Butylphthalate	10.847	149	150	104	4
Fluoranthene	11.659	202	203	101	4
Benzidine	11.926	184	92	185	5
Pyrene	12.006	202	200	203	5
Butylbenzylphthalate	13.214	149	91	206	5
3,3'-Dichlorobenzidine	13.892	252	254	126	5
Benzo(a)Anthracene	13.866	228	229	226	5
Bis(2-ethylhexyl)phthalate	14.111	149	167	279	5
Chrysene	13.924	228	226	229	5
Di-n-octylphthalate	14.971	149	43		5
Benzo(b)fluoranthene	15.367	252	253	125	6
Benzo(k)fluoranthene	15.399	252	253	125	6
Benzo(a)pyrene	15.783	252	125	253	6
Indeno(1,2,3-cd)pyrene	17.284	276	139		6
Dibenzo(a,h)anthracene	17.317	278	139	279	6
Benzo(g,h,i)perylene	17.674	276	277	138	6
SURROGATES					
2-Fluorophenol	3.032	112	64		1
Phenol-d5	3.785	99	71		1
Nitrobenzene-d5	4.586	82	128	54	2
2-Fluorobiphenyl	6.643	172	171		3
2,4,6-Tribromophenol	8.732	330	332	141	3
Terphenyl-d14	12.332	244	122	212	5
INTERNAL STANDARDS					
1,4-Dichlorobenzene-d4	4.057	152	150	115	1
Naphthalene-d8	5.302	136	68		2
Acenaphthene-d10	7.556	164	162	160	3
Phenanthrene-d10	9.747	188	94	80	4
Chrysene-d12	13.887	240	236	120	5
Perylene-d12	15.858	264	265	260	6

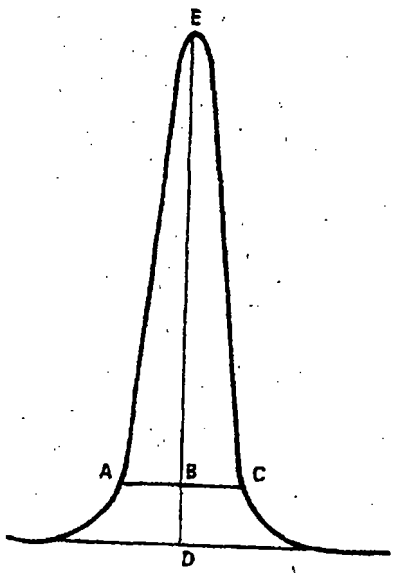
APPENDIX B- TARGET COMPOUNDS

APPENDIX IX TARGET LIST

PARAMETER	RT	Quant Ion	Secondary Ions			ISTD
1,4-Dioxane	1.933	88	58	45		1
Pyridine	2.178	79	52	51		1
2-Picoline	2.664	93	66			1
1,4-Benzoquinone	**4.466**	54	108	82		1
N-Nitrosomethylethylamine	2.739	88	42	43	56	1
Methyl methanesulfonate	2.964	80	79	65		1
N-Nitrosodiethylamine	3.268	102	42	44	57	1
Ethyl methanesulfonate	3.503	79	109	97	45	1
N-Nitrosopyrrolidine	4.481	100	41	42		2
Acetophenone	4.486	105	77	51		2
N-Nitrosomorpholine	4.497	56	86			1
O-Toluidine	4.529	106	107	79		2
Phorate	9.123	75	121			4
N-Nitrosopiperidine	4.796	114	42	55	56	2
O,O,O-Triethyphosphorothioate	5.122	65	97	93		2
2,6-Dichlorophenol	5.469	162	164	98		2
Hexachloropropene	5.507	213	211	215	117	2
1,2,4,5-Tetrachlorobenzene	6.447	216	214	179		3
a,a-Dimethylphenethylamine	5.619	58	91	42		2
N-Nitroso-di-n-butylamine	5.875	84	57	41		2
1,4-Phenylenediamine	5.864	108	80	107		2
Safrole	6.094	162	104	135	103	2
Isosafrole	6.757	162	104	131		2
1,1-Biphenyl	6.805	154	76			3
1,4-Naphthoquinone	7.056	158	104	76		3
m-Dinitrobenzene	7.317	168	76	50		3
Pentachlorobenzene	7.916	250	248	252	215	3
1-Naphthylamine	8.001	143	115	116		3
2-Naphthylamine	8.113	143	115	116		3
2,3,4,6-Tetrachlorophenol	8.140	232	230			3
5-Nitro-o-toluidine	8.466	152	77	106		3
Thionazin	8.471	107	96	97		4
Sulfotepp	9.032	97	65			4
1,3,5-Trinitrobenzene	9.091	213	74	120		4
1-Diallate	9.118	86	43	234		4
Phenacetin	9.161	108	109	179		3
2-Diallate	9.235	86	43	234		4
Dimethoate	9.396	87	93	125		4
4-Aminobiphenyl	9.556	169	168	170		4
Pronamide	9.748	173	175	145		4
Pentachloronitrobenzene	9.748	237	295	142	214	4
Disulfoton	9.935	88	60			4
Dinoseb	9.957	211	163	147		4
Methyl parathion	10.517	109	125			4
4-Nitroquinoline-1-oxide	11.094	174	101	128	75	4
Parathion	11.158	109	97			4
Famphur	**13.178**	218	93	125		4

Methapyrilene	11.388	97	58	191		4
Aramite-1	12.435	185	191	319		5
Aramite-2	12.563	185	191	319		5
p-Dimethylaminoazobenzene	12.638	120	225	77		5
Chlorbenzilate	12.745	139	251	75		4
Kepone	**17.739**	272	270	237		5
3,3'-Dimethylbenzidine	13.167	212	196	106		5
2-Acetylaminofluorene	13.562	181	180	223		5
7,12-Dimethylbenz(a)anthracene	15.438	256	239	241		6
Hexachlorophene	15.747	196	198			6
3-Methylcholanthrene	16.324	268	252	253		6
INTERNAL STANDARDS						
1,4-Dichlorobenzene-d4	4.102	152	150	115		1
Naphthalene-d8	5.346	136	68			2
Acenaphthene-d10	7.601	164	162	160		3
Phenanthrene-d10	9.802	188	94	189		4
Chrysene-d12	13.926	240	236	120		5
Perylene-d12	15.902	264	265	260		6

FIGURE 1 – Tailing Factor Calculation



TAILING FACTOR = $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

EXTRACTABLE ORGANIC HALIDES (EOX)

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Approved by:

R. Wayne Robbins — Dec 2, 1999

Title: STL-SL QA Manager — Date

1.0 SCOPE AND APPLICATION

1.1 This procedure can be used to determine the concentration of extractable organic halides (EOX) in soils and solids. Organically bound halides (chlorine, bromine, and iodine) are measured as equivalent concentrations of organic chloride.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria are given in Section 5 of the current revision of the STL-SL LQM.

2.0 SUMMARY OF METHOD

2.1 The organic halides present in soils and solids are extracted with ethyl acetate. An aliquot of the extract is injected into the pyrolysis oven of the TOX instrument where the OX is converted to hydrogen halide. The hydrogen halide is swept into the titration cell of a calibrated micro-coulometric detector and the concentration of the organic halide detected is reported as an equivalent concentration of organically bound chloride.

2.2 This method is based on the guidance in SW-846 Method 9023. This SOP contains a modification from the referenced method. 2,4,6-trichlorophenol is used as the standard in place of 1,2,4-trichlorobenzene. 1,2,4-trichlorobenzene is volatile and does not extract efficiently under the method conditions.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or will put yourself or others in a potentially unsafe situation. When handling samples and standards for analysis, the analyst must wear a lab coat or apron, safety glasses, and latex gloves.

3.2 Care must be taken when handling 2,4,6-trichlorophenol, which is used to prepare the stock calibration standards. This material is a suspected carcinogen and may be harmful if inhaled.

3.3 Glacial acetic acid can cause nose and throat irritation upon inhalation. Handling of this material must take place under a ventilated fume hood.

3.4 Field samples may have high concentrations of volatile compounds. Open the samples under a ventilated fume hood if the nature of the sample is not known.

3.5 The analyst must be familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in this procedure. The MSDS denote the type of hazard that each reagent poses and provide guidance for safely handling these compounds.

4.0 INTERFERENCES

4.1 Reagents and gases must be of the highest purity to minimize contamination. The lab should be free from halogenated solvents (such as chloroform and methylene chloride) which will cause a positive interference.

4.2 Contamination of glassware is diminished through scrupulous cleaning. If the reagent blanks show no detectable organic halide (OX), the cleaning steps are sufficient. If not, all glassware must be cleaned as soon as possible after use with a Nochromix solution. After the Nochromix cleaning, glassware must be washed with detergent (Liquinox) in hot water. Rinse glassware thoroughly with tap water, rinse

thoroughly with DI water, and allow to dry.

4.3 Loss of volatile components is diminished if sample is taken with zero headspace in the sampling container. Minimum handling of the sample also avoids loss of volatile organohalides (OX) as well as reduces the possibility of contamination.

4.4 Some inorganic salts, such as mercuric chloride, may be soluble in the ethyl acetate and cause a positive interference.

5.0 SAMPLE COLLECTION, HANDLING AND PRESERVATION

Soils and solid sample are collected in glass containers equipped with Teflon-lined caps. The samples should be collected and stored with minimum headspace to minimize the loss of volatile OX. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples) in the lab until the time of extraction and analysis. The samples must be extracted and analyzed within 28 days of collection.

6.0 APPARATUS AND MATERIALS

6.1 TOX microcoulometric analyzer: Dohrmann MC-3, or equivalent TOX/EOX analyzer

6.1.1 Sample boat

6.1.2 Pyrolysis furnace

6.1.3 Microcoulometric detector with integrator

6.1.4 Titration vessel

6.2 Top loading balance

6.3 Analytical balance

6.4 Microsyringes-various volumes with extended syringe bodies so that standards can be added under the surface of the liquid in volumetric flasks.

6.5 Centrifuge

6.6 15-mL conical centrifuge tubes

6.7 Sonicator

6.8 Scintillation or VOA vials

7.0 REAGENTS

Reagents must be tracked in accordance with STL-SL SOP AN44.

7.1 Reagent water - lab generated deionized (DI) water

7.2 Glacial acetic acid (CH_3COOH) - reagent grade.

7.3 Acetic acid, 70% (Titration cell electrolyte) - Transfer 70mL of glacial acetic acid to a 100mL volumetric flask. Dilute to volume with DI water. Transfer to a glass container with a Teflon lined cap.

CAUTION: GLACIAL ACETIC AICD WILL CAUSE EYE, NOSE, AND THROAT IRRITATION. THIS REAGENT MUST BE PREPARED UNDER A WELL VENTILATED HOOD.

7.4 Oxygen: 99.9% pure

7.5 Carbon dioxide: 99.9% pure

7.6 Ethyl acetate-residue grade. This solvent is used to extract organic halides from the sample matrix and must be protected from potential sources of halogenated organic materials such as chloroform and methylene chloride.

8.0 STANDARDS

The preparation of standards must be documented in accordance with STL-SL SOP AN41:*Standard Material Traceability*.

8.1 Sodium chloride-reagent grade

8.2 Sodium chloride stock standard (1000mg/L)-Weigh 0.1648g of sodium chloride into a 100-mL volumetric flask and dilute to volume with reagent water. This solution is used to calibrate the titration cell prior to the analysis of EOX.

8.3 Sodium chloride calibration standard (100mg/L)-Dilute 10mL of the 1000mg/L sodium chloride stock to 100mL in a 100-mL volumetric flask.

8.4 Sodium chloride calibration standard (10mg/L)-Dilute 1.0mL of the 1000mg/L sodium chloride stock to 100mL in a 100-mL volumetric flask.

8.5 2,4,6-Trichlorophenol-reagent grade

8.6 EOX/TCP Stock standard-10000 mg Cl /L. Transfer 1.856 g 2,4,6-trichlorophenol to a 100-mL volumetric flask containing 80mL of ethyl acetate. Dilute to volume with ethyl acetate. Transfer the stock standard to 40-mL VOA vials equipped with Teflon-lined septa. The stock standard is stored with minimum headspace to minimize the volatilization of the solvent and standard material. Store the solution at 4C in the dark.

NOTE: If the weight of 2,4,6-trichlorophenol is not exactly 1.856 g, the concentration of the stock (Cstock) can be calculated from the following equation:

$$Cstock(mg/L) = \frac{Wtcb \otimes \frac{106.5g}{197.4g}}{0.100L} \otimes 1000mg/g$$

where
Wtcb = weight of 2,4,6-trichlorophenol added to the volumetric flask(g)

8.7 EOX /TCP Spiking Solution, 400mgCl /L. Add 1 mL of the 10000 mg Cl /L EOX stock to 24 mL ethyl acetate. Transfer the stock standard to 40-mL VOA vials equipped with Teflon-lined septa. The stock standard is stored with minimum headspace to minimize the volatilization of the solvent and standard material. Store the solution at 4C in the dark.

NOTE: If the concentration of the stock solution is not 10000 mg Cl /L, the volume of stock required to prepare 25 mL of the 400mgCl /L working standard can be determined from the following equation:

$$Vs(mL) = \frac{25mL \otimes 400mg/L}{Cs(mg/L)}$$

where
Vs (mL) = volume of stock required in mL
Cs (mg/L) = concentration of the stock solution in mg Cl/L

9.0 SAMPLE PREPARATION

9.1 Remove the samples from the storage refrigerator and allow the samples to equilibrate to room temperature. Collect the required glassware and reagents and complete as much of the analysis log as possible while the samples are warming up.

9.2 Homogenize the samples by stirring with a stainless steel spatula. Stir in any water that has collected on top of the samples. Perform this step quickly to minimize loss of volatile compounds.

9.3 Using a stainless steel spatula or glass pipette; weigh 2g +/-0.1g of each soil or waste sample into separate 40mL VOA vial. Record the weight to the nearest 0.1g. For each batch of twenty or fewer samples, prepare two additional aliquots of the sample selected as the MS and MSD.

9.4 Prepare the method blank and LCS by weighing 2g of blank sand or blank soil into each of two extraction vials. (Assume that the weight of the method blank and LCS are 2g even if the weight is slightly different from 2g.)

9.5 Add 0.25mL (250uL) of the EOX spiking solution to the LCS, the MS, and the MSD. The theoretical concentration of the spike for a 2g sample is:

$$Ct(mg/kg,dw) = \frac{0.25mL \otimes 400mg/L}{2.0g \otimes solids} = \frac{0.25mL \otimes 400ug/mL}{2.0g \otimes solids} = \frac{100ug}{2g \otimes solids} = \frac{50mg}{kg \otimes solids}$$

9.6 Add 10mL of ethyl acetate to each sample, blank, LCS, and MS/MSD.

9.7 Close each vial and shake vigorously for 30 seconds.

9.8 Place the vials in an ultrasonic bath containing about 1 inch of water and sonicate for 15 minutes.

9.9 After the sonication, allow the samples to sit for 10 minutes. The particulates will settle out.

9.10 Decant the upper layer of extract into a 15-mL conical centrifuge tube. The water, soil, and solvent remaining in the vial can be discarded.

9.11 Centrifuge each sample and QC item at half power for 10 minutes.

9.12 Transfer the extract (upper layer) into a labeled scintillation vial equipped with a Teflon-lined cap and store at 4C in the dark until the time of analysis.

10.0 PROCEDURE

10.3 Routine Start-up and Cell Equilibration for EOX

10.3.1 Prepare the analyzer for use in the direct injection mode for TOX according to the directions in the Dorhmann instruction manual.

10.3.2 Turn the instrument on and open the CO2 and O2 tanks. Both regulators should be preset at 25psi.

10.3.3 While the furnace is heating up to 800C, perform the following checks:

-the FUNCTION select button on the front of the panel is set to STANDBY
-the GAIN control button on the front of the instrument is set at 30.
-the BIAS control button on the front of the instrument is set at 250
-ensure that the titration cell electrodes and the heater tape leads are properly connected
-ensure that the clamp on the titration cell ball joint is forming a tight seal
-verify that the input CO2 and O2 gas pressures are at 25psi.
-observe the gas bubbles in the titration cell. If no bubbles are observed, see Section 13 of STL-SL SOP BA12 or BA14 for guidance in troubleshooting the problem.

10.3.4 Flush the titration cell twice with 70% acetic acid.

10.3.5 Fill the titration cell with electrolyte to the fill line.

10.3.6 Check the baseline reading on the front panel. If a negative reading is displayed, continue to flush the titration cell with 70% acetic acid until a positive reading is displayed.

10.3.7 If the cell is flushed more that three times and a negative reading is still displayed, refer to Section 13 of STL-SL SOP BA12 or BA14 for guidance on troubleshooting the problem. If the problem cannot be resolved quickly, contact the immediate supervisor for assistance.

10.3.8 When a positive baseline is achieved, set the FUNCTION button to DET and the MODE button to POX.

10.3.9 Allow the baseline to stabilize. The baseline is stable when it varies by less than 2 digits.

-if the baseline fails to stabilize within 2-3 minutes, increase the GAIN adjustment slightly.

-if the baseline continues to fluctuate more than 2 digits, see Section 13 of this SOP for guidance in troubleshooting the problem. If the problem cannot be resolved quickly, contact the immediate supervisor.

10.3.10 After the baseline has stabilized, set the MODE button to the EOX mode and the FUNCTION setting to INT.

10.3.11 Set the analysis time to five minutes and verify that the READY lamp on the front panel is illuminated. If the READY lamp is not on, press the CANCEL button once or twice to reset.

10.4 EOX Sample Analyses

ANALYTICAL SEQUENCE

Initial Calibration	Direct injection of sodium chloride standards into titration cell at 0.10, 0.20, 0.50,1.0, 2.0, 4.0 and 8.0ug Cl
System Blank (Method Blank)	40uL blank extract
Calibration Verification (LCS)	40uL of 50 mg/kg EOX/TCP Calibration Standard
Sample Analyses-twenty sample analyses	All samples are analyzed in duplicate at 40uL.

NOTE: Cell maintenance or other changes to the analytical system that affect the system performance may not be performed during sample analysis. The calibration must be verified by the analysis of the LCS standard and system blank after instrument maintenance is performed.

10.4.1 Calibrate the TOX analyzer by injecting various amounts of the 10mg/L sodium chloride stock and 100mg/L sodium chloride calibration solutions directly into the titration cell. The analyzer is operated in the POX mode during the cell calibration.

Calibration Standard	Stock	Volume (uL) Injected	ng Cl	ug Cl
EOX-1	10mg/L	10	100	0.10
EOX-2	10mg/L	20	200	0.20
EOX-3	10mg/L	50	500	0.50
EOX-4	100mg/L	10	1000	1.0
EOX-5	100mg/L	20	2000	2.0
EOX-6	100mg/L	40	4000	4.0
EOX-7	100mg/L	80	8000	8.0

10.4.1.1 Calculate the response factor for each calibration standard using the following equation:

$$RF = \frac{\text{concentration from the analysis of the cal std (ug/L)}}{\text{true concentration of the cal std (ug/L)}}$$

10.4.1.2 Calculate the average response (or calibration) factor for the initial calibration standards:

$$RF_{avg} = \frac{RF_1 + RF_2 + \ldots + RF_n}{n}$$

where n = number of standards in the initial calibration

10.4.1.3 Calculate the standard deviation of the five calibration levels for each target.

$$Standard\ Deviation = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RFavg})^2}{n-1}}$$

where

RF_i = response factor of the individual calibration level

RFavg = average response factor

n = number of calibration standards in the initial calibration

10.4.1.4 Calculate the relative standard deviation (% RSD):

$$\%\,RSD = \frac{standard\ deviation}{RFavg} \otimes 100$$

If the % RSD is less than 20% in the initial curve, the calibration is considered linear and the average response factor (or calibration factor) is used for quantitation.

10.4.1.5 After the initial calibration has been evaluated, each calibration standard is recalculated using the average response factor from the curve:

$$C(recal - ug/L) = \frac{\text{concentration from the analysis (ug/L)}}{RFavg}$$

The "recalculated concentration" for each calibration point must be within 5% of the true concentration or within 50 ng of the true value.

10.4.2 Verify the calibration by analyzing three 40uL aliquots of the EOX /TCP calibration standard. All three standards must be ±40% of the true value.

10.4.3 Remove the extracts from the storage refrigerator and allow the extracts to come to room temperature.

10.4.4 Draw 45uL of the extract into a 50uL microsyringe. If air bubbles are introduced into the syringe, expel the extract and draw up another aliquot of the extract. Adjust the volume to the 40uL mark. Pull the plunger out until all of the extract is contained in the body of the syringe.

10.4.5 Press START. The READY light should go out and the INT light should be illuminated. Wait four seconds for baseline memorization.

10.4.6 Inject the extract through the septum at the end of the glass-to-ball connector at a rate of about 5uL/sec.

10.4.7 When the READY light on the front panel comes on, record the reading on the EOX log. Note that the reading is in nanograms. If the reading exceeds 9999 nanograms, the display will blink and zeros will be displayed, indicating that the weight of OX in the extract has exceeded the capacity of the titration cell and that the extract will require dilution and reanalysis.

11.0 CALCULATIONS

11.4 Soils (EOX)

$$EOX(mg/kg,dw) = \frac{TX}{\frac{W \otimes solids}{Vext} \otimes Vinj} \otimes DF$$

where
TX = weight of halogen detected in the extract (ng)
W = weight of sample extracted (g)
solids = (percent solids)/100
Vext = volume of solvent used to extract the sample (mL)
Vinj = volume of extract (mL)
DF = dilution factor (if dilution of the extract is required)

11.1 Matrix spike recovery

$$\%recovery = \frac{Cms - Csample}{T} \otimes 100$$

where
Cms = concentration of the spiked sample (mg/kg,dw)
Csample = concentration of the unspiked sample (mg/kg,dw)
T = true value of the spike (mg/kg,dw)

The equation can also be used to calculate the recovery of the LCS where Csample = 0.

The true value (concentration) of the spike is calculated:

$$T = \frac{Cs \otimes Vs}{W \otimes solids}$$

where
Cs = concentration of the spiking solution(ug/mL)
Vs = volume of the spiking solution added to the sample(mL)
W = weight of sample spiked (g)
solids = (percent solids)/100

(recall that mg/L = ug/mL)

11.5 Precision as %RPD

$$\%RPD = \left| \frac{Cms - Cmsd}{\frac{Cms + Cmsd}{2}} \right| \otimes 100$$

where
Cms = concentration of MS
Cmsd = concentration of MSD

12.0 QUALITY ASSURANCE/QUALITY CONTROL

12.1 See STL-SL SOP AN02: *Analytical Batching* for guidance in establishing and evaluating batch QC. MS and MSD must be performed at a minimum frequency of 5% of samples. Each batch will have a minimum of a method blank and a LCS.

12.2 Each analyst must demonstrate the ability to generate acceptable results using this procedure-the initial demonstration of capability (IDOC).

-Weigh five 2-g aliquots of a blank sand or soil into extraction vessels.

-Add 0.25 mL of the 400mg/L TCP standard to four of the vials. The theoretical concentration is

$$Ct(mg/kg) = \frac{400mg/L \otimes 0.25mL}{2.0g} = \frac{400ug/mL \otimes 0.25mL}{2.0g} = 50ug/g = 50mg/kg$$

-Add 10mL of ethyl acetate to each spiked sample and the blank.

-Extract the samples as described in Section 9 and analyze the samples as described in Section 10.

-Calculate the concentration of each sample, the average recovery, and the standard deviation. The following criteria should be met to demonstrate capability:

Average recovery (mg/kg)	Standard Deviation(mg/kg)
44-56	<5

This criteria is based on the recovery of the CCV specified in Method 9023 and represents a recovery range of 88-112%. The standard deviation criteria was selected at 10% of the true value.

12.3 The method detection limit (MDL) must be determined annually in accordance with STL-SL SOP CA90.

13.0 MAINTENANCE, TROUBLESHOOTING, AND GENERAL CONCEPTS

13.1 Microcoulometric Titrations

13.1.1 Theory of Microcoulometry

In the titration cell, the acid halide species are titrated within the cell with an internally generated titrant. There are two pair of electrodes contained in the titration cell. The generating pair of electrodes generates the titrant (silver ions). These electrodes are called the working and auxiliary electrodes. The sensor/reference pair of electrodes monitors the concentration of the titrant at all times. All of the electrodes with the exception of the generator auxiliary are made of solid silver. The generator auxiliary electrode is platinum wire. The cell electrolyte is 70% acetic acid.

13.1.2 Principles of Operation of the Titration Cell and Microcoulometric Detector

13.1.2.1 The titration cell is designed to maintain a constant titrant (silver ion) concentration. When a halide such as chloride, bromide, or iodide enters the titration cell, the silver halide is formed so the silver ion concentration decreases. This decrease in silver ion is detected by the reference and sensor electrodes.

13.3.2.2 The mV output is directly related to the silver ion concentration.

13.3.2.3 The reference electrode is mounted in silver acetate. This electrode generates a constant mV output used as the reference voltage within the cell.

13.3.2.4 The silver sensor electrode is positioned directly above the gas stream coming from the pyrolysis tube, to ensure that the halides present pass over it.

13.3.2.5 The working generator electrode is also positioned directly above the gas stream coming from the pyrolysis tube, to ensure that the halides present pass over it.

13.3.2.6 The sensor electrode and the working electrode are coated with a silver chloride coating. Silver ions are continuously released into the electrolyte to maintain a constant silver ion concentration when halides are not present.

13.3.2.7 The working electrode and the auxiliary electrode work together to generate or remove silver ions in the stirred electrolyte which permits the restoration of the silver ion to its original concentration whenever a change is detected by the reference/sensor electrode pair.

13.3.2.8 The microcoulometric detector will detect zero OX when the voltage at the reference electrode is exactly equal to the voltage determined at the sensor electrode. A change in the voltage at the sensor electrode (a decrease in silver ion concentration) is translated by the detector as a positive TOX result.

13.2 Cell Maintenance and Troubleshooting

13.2.1 Cell Performance Check

13.2.1.1 The cell performance check must be performed daily after the cell has been flushed and filled with fresh electrolyte. The results of the performance check should be recorded into the TOX or EOX analysis log.

13.2.1.2 Prepare a 1000ppm sodium chloride (NaCl) solution by dissolving 0.1648g of NaCl in approximately 80mL of DI water placed in a 100mL volumetric flask. Mix. Dilute to 100mL with DI water.

13.2.1.3 Set the FUNCTION knob to POX, and set the MODE to DET, and the output units to ng.

13.2.1.4 With the titration cell connected to the pyrolysis tube, verify that the baseline is stable.

13.2.1.5 Change the FUNCTION knob to INT.

13.2.1.6 Press START and wait 4 seconds for baseline memorization.

13.2.1.7 Remove the glass cap from the top of the titration cell. Using a 100uL or 50uL syringe, inject 5uL of the 1000ppm sodium chloride (NaCl) solution directly into the top of the titration cell. Replace the titration cap.
**NOTE--The syringe tip should be submerged in the electrolyte when the NaCl is injected.

13.2.1.8 The halide measurement should fall within 2% of the true value injected.

13.2.1.9 The true value of the standard is calculated as follows:

Ideal reading = (1000ng/uL) x 5uL = 5000ng

(Recall that 1000mg/L = 1000ng/uL)

13.2.1.10 If the true value of the chloride standard is not within 2%, the cell must be flushed and the performance check should be performed again.

13.2.2 Flushing the Cell and Disposal of Electrolyte

A drain vessel is placed below the titration cell which is large enough to hold approximately 200mL of electrolyte. Place about 2 teaspoons of sodium carbonate in to the bottom of the vessel to neutralize the acetic acid. When flushing the titration cell, allow the acetic acid to drain into this vessel and neutralize. Once the solution is neutralized it may be disposed of in a sink while running plenty of water behind.

13.2.3 Whenever the titration cell is connected to the pyrolysis tube and NO gas stream is flowing through the cell inlet, the heater tape must ALWAYS be de-energized. This can be done by switching the FUNCTION knob to "STANDBY".

13.2.4 The titration cell must ALWAYS be stored with electrolyte. The electrodes must not be allowed to dry.

13.2.5 The analyst should be checking for bubbles in the titration sidearms continuously throughout sample analysis. The presence of air bubbles in the sidearms will cause erratic and consistent results since the continuity of the electrical charge will potentially be broken.

13.2.6 Bubbles in the titration sidearms (except in the reference sidearm) can be dislodged by opening the stopcock closest to the sidearm containing the bubble, while tilting the cell so the stopcock is pointing upward. Gently tap the cell body until the bubble becomes dislodged and passes through the stopcock. Close the stopcock and reposition the cell.

13.2.7 A negative baseline reading can be from an excess of ions in the cell solution. Flush the cell with fresh electrolyte and perform the cell performance check with the NaCl. The cell performance check should be +/- 2% of the true value.

A negative baseline can also be from contaminated gas or low gas pressure. Replace gas source.

13.2.8 If the baseline is too high or too noisy, check for air bubbles which may be lodged in the electrode sidearms. Dislodge any bubbles according to 13.4.6.

13.2.9 A high or noisy baseline may also be caused by a dirty titration cell, or a titration cell which is low on electrolyte. Clean (13.5) the titration cell and do the performance check.

13.3 Titration Cell Cleaning

13.3.1 Empty the cell of electrolyte and disconnect from the pyrolysis tube. Remove the heater tape.

13.3.2 Unplug all BUT the reference electrodes from their ports. Replug these three ports with a silicone plug.

13.3.3 Open the reference sidearm stopcock briefly to lodge a pocket of air in the capillary and prevent any other material other than electrolyte from coming into the reference arm. Then rinse the cell body and reservoir with DI water. Fill the cell body with 5 to 10mL of Nochromix solution.

13.3.4 Using a suction bulb, draw the acid up and down the capillary inlet until clean.

13.3.5 Rinse the cell thoroughly with DI water.

13.3.6 Re-install the three electrodes in their proper ports.

13.3.7 Flush the cell thoroughly with electrolyte, then restore the electrolyte to the proper level.

13.3.8 *Eliminate any bubbles in the sidearms, including the bubble in the reference sidearm.*

13.3.9 If the cell performance check yields values greater than +/- 2% of the true value, check or replace the o-rings at the exit tube. Once the o-rings are replaced, verify a constant gas flow.

13.4 Cleaning and Reconditioning the Cell Electrodes.

13.4.1 Drain the cell electrolyte and remove the black and green electrodes.

13.4.2 Clean the sensor and working (green and black, respectively) electrodes: Pull electrodes through the red/white septa. Sand the electrodes lightly with 4/0 emery cloth or immerse exposed silver parts in NH4OH solution, under a hood, until the silver gets shiny, then rinse thoroughly with DI water.

13.4.3 Reinsert sensor (green) and working (black) electrodes into their red/white septa and install the sensor and working electrodes in their normal ports in the cell body.

13.4.4 Turn on gases.

13.4.5 Mount the cell on the combustion tube.

13.4.6 Fill the cell with electrolyte. Make sure gas is bubbling through the cell.

13.4.7 The sensor (green) electrode will be coated first. Plug the white and red electrodes into their corresponding white and red jacket positions. Plug the green and blank electrodes into the REVERSE jacket positions (green to black and black to green).

13.4.8 Switch the function knob to DET. Wait for the baseline to somewhat stabilize.

13.4.9 Inject 5uL of 1000mg/L NaCl directly into the cell electrolyte. Integrate the result and record the data. (Five minute analysis time is sufficient).

13.4.10 Repeat 13.6.9 until the recovery of the NaCl stabilizes close to 100%.

13.4.11 Switch the function knob to STANDBY. Drain electrolyte and restore the sensor (green) electrode and the working (black) electrode to their normal ports and restore the green-green and black-black pin connectors.

13.4.12 Fill the cell with electrolyte and repeat steps 13.6.9 and 13.6.10.

13.4.13 Flush the cell and begin analysis.

13.5 Repacking the Reference Electrode Chamber

13.5.1 Drain, then disconnect the cell by unclamping it from the pyrolysis tube. Unplug the heater tape and four electrode leads. Take off the heater tape.

13.5.2 Gently remove the reference electrode and its septum from the cell, keeping the assembly intact.

13.5.3 Remove and discard the quartz wool and silver acetate from the reference electrode chamber.

13.5.4 Rinse the cell with electrolyte and clean if necessary.

13.5.5 Place a small tuft of quartz wool in to the reference electrode chamber. Add electrolyte to the cell body so that it just covers the quartz wool. Drain some electrolyte through the reference arm, if necessary, to establish fluid continuity between the cell body and the reference arm. Carefully poke the quartz wool with a small diameter rod to release any bubbles trapped in the wool. Make sure there are no bubbles in the capillary leading to the reference chamber.

13.5.6 Fill the reference chamber with silver acetate to a level which will nearly cover the entire electrode when inserted.

13.5.7 Completely fill the cell with electrolyte. Note that this will cause the electrolyte to overflow through the reference chamber. Wearing gloves for this procedure is strongly recommended.

13.5.8 Eliminate any bubbles which may be present in the reference chamber by stirring the silver acetate packing gently with the reference electrode. When bubbles are gone, be sure electrolyte is overflowing through the reference chamber, then slowly insert the reference electrode septum followed by the reference electrode.

13.5.9 Flush the cell and begin analysis.

13.6 Removing Bubbles from Reference Electrode

13.6.1 Fill the titration cell so that the electrolyte level is above the reference electrode chamber. Drain a small amount of electrolyte from the reference arm, if necessary, to establish fluid continuity between the cell body and the reference chamber.

13.6.2 Slide the reference electrode out of its septum, then remove the septum from the chamber. Using the electrode, gently stir or probe the silver acetate and quartz wool to dislodge any bubbles from the electrode chamber.

13.6.3 Once the chamber is free of bubbles, add a few drops of electrolyte to fill the chamber, reinsert the septum, rinse the electrode with DI water, and then reinsert electrode through the septum.

13.6.4 Inspect the chamber to ensure that no bubbles are present. Remove any spilled electrolyte.

13.7 Filling the Titration Cell

13.7.1 Remove the white reference electrode and septum as a unit from the reference chamber. Pyrex wool and silver acetate are already in place in the reference chamber so care should be taken in removing the white reference electrode. Open the reference stopcock. Slowly fill the cell with electrolyte through the main cell body. When the reference arm is full of electrolyte and there are no bubbles present in the arm, close the stopcock.

13.7.2 Continue filling the cell slowly until the fluid level is above the top of the reference chamber. As the chamber fills with electrolyte, the silver acetate may have to be stirred gently with a clean stainless steel syringe needle. When the electrolyte level reaches the top of the chamber, replace the reference electrode.

13.7.3 Look for bubbles. Remove any bubbles sitting on top of the silver acetate by repeating 13.9.2. Then confirm that no bubbles exist under the Pyrex wool or in the reference capillary. To remove existing bubbles, carefully tip the cell so that the top points towards you with the reference stopcock uppermost. Gently push on the reference electrode to pump the bubble out of the capillary.

CAUTION**DO NOT FORCE THE ELECTRODE THROUGH THE PYREX WOOL.

13.7.4 The cell is ready for initial startup.

13.8 Pyrolysis Tube

13.8.1 The exit tube and quartz wool should be visually checked daily for signs of coking (dark residue). If coking is present clean the exit tube, and replace the quartz wool and the o-rings.

13.8.2 The exit tube may be cleaned by soaking the tube in Nochromix for several hours then rinsing thoroughly with tap water. Finally rinse three times with DI water, and allow the exit tube to air dry prior to reinstallation.

14.0 TROUBLESHOOTING

This section has been incorporated into section 13 in this SOP.

15.0 REFERENCES

15.1 *Savannah Laboratories' Comprehensive Quality Assurance Plan* and Savannah Laboratories' *Corporate Quality Assurance Plan*, current revisions

15.2 *Test Methods for Evaluating Solid Waste, Third Edition with Revisions and Updates, SW-846*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC. (Update III)

Method Summary- 9023-EOX (Extraction for soils and wastes)

HOLD/STORAGE

Container	500mL amber glass with Teflon-lined cap to seal the bottle with minimum headspace
Preservative	None
Storage*	4C from collection until analysis
Hold Time	The analysis must be completed within 28 days of collection

*The control temperature is less than 6C with no frozen samples

SAMPLE PREPARATION

Extraction, 2g to 10mL with ethyl acetate, followed by direct injection of the extract into the pyrolysis chamber.

ANALYTICAL SEQUENCE

Initial Calibration	Direct injection of sodium chloride standards into titration cell at 1,5,10,50, and 80ug Cl
System Blank (Method Blank)	40uL ethyl acetate extraction blank
Calibration Verification (LCS)	40 uL of extracted lab control standard
Sample Analyses-twenty sample analyses	All samples are analyzed in duplicate at 40uL.

QC Batch

Method blank
LCS
MS/MSD at a frequency of 5% of samples

QC Check	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	Initially and when CCV fails	Less than 5% difference or within 0.05ug of the true value (against the average response)	-evaluate instrument and repeat analysis of one or more calibration standards
Method blank (ethyl acetate)	After LCS	<10 mg/kg	-evaluate instrument and repeat analysis of method blank -evaluate according to STL-SL SOP AN02
Calibration verification (LCS)	After initial calibration and once per batch	44-56 mg/kg %RSD: <5%	-evaluate instrument and repeat analysis of CCV -re-calibrate -maintenance instrument and re-calibrate
MS/MSD	At a frequency of 5% of samples	Within STL-SL QAP limits	-evaluate according to STL-SL SOP AN02
Initial demonstration of Capability (IDOC)	Initially and when new analysts are trained	Section 12	-evaluate instrument and repeat IDOC
Method Detection Limit (MDL)	Annually	See CA90	CA90

SOP SUMMARY FORM

SOP#: BA13:11.30.99:2	SOP Description: Extractable Organic Halides (EOX)

Revisions:

___Minor _X__Significant ___Complete Re-write ___New SOP

Summary of Revision(s):
-Section 8.5 through 8.7 - standard preparation revised to reflect change in calibration compound from tirchlorobenzene to trichlorophenol.
-Section 9.3 - Sample weight increased to 2 g ± 0.1 g.
-Section 9.5 - equation revised. Spiking level is 50 mg/kg (50ug/g).
-Section 10.4 - analytical sequence revised.
-Section 10.4.2 - revised calibration verification to method criteria.
-Section 12.2 - revised IDOC spiking solution and weight of sample. Revised recovery and precision criteria to method requirements.
-SOP Summary - revised analytical sequence; revised LCS frequency and acceptance criteria; revised method blank criteria to <10 mg/kg.

IDOCs Required:	_X__Yes	___No
MDLs Required:	_X__Yes	___No
SOP Implementation Date:	12.30.99	
Target Training Completion Date:	1.13.99	

Prepared by : R. Wayne Rabb

Title: STL-SL QA Manager

Date: Dec 2, 1999

Division Approval: [signature]

Title: Laboratory Director

Date: 12-13-99

FAN057:08.03.99:1

Savannah Laboratories

PERCENT SOLIDS DETERMINATION

(Methods: SW-846 3050 & 3550, and EPA 160.3)

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1.0 SCOPE AND APPLICATION

This SOP describes the procedures for the determination of the percent solids in soils, sediments, sludges, and other solid materials that must be reported on a "dry weight basis".

This SOP was written by and for STL Savannah.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 A well-mixed sample is transferred to a tared aluminum weighing pan or crucible. The sample is placed in an oven maintained at 103°C-105°C. The residue that remains after the liquid has been evaporated is the solids portion of the sample. The solids portion is routinely expressed as the percent solids, but it can also be expressed as the percent moisture. Equations for both the percent moisture and percent solids determination are described in Section 11 of this SOP.

2.2 This procedure is based on the percent solids determination in SW-846 Methods 3050 and 3550 and EPA 160.3.

2.3 Definitions – Refer to SOP AN99: *Definitions, Terms, and Acronyms* for a complete listing of applicable definitions.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Waste Disposal SOP, and this document.

3.1 Specific Safety Concerns or Requirements

All samples must be treated as if they are hazardous. The analyst must protect himself/herself from exposure to the sample matrix. Many of the samples that are tested for percent solids may contain hazardous chemical compounds or biological organisms. The analyst must wear protective clothing (lab coat or apron), eye protection (glasses or face shield), and disposable gloves when handling these samples.

The analyst should handle samples that have been dried at 103C - 105C with caution. This temperature can cause skin burns.

4.0 INTERFERENCES

The primary cause of interferences comes from glassware or other containers that have not been properly cleaned or prepared prior to the analysis. The basis of this procedure is the difference in the weight of the aluminum pan or crucible containing the residue and the tare weight of the crucible. Thus, care must be taken to ensure the aluminum pan or crucible is not treated in such a manner as to add or lose weight.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Aliquots of samples for the determination of percent solids are routinely sub-sampled from the 100-mL to 500-mL widemouth containers collected for metals or organic extractable analyses. The samples

are iced at the time of collection and are maintained at 4°C ± 2°C until the time of analysis. The percent solids should be determined as soon as possible.

6.0 APPARATUS AND MATERIALS

6.1 Aluminum pans

6.2 Top-loading balance: capable of weighing to the nearest 0.01g

6.3 Drying oven: capable of maintaining a temperature of 103°C - 105°C

6.4 Spatula or other utensil for transferring sample

7.0 REAGENTS

No reagents are required for this procedure.

8.0 STANDARDS

Calibration and check standards are not required for this procedure.

9.0 SAMPLE PREPARATION

Sample preparation steps are included in Section 10.

10.0 ANALYTICAL PROCEDURES

10.1 Calibrate and verify that the top loading balance is working within the proper parameters in accordance with SOP AN10: *Balance Calibration and Use.*

10.2 Label an aluminum pan with an identification number. Weigh the pan on the top loading balance. Record the ID and the weight (to the nearest 0.01g) of the aluminum pan on the bench sheet.

10.3 Tare the balance by pressing the auto tare button. This will zero the balance.

10.4 Thoroughly mix the sample with a stainless steel spatula or glass rod. It is important to obtain a homogeneous mixture prior to sub-sampling so that the sub-sample will accurately reflect the composition of the sample. Leaves, rocks, and other foreign materials should not be included in the sub-sample.

NOTE: If there is any doubt as to how to treat a given sample, contact the immediate supervisor to determine the proper course of action. SOP AN70: *Compositing, Homogenization, and Segregation Samples* provides guidance for homogenizing samples.

10.5 Add a 9.95 - 10.05g aliquot of the well-mixed sample to the tared aluminum pan. Record the sample identification and weight to the nearest 0.01g on the analysis log.

NOTE: The LIMS percent solids program assumes 10.0g initial weight.

10.6 Place the sample in the drying oven, maintained at 103-105°C, for at least 12 hours.

10.7 Remove the aluminum pan from the oven and allow to cool. Remember not to place the aluminum pan on a surface that can cause dirt or other foreign objects to adhere to the pan. Ensure that the surface that the pan is placed on can handle the temperature of the aluminum pan without damage.

10.8 Weigh the aluminum pan containing the sample residue on the top-loading balance and record the weight to the nearest 0.01g.

11.0 DATA ANALYSIS AND CALCULATIONS

The LIMS program automatically calculates the results according to the equations listed below:

11.1 The percent solids is calculated using the following equation:

$$percent\ solids = \frac{A - B}{W} x\ 100$$

where

A = weight of sample residue and aluminum pan (g)
B = weight of aluminum pan (g)
W = weight of sample used to determine the percent solids (g)

To express the percent solids as a decimal equivalent ("solids") for calculating sample results on a "dry weight basis":

$$\text{Soilds} = \frac{\text{percent solids}}{100}$$

To express the percent solids as percent moisture:

$$\text{Percent moisture} = 100 - \text{percent solids}$$

11.2 The LIMS program prints out a log containing the percent solids results. This log is kept in a 3-ring binder.

12.0 QUALITY CONTROL AND DATA ASSESSMENT

12.1 The balance must be checked in accordance with ~~SL~~ SOP AN10: *Balance Calibration and Use* prior to use.

12.2 Refer to the analytical SOPs for quality control and data assessment information.

13.0 METHOD PERFORMANCE

13.1 Refer to the analytical SOPs for method performance information.

14.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

Refer to SOP AN53: *Maintenance Procedures for Laboratory Instrumentation* for routine preventive maintenance and the manufacturer's guides for trouble-shooting items.

15.0 WASTE MANAGEMENT AND POLLUTION CONTROL

All waste will be disposed of in accordance with Federal, State and Local regulations. Follow the guidance for disposal in SOP CA70: *Waste Disposal*. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

15.1 Waste Streams Produced by the Method

Excess samples, reagents, and standards must be disposed in accordance with SOP CA70: *Waste Management*.

The following waste streams are produced when this method is carried out.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets

16.0 REFERENCES

16.1 STL Savannah's *Laboratory Quality Manual (LQM)*, current revision.

16.2 *Test Methods for Evaluating Solids Waste, Third Edition*, SW-846; USEPA Office of Solids Waste and Emergency response, Washington, D.C.

17.0 TABLES, DIAGRAMS, AND VALIDATION DATA

There are no tables, diagrams, or validation data included in this SOP.

SEVERN TRENT STL

SOP SUMMARY FORM

SOP#: BA51:02.18.04:2	**SOP Description**: PERCENT SOLIDS DETERMINATION

Revisions:

___Minor _X_Significant ___Complete Re-write ___New SOP

Summary of Revision(s):

- Changed title of SOP
- Revised format to be consistent with current STL Savannah SOP format and NELAC requirements
- Revised safety information to be consistent with current STL format
- Added requirement for samples to be dried at 103-105°C for at least 12 hours
- Added waste management information

IDOCs Required:	___Yes	_X_ No	___NA
MDLs Required:	___Yes	_X_ No	___NA
SOP Implementation Date: 03.18.04			
Target Training Completion Date: 03.18.04			

Approved by: Andrea Teal

Title: Quality Assurance Manager

Date: 02/20/04

Division Approval: [signature]

Title: Lab Director

Date: 2/25/04

STANDARD OPERATING PROCEDURE
PARTICLE-SIZE ANALYSIS OF SOILS
ASTM D422-63

Applicable Matrix: Soil

APPROVAL SIGNATURES

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QA Manager:	Kirstin L. McCracken	Date: 01/28/05
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1.0 SCOPE AND APPLICATION

1.1. This SOP describes the laboratory procedure for the determination of particle size distribution in soil samples that contain sand, silt, clay and gravel.

2.0 SUMMARY OF METHOD

2.1. A soil sample submitted for particle size analysis is prepared according to laboratory SOP LM-SL-D421 *Dry Preparation of Soil for Particle Size Analysis* or LM-SL-D2217 *Wet Preparation of Soil Samples for Particle Size Analysis.* Particles greater than 75um (gravels to fine sands) are determined by sieve analysis while particles less than 75um (silts and clays) are determined by sedimentation using a hydrometer followed by sieve analysis.

After wet or dry sample preparation, the sample is passed through No.10 sieve. The particles retained on the No.10 sieve (greater than 2.00mm) are further separated by sieve analysis. A portion of the sample that passed through the No.10 sieve is transferred to a glass sedimentation cylinder to which distilled water has been added. Seven hydrometer readings are taken over 24 hours. After the final hydrometer reading, the suspension is rinsed over a No. 200 (75 um) sieve, dried, and further separated by sieve analysis.

Particle size determinations for each sieve measurement and hydrometer reading are calculated and corrected for hygroscopic moisture and specific gravity. Unless a separate analysis for specific gravity is requested, the specific gravity is s assumed to be 2.65.

2.2. This procedure is based on ASTM D422-63.

3.0 DEFINITIONS

Not Applicable

4.0 INTERFERENCES

Not Applicable

5.0 SAFETY

5.1. Care should be taken to avoid exposure to the sample matrix since all environmental samples are potentially hazardous. Protective clothing, eye protection and disposable gloves should be worn when handling samples. All laboratory personnel must be familiar with the environmental health and safety plan described in the STL Chemical Safety Manual.

6.0 EQUIPMENT AND SUPPLIES

6.1. Top-Loading Balance sensitive to 0.01 g

6.2. Mechanical Stirring Apparatus and Dispersion Cup

6.3. Sedimentation Cylinder(s) 1000 mL

6.4. Hydrometer: ASTM 151H in specification E 100.

6.5. Thermometer: Accurate to 0.5°C

6.6. Mortar and Rubber Tipped Pestle

6.7. Sieves of the following size(s):

3.0 in (75.00mm)	No. 20 (850.0um)
2.0 in (50.00mm)	No. 40 (425um)
1.5 in (37.50mm)	No. 60 (250.0um)
1.0 in (25.00mm)	No. 80 (180.0um)
3/4 in (19.00mm)	No. 100 (150.0um)
3/8 in (9.50mm)	No. 200 (75.0um)
No. 4 (4.75mm)	
No. 10 (2.00mm)	

6.8. Oven with temperature range of 60° C to 110° C

6.9. Timing Device with second hand and capable of counting up to 25 hours

6.10. Stainless steel spatulas, spoons, metal and bristle brushes

6.11. Ro-tap machine

7.0 REAGENTS AND STANDARDS

7.1. Reagents

Deionized (DI) Water: Milli-Q System

Sodium Hexametaphosphate Solution: Combine 2940 g of DI water with 120 g of sodium hexametaphosphate in an appropriate container. Mix until the solution is homogeneous. Assign an expiration date of 30 days from date of preparation.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1. At least 500 grams of soil sample should be collected in glass or polyethylene jars. Immediately following collection the sample should be sealed and cooled to 4°C in order to preserve the moisture content of the sample.

8.2. Samples are stored from the time of receipt in the laboratory until 30 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or

client-specific protocol, samples are disposed of after 30 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

Not Applicable

10.0 CALIBRATION AND STANDARDIZATION

10.1. Calibrate the balance on each day of use, prior to use.

10.2 Calibrate the hydrometers every two years following the procedure given in LM-SL-001.

11.0 PROCEDURE

11.1 Sample Preparation

Prepare the sample following either laboratory SOP LM-SL-D421 (Dry Preparation) or LM-SL-D2217 (Wet Preparation).

11.2 Sample Analysis

11.2.1 Hydrometer Test

Transfer the sample/sodium hexametaphosphate mixture into a dispersion cup ensuring a quantitative transfer using DI water. Fill the dispersion cup ~half full with DI water. Mix the sample for one minute using the immersion blender.

Pour the contents of the dispersion cup through a #10 sieve into a 1000 mL sedimentation cylinder (1000 mL graduated cylinder). Rinse the cup with DI water, to ensure that the entire sample is transferred to the sedimentation cylinder.

Add DI water to the sedimentation cylinder until the volume is 1000 mL then cover the cylinder with a sheet of parafilm. Allow the sample to stabilize to ambient temperature.

Transfer the material retained on the No. 10 sieve to a labeled medium-size aluminum dish, and place the aluminum dish into an oven maintained at a temperature of 105ºC for a minimum of 16 hours.

After up to 12 sedimentation cylinders have been prepared, ensure that each cylinder is filled to the reference line with DI water, covered with parafilm, and that there is sufficient clean DI water available to rinse the hydrometer.

Record the ID of the hydrometer that you intend to use. Record the start time and set the timer for elapsed time.

Use the hydrometer reading table used to perform the activities as indicated (shake, place or read) for each 1000 mL cylinder.

To shake, rotate the flask up and down for one minute approximating at least 60 turns (one turn upside down and then right side up constitutes two turns).

To take a reading, gently insert the hydrometer into the cylinder then wait ~ 20 seconds. Read the hydrometer at the top of the meniscus to the nearest 0.0005. Enter the hydrometer reading into the appropriate cell on the benchsheet. Clean the hydrometer by twisting and dropping into a clean DI water bath.

Insert a temperature sensor into the cylinder to the depth the hydrometer reached. Read the temperature to the nearest 0.5°C. Enter the temperature reading into the appropriate cell on the benchsheet. After reading, rinse the sensor in a DI water bath.

Take readings every 2, 5, 15, 30, 60, 240 and 1440 minutes. Record each reading on the benchsheet, then transfer this information into the appropriate cell of the EXCEL worksheet.

11.2.2 Large Sieves

Tare the balance and weigh an aluminum dish. Enter the weight measurement in the non-material section of the EXCEL worksheet in the cell labeled "Pan, g".

Carefully transfer the non-soil material (e.g.- sticks, grass, wood, plastic) from the drying dish to the pre-weighed dish and enter the weight measurement in the non-soil material section of the EXCEL worksheet in the cell labeled "Pan/Dry Sample, g".

Enter a brief description of the type of non-soil material (e.g.- sticks, grass, wood, plastic) in the non-soil material section of the EXCEL worksheet in the cell labeled "Description".

Tare the balance and weigh each of the 3/4", 3/8", #4 and #10 sieves. Record the weight measurements in the EXCEL worksheet in the cells labeled "Sieves (Tares)". Also weigh any larger sieves if necessary.

Stack the sieves then transfer the soil material retained on the #10 sieve into the sieve stack. Shake for 2 minutes. If there is greater than ~30 g of material, place the sieve stack into the Ro-tap machine and shake for 10 minutes.

Weigh each sieve along with the material retained on it. Enter these weight measurements in the "Sieve + Sample Weights" section of the Excel worksheet.

Determine the average hardness of the particles retained on the #10 sieve by dropping a hammer on the particle from a height of approximately one foot. Hardness qualifiers are hard, soft or brittle. Record the hardness qualifier in the "Description of >#10 Particles" section of the Excel worksheet.

Observe and record the shape of the particles in the "Description of >#10 Particles" section of the Excel worksheet. Shape qualifiers are well rounded, rounded, subrounded, subangular, and angular.

11.2.3 Small Sieves

When the hydrometer test is complete, transfer the soil from the sedimentation cylinder to a #200 wet wash sieve.

Wash the soil through the #200 sieve until the water from the bottom of the sieve runs clear. Carefully transfer the material retained on the sieve to a labeled 250 mL glass beaker.

Place the beaker into the oven. Dry at a temperature of 105ºC for at least 16 hours. After 16 hours, remove the beaker from the oven and allow it to cool.

Gently mix the dried contents of the beaker with a rubber-tipped pestle to break any soil aggregates that may have formed during the drying stage.

Tare the balance and weigh each of the sieves between #20 and #200. Record the weight measurements in the EXCEL worksheet in the cells labeled "Sieves (Tares)".

Transfer the dry sample into the sieve stack, ensuring that all material is transferred. Use hair or wire brushes to clean the beaker.

Place the sieve stack on the Rotap machine and shake for ten minutes.

Weigh each sieve along with the material retained on it. Enter these weight measurements in the "Sieve + Sample Weights" section of the Excel worksheet.

Determine particle size using the following formula.

12.0 CALCULATIONS

12.1. Sample Used (SU)

<u>Wet Method</u>

$$SU = (pan + wet\ sample - pan) \otimes PS$$

Where:

PS = Percent solids

Note: for hydrometer SU, subtract the dry weight of any material retained on the No. 10 sieve.

Dry Method

$$SU = (pan + dry\ sample - pan) - (pan + non - soil\ material - pan) \otimes HMCF$$

Where:

HMCF = Hygroscopic moisture correction factor

12.2 Sieve Analysis (Percent Finer = PF)

Large Sieves:

3 inch: PF = 100-100 (Sieve and Sample (3 inch) - Sieve (3 inch))/SU*

2 inch: PF = PF (3 inch) - 100(Sieve and Sample (2 inch) - Sieve (2 inch))/SU and so on through the #10 Sieve.*

Small Sieves:

#20: PF = PF(#10) - 100(mass passing #10/sample mass (Hyd))*(sieve and sample (#20) - sieve(#20))/sample used*

#40: PF = PF (#20) - 100(mass passing #10/sample mass (Hyd))*(sieve and sample (#40) - sieve (#40))/sample used and so on up through #10 sieve.*

12.5 Hydrometer Analysis

Particle size, Micron

1000*sqrt [930*viscosity/980*(SG-1))*(effective depth/time)]

Viscosity at sample temperature, poises
Effective Depth, cm = 16.29-264.5*(actual Hydrometer reading - 1) above equation for effective depth based on equation found with table 2 in method, in which 16.29 = 0.5*(14.0-67.0/27.8)+10.5 and 264.5 = (10.5-2.3)/0.031
Time, minutes = Time of hydrometer reading from beginning of sedimentation
Sqrt - square root
SG - Specific Gravity of soil
Viscosity - is the resistance of a liquid to flow

12.6 Percent Finer (PF):

PF = Constant*(actual hydrometer reading - hydrometer correction factor - 1)

Where:

Constant = (100,00/W)*SG/(SG-1)
W = (Total sample used *sample used for hydrometer analysis*HMCF)/Amount of total sample passing #10 sieve
Hydrometer Correction = slope*sample temperature + Intercept
Slope = ((low temp. reading -1)-(high temp. reading -1)/(low temp. - high temp.))
Intercept = (low temp. reading -1) - (low temp. * slope)

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.0. Complete the sample preparation benchsheet and EXCEL spreadsheet. Document any problems encountered during sample analysis so they may be properly addressed in the project narrative. Perform primary and secondary data review following the guidance given in laboratory SOP LP-LB-003 *Data Review*.

14.0 METHOD PERFORMANCE

Not Applicable

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1. The laboratory optimizes technology to minimize pollution and reduce the production of hazardous waste whenever possible.

15.2. The laboratory procedures for waste management comply with applicable federal, state and local regulations and are described in SOP LP-LB-001HAZWD.

16.0 REFERENCES

16.1. Standard Test Method for Particle-Size Analysis of Soils, ASTM D422-63, Volume 04.08 Soil and Rock, American Society for Testing and Materials, Philadelphia, Pa., 1998.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

17.1 Table 1: Hydrometer Reading Table

Table 2: Hydrometer Reading Table (For up to 12 Sedimentation Cylinders)

Elapsed Time (hr:min)	Task	Cyl. No.	Actual Time (min)	Elapsed Time (hr:min)	Task	Cyl. No.	Actual Time (min)
0:00	Shake			1:01	Read	10	5
0:01	**Place**	**1**		1:02	Shake		
0:01	Shake			**1:03**	Place	11	
0:02	Place	2		1:04	Read	9	15
0:03	Read	1	2	1:05	Read	11	2
0:04	Read	2	2	1:06	Read	7	31
0:06	Read	1	5	1:07	Read	3	58
0:07	Read	2	5	1:08	Read	11	5
0:08	Shake			1:09	Shake		
0:09	**Place**	**3**		**1:10**	Place	12	
0:09	Shake			1:11	Read	10	15
0:10	Place	4		1:12	Read	12	2
0:11	Read	3	2	1:13	Read	4	63
0:12	Read	4	2	1:14	Read	8	32
0:14	Read	3	5	1:15	Read	12	5
0:15	Read	4	5	1:18	Read	11	15
0:16	Read	1	15	1:19	Read	9	30
0:17	Read	2	15	1:21	Read	5	60
0:20	Shake			1:25	Read	12	15
0:21	Place	5		1:26	Read	10	30
0:23	Read	5	2	1:27	Read	6	59
0:24	Read	3	15	1:33	Read	11	30
0:25	Read	4	15	1:34	Read	7	59
0:26	Read	5	5	1:41	Read	12	31
0:27	Shake			1:42	Read	8	60
0:28	Place	6		1:52	Read	9	63
0:30	Read	6	2	1:53	Read	10	57
0:31	Read	1	30	2:06	Read	11	63
0:32	Read	2	30	2:07	Read	12	57
0:33	Read	6	5	4:17	Read	1	256
0:34	Shake			4:18	Read	2	256
0:35	Place	7		4:19	Read	3	250
0:36	Read	5	15	4:20	Read	4	250
0:37	Read	7	2	4:21	Read	5	240
0:38	Read	3	29	4:22	Read	6	234
0:39	Read	4	29	5:00	Read	7	265
0:40	Read	7	5	5:01	Read	8	259
0:41	Shake			5:02	Read	9	253
0:42	Place	8		5:03	Read	10	247
0:43	Read	6	15	5:04	Read	11	241
0:44	Read	8	2	5:05	Read	12	235
0:47	Read	8	5	24:01	Read	1	1440
0:48	Shake			24:02	Read	2	1440
0:49	Place	9		24:03	Read	3	1434
0:50	Read	7	15	24:04	Read	4	1434
0:51	Read	9	2	24:05	Read	5	1424
0:52	Read	5	31	24:06	Read	6	1418
0:54	Read	9	5	24:07	Read	7	1412
0:55	Shake			24:08	Read	8	1406
0:56	Place	10		24:09	Read	9	1400
0:57	Read	8	15	24:10	Read	10	1394
0:58	Read	10	2	24:11	Read	11	1388
0:59	Read	6	31	24:12	Read	12	1382
1:00	**Read**	**1**	**59**				
1:00	**Read**	**2**	**58**				

Source: Laboratory Prepared Reference Document

STANDARD OPERATING PROCEDURE
HYDRAULIC CONDUCTIVITY OF SATURATED POROUS MATERIALS USING A FLEXIBLE WALL PERMEAMETER
ASTM 5084

Applicable Matrix: Clay, Silt

APPROVAL SIGNATURES

Laboratory Director:	Michael F. Wheeler, Ph.D.	Date: 5/5/05
QA Manager:	Kirstin L. McCracken	Date: 5-5-05
Department Manager:	Jon K. Jagmuntowicz	Date: 5/6/05
Technical Director: Geotechnical Lab	Matthew R. Duquette	Date: 5-5-05

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of the coefficient of hydraulic conductivity (permeability) of water-saturated porous materials with a flexible wall permeameter. It is applicable to silts and clays with a hydraulic conductivity less than or equal to 1×10^{-5} m/s that are collected in a Shelby tube or other method which maintains the soil in an undisturbed state. The procedure may be performed for disturbed soil samples, after the soil is compacted into a mold to represent a minimum or maximum density. More permeable soils should be tested using ASTM D 2434.

2.0 SUMMARY OF METHOD

2.1 Hydraulic conductivity is measured as flow of water over time through a sample. The sample is assembled in a hydraulic conductivity apparatus, and water permeates through under pressure. Burette readings are taken to measure the amount of water flowing through the soil.

2.2 This procedure is based on ASTM Method D5084.

3.0 DEFINITIONS

Not Applicable

4.0 INTERFERENCES

Not Applicable

5.0 SAFETY

5.1. Care should be taken to avoid exposure to the sample matrix since all environmental samples are potentially hazardous. Protective clothing, eye protection and disposable gloves should be worn when handling samples. All laboratory personnel must be familiar with the environmental health and safety plan described in the STL Chemical Safety Manual.

6.0 EQUIPMENT AND SUPPLIES

6.1 ELE/Soiltest Tri-Flex 2, Permeability Test System

6.2 ELE Master control panel

6.3 Trautwein Standard panel M100000

6.4 Trautwein Standard Add-on panel M116000

6.5 De-aired, deionized water

6.6 Flexible-Wall Permeability test cell

6.7 Filter paper

6.8 Latex membranes

6.9 Vacuum pump membrane assembly

6.10 High-vacuum grease

6.11 Sample extractor

6.12 Stainless steel spatulas/spoons

6.13 3" Shelby Tube Mold

7.0 REAGENTS AND STANDARDS

Not Applicable

8.0 SAMPLE HANDLING AND PRESERVATION

8.1 Samples should be collected using a Shelby tube or equivalent, of 3" diameter and at least 6" in length. Alternatively, a sample volume of approximately 500 g (dry weight) should be collected in a container that will maintain the soil's moisture content.

8.2 Samples are stored from the time of receipt in the laboratory until 30 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or client-specific protocol, samples are disposed of after 30 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

Not Applicable

10.0 CALIBRATION AND STANDARDIZATION

10.1. Calibrate the balance on each day of use prior to use.

10.2. Check the calibration of the mold apparatus annually following the procedure given in Appendix A.

11.0 PROCEDURE

Determine the soil moisture content of the sample following laboratory SOP LM-SL-D2216. Enter the moisture content value into the Excel spreadsheet as "Initial Moisture content (%)".

Place the porous end pieces of the chamber in deionized water during sample preparation.

If the sample is undisturbed (in Shelby Tube), prepare the test specimen by cutting a length of Shelby tube at least 6 times greater than the largest particle size in the sample.

If the sample is disturbed (other sample container), compact the sample in a 3" Shelby Tube Mold, building layers of soil and scarifying each previous layer with a stainless spatula or fork.

Using the sample extractor, carefully push out the soil cores, trimming the ends if voids cause the length to vary by more than 5%

Measure the initial length of the soil (cm) and enter the value into the Excel spreadsheet as "initial length (cm)".

Measure the initial width of the soil, and enter the value into the Excel spreadsheet as "initial width (cm)".

Weigh the sample, and record the weight as "initial mass, (g)" in the Excel spreadsheet.

Lightly grease the base plate, place a porous end piece on the base of the chamber, and a circle of filter paper on top. Set the sample core on the filter paper, top the sample with filter paper, porous end piece, and the lightly greased top cap.

Using the vacuum pump membrane assembly, carefully surround the sample with the latex membrane. Secure the latex membrane with rubber o-rings. Affix both top cap water lines. Lightly grease the chamber o-rings, top and bottom. Assemble the chamber and tighten retaining rods hand-tight.

Using a drain line, vent the top valve of the chamber to a catch basin. Attach the lower cell line to the water port on the master panel. Fill the cell with water, checking top and bottom seals for leaks.

Note: Ensure that there is no air in the system after venting the top valve. If a leak occurs, it may be necessary to reassemble the apparatus.

Re-attach the cell line to the appropriate chamber controls on the master panel, and check to ensure that all pipettes are approximately ½ full with de-aired water.

With all chamber valves closed, set the cell to a confining pressure, usually 20psi. Establish a pressure gradient across the sample, usually 15psi lower, 10psi upper.

First open the cell chamber valve, then open the lower valve, and then open the upper valve. Again, check for leaks. If a leak occurs at this point, reassemble the apparatus.

Remove the air from the sample lines by attaching the drain line to the drain valves, and opening the drain valves. Only de-air one line at a time, and take care to not allow the water in the pipette to empty.

Allow the sample to saturate with water for at least 24 hours. After saturation, de-air the lines again, and set the water levels in the panel pipettes to prepare for readings. Drain most of the water out of the "upper" pipette, and fill the "lower" pipette.

Turn all three control panel valves to "pipette", take a base reading of pressures (PSI) and pipette levels (mL), and start a count-up timer (hr/min/sec). Pressures may have to be adjusted to prevent leaks, if pressures are changed, reset pipette levels and timer, and re-establish the baseline reading.

Record the room temperature as "initial Temperature (ºC)" in the Excel spreadsheet.

Take readings as conditions permit (i.e. when there is an appreciable difference (>1/10 mL) in pipette levels). The time intervals between will vary greatly between samples but a minimum of 6 readings must be taken.

Enter the burette readings for each pipette into the Excel spreadsheet as "Burette, mL". Pressure readings for each reading should be recorded as "Pressure, psi" in the Excel spreadsheet. Times for each reading are entered into the spreadsheet in hours, minutes and seconds.

Calculate hydraulic conductivity using the equation given in Section 12.0.

The test is considered complete when the Hydraulic conductivities of 4 trials are within 25% of the mean hydraulic conductivity.

Upon completion of the testing, record the room temperature as "Final Temperature (ºC)" in the Excel spreadsheet.

After completion of the hydraulic conductivity testing, disassemble the chamber using the reverse procedure of the set-up.

Using a sharp razor blade, cut and remove the rubber membrane from around the sample. Remove the filter paper and porous disks from the sample as well.

Measure the final length of the soil (cm) and enter the value into the Excel spreadsheet as "final length (cm)".

Measure the final width of the soil, and enter the value into the Excel spreadsheet as "final width (cm)".

Weigh the sample, and record the weight as "final mass, (g)" in the Excel spreadsheet.

Determine the soil moisture content of the sample following laboratory SOP LM-SL-D2216. Enter the moisture content value into the Excel spreadsheet as "final Moisture content (%)".

12.0 CALCULATIONS

12.1 Hydraulic Conductivity (k):

$k = QL/Ath$

Where
Q = quantity of water discharged
L = distance between manometers
A = cross-sectional area of specimen
t = total time of discharge
h = difference in head on manometers

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Perform primary review of your work following the procedures given in the laboratory SOP for data review. All data undergoes secondary review by a senior analyst or a data review analyst. Problems encountered during analysis are documented and reported in the case narrative provided with the data package report. For additional guidance regarding the laboratory's protocol and required elements for each level of data review (primary, secondary, and tertiary) refer to laboratory SOP LP-LB-003 *Data Review.*

14.0 METHOD PERFORMANCE

Not Applicable

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably possible technology changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 No waste streams are produced when this method is carried out.

16.0 REFERENCES

16.1 Standard Test Method Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter, ASTM D5084-03, volume 04.08 Soil and Rock, American Society for Testing and Materials, Philadelphia, PA.

16.2 Tri-Flex 2 Permeability Test System Owner's Manual, ELE/Soiltest, Revision 2, September 1995.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

Not Applicable

APPENDIX A: Calibration Check for Mold Apparatus

The volume of the compaction mold is checked annually using a water-filled method checked by linear measurement.

Equipment & Supplies

- Vernier or Dial Caliper with a range of at least 0-6 in. (0-150 mm). Readable to at least 0.001 in. (0.02 mm).
- Inside micrometer with a range of at least 2-12 in. (50-300 mm). Readable to at least 0.001 in. (0.02 mm).
- Plastic or glass plate approximately 8 in. square by ¼ in. thick (200 by 200 mm by 6 mm).
- Thermometer 0-50°C range, 0.5°C readability.
- Stopcock or high vacuum grease.
- 4 in. compaction mold
- Top loading balance

Procedure

Water Fill Method

1) Lightly grease the bottom of the mold, assemble the base plate and mold, and secure the mold to the base plate.
2) Lightly grease the top of the mold.
3) Weigh the greased mold and glass plate to the nearest 1 g and record.
4) Place the mold on a firm, level surface and fill the mold with water to slightly above the rim.
5) Slide the glass plate over the top surface of the mold so that the mold remains completely filled with water and air bubbles are not entrapped.
6) Completely dry any excess water from the outside of the mold and plates.
7) Weigh the mold, plate and water and record to the nearest 1 g.
8) Determine the temperature of the water in the mold to the nearest 1°C.
9) Repeat steps 1-8

Linear Measurement Method

1) Using the Vernier caliper, measure the inside diameter of the mold 6 times at the top of the mold and 6 times at the bottom of the mold. Record the values to the nearest 0.001-in. (0.02-mm)

2) Using the Vernier caliper, measure the inside height of the mold by making three measurements equally spaced around the circumference of the mold. Record the values to the nearest 0.001-in. (0.02-mm).

Calculations

Water Fill Method

$V = (M_1 - M_2)/D_1$

Where:
V = volume of mold
M_1 = mass of mold, plate and water
M_2 = mass of mold and plate
D_1 = density of water at recorded temperature (from table 1)

Linear measurement method

$$V = \frac{(\pi)(h)(d_t + d_b)^2}{(16)(1728)} \quad \text{(inch-pound)}$$

$$V = \frac{(\pi)(h)(d_t + d_b)^2}{(16)(10^3)} \quad \text{(SI)}$$

Where:
V = volume of mold, ft^3 (cm^3)
H = average height, in. (mm)
d_t = average top diameter, in. (mm)
d_b = average bottom diameter, in. (mm)
1/1728 = constant to convert in^3 to ft^3
$1/10^3$ = constant to convert mm^3 to cm^3

STANDARD OPERATING PROCEDURE
PERMEABILITY OF GRANULAR SOILS (CONSTANT HEAD)

Applicable Matrix: Soil

APPROVAL SIGNATURES

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QA Manager:	Kirstin L. McCracken	Date: 5/6/05
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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of the coefficient of permeability by a constant-head method for the laminar flow of water through granular soils. In order to limit consolidation influences during testing, this procedure is limited to disturbed granular soils containing not more than 10% soil passing the 75 um (No. 200) sieve.

2.0 SUMMARY OF METHOD

2.1 The sample's moisture content is determined following laboratory SOP LM-SL-D2216. A portion of sample is air dried and layered into a constant-head permeameter chamber. Water from the constant-head filter tank is allowed to flow through the test sample with the flow rate measured from the outlet port. The test is repeated five times increasing the constant head (hydraulic head) with each subsequent test. Average permeability is then calculated.

2.2 This procedure is based on ASTM Method D2434.

3.0 DEFINITIONS

Not Applicable

4.0 INTERFERENCES

Not Applicable

5.0 SAFETY

5.1. Care should be taken to avoid exposure to the sample matrix since all environmental samples are potentially hazardous. Protective clothing, eye protection and disposable gloves should be worn when handling samples. All laboratory personnel must be familiar with the environmental health and safety plan described in the STL Chemical Safety Manual.

6.0 EQUIPMENT AND SUPPLIES

6.1 Constant-head permeameter

6.2 Top loading balance

6.3 Aluminum measuring pans

6.4 Stainless steel spoons and spatulas

6.5 100 mL graduated cylinder

6.6 Assorted size funnels

6.7 Thermometer

6.8 ¾"Flat solid steel cylinder

7.0 REAGENTS AND STANDARDS

Not Applicable

8.0 SAMPLE HANDLING AND PRESERVATION

8.1. At least 500 grams of soil sample should be collected in glass or polyethylene jars. Immediately following collection the sample should be sealed and cooled to 4°C in order to preserve the moisture content of the sample.

8.2. Samples are stored from the time of receipt in the laboratory until 30 days after delivery of the reconciled data package report. Unless otherwise specified by a federal, state or client-specific protocol, samples are disposed of after 30 days in a manner that complies with all applicable regulations.

9.0 QUALITY CONTROL

Not Applicable

10.0 CALIBRATION AND STANDARDIZATION

10.1. Calibrate the balance on each day of use prior to use using 2 Class S weights that bracket the range of use. Record the check in the logbook designated for this purpose.

10.2 Check the calibration of the mold apparatus using the procedures given in Appendix A.

11.0 PROCEDURE

11.1 Analysis

Determine the moisture content of the sample following laboratory SOP LM-SL-D2216. Enter the results from analysis in the "Moisture Content" section of the Excel worksheet.

Select and air-dry a portion of sample equal to twice the amount needed to fill the permeameter chamber. Remove any particles larger than 19 mm (3/4 in.).

Place the permeability chamber in the base of the apparatus and assemble the lower porous disc and spacer.

Place the soil sample in the chamber, in uniform thin layers that are approximately equal in thickness to the maximum particle size, but not less than 15mm.

Using the steel cylinder, lightly tamp each layer uniformly over the surface of the soil until there is no visible motion of surface particles at the edges of the tamping foot.

Level the upper surface of the soil, place the top porous disc on the sample and assemble the permeameter.

Measure the final height of the sample (cm), and record as "Soil Length" in the Excel worksheet.

Using a vacuum pump, evacuate the sample for 15 minutes to remove any air that is adhering to soil particles and from the voids.

Slowly saturate with water the sample from the bottom upward, removing any remaining trapped air.

Stabilize the head in the inlet funnel by adjusting the inflow of water to equal the outflow. Record the initial head reading in the Excel spreadsheet as "H initial, cm."

Once the outflow has stabilized, start the timer and place a 100 mL graduated cylinder under the outflow port in order to measure the quantity of water discharged.

When at least 20 mL of water has been collected, record the time elapsed as "Time (t)(seconds)," the quantity of water collected as "Q, cm3 (mL)" and record the temperature(°C) of the water in the Excel spreadsheet.

Repeat the procedure 5 times, increasing the head ½ cm to 1 cm with each subsequent trial.

Calculate the coefficient of permeability using the equation given in Section 12.0.

12.0 CALCULATIONS

12.1 Moisture Content

$w = [(M_{cws} - M_{cs})/(M_{cs} - M_c)]*100$

Where:
w = water content, %
M_{cws} = mass of container and wet sample, g
M_{cs} = mass of container and oven dry sample, g
M_c = mass of container, g

12.1 Coefficient of Permeability (k):

$k = QL/Ath$

Where
Q = quantity of water discharged

L = distance between manometers
A = cross-sectional area of specimen
t = total time of discharge
h = difference in head on manometers

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Perform primary review of your work following the procedures given in the laboratory SOP for data review. All data undergoes secondary review by a senior analyst or a data review analyst. Problems encountered during analysis are documented and reported in the case narrative provided with the data package report. For additional guidance regarding the laboratory's protocol and required elements for each level of data review (primary, secondary, and tertiary) refer to laboratory SOP LP-LB-003 *Data Review.*

14.0 METHOD PERFORMANCE

Not Applicable

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably possible technology changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 No waste streams are produced when this method is carried out.

16.0 REFERENCES

16.1 Standard Test Method for Permeability of Granular Soils (Constant Head), ASTM D2434 - 68, volume 04.08 Soil and Rock, American Society for Testing and Materials, Philadelphia, Pa., March, 2000.

17.0 TABLES, DIAGRAMS, FLOWCHARTS

Not Applicable

APPENDIX A: Calibration Check for Mold Apparatus

Check the volume of the compaction mold annually using a water-filled method checked by linear measurement.

Equipment & Supplies

- Vernier or Dial Caliper with a range of at least 0-6 in. (0-150 mm). Readable to at least 0.001 in. (0.02 mm).
- Inside micrometer with a range of at least 2-12 in. (50-300 mm). Readable to at least 0.001 in. (0.02 mm).
- Plastic or glass plate approximately 8 in. square by ¼ in. thick (200 by 200 mm by 6 mm).
- Thermometer 0-50°C range, 0.5°C readability.
- Stopcock or high vacuum grease.
- 4 in. compaction mold
- Top loading balance

Procedure

Water Fill Method

1) Lightly grease the bottom of the mold, assemble the base plate and mold, and secure the mold to the base plate.
2) Lightly grease the top of the mold.
3) Weigh the greased mold and glass plate to the nearest 1g and record.
4) Place the mold on a firm, level surface and fill the mold with water to slightly above the rim.
5) Slide the glass plate over the top surface of the mold so that the mold remains completely filled with water and air bubbles are not entrapped.
6) Completely dry any excess water from the outside of the mold and plates.
7) Weigh the mold, plate and water and record to the nearest 1g.
8) Determine the temperature of the water in the mold to the nearest 1°C.
9) Repeat steps 1-8

Linear Measurement Method

1) Using the Vernier caliper, measure the inside diameter of the mold 6 times at the top of the mold and 6 times at the bottom of the mold. Record the values to the nearest 0.001-in. (0.02-mm)

2) Using the Vernier caliper, measure the inside height of the mold by making three measurements equally spaced around the circumference of the mold. Record the values to the nearest 0.001-in. (0.02-mm).

Calculations

Water Fill Method

$V = (M_1 - M_2)/D_1$

Where:
V = volume of mold
M_1 = mass of mold, plate and water
M_2 = mass of mold and plate
D_1 = density of water at recorded temperature (from table 1)

Linear measurement method

$$V = \frac{(\pi)(h)(d_t + d_b)^2}{(16)(1728)} \quad \text{(inch-pound)}$$

$$V = \frac{(\pi)(h)(d_t + d_b)^2}{(16)(10^3)} \quad \text{(SI)}$$

Where:
V = volume of mold, ft^3 (cm^3)
H = average height, in. (mm)
d_t = average top diameter, in. (mm)
d_b = average bottom diameter, in. (mm)
1/1728 = constant to convert in^3 to ft^3
$1/10^3$ = constant to convert mm^3 to cm^3

APPENDIX C

Chain of Custody

Chain of Custody Record

P.O. No.

PROJECT NUMBER | PROJECT NAME

SAMPLERS: (Signatures)

Sample No.	DATE	TIME	LOCATION	Number of Containers	Type of Analysis										Type of Preservation	Remarks

Relinquished By:	Received By:	Date	Remarks
Signature	Signature	/ /	
Printed Name	Printed Name	Time	
Company	Company		
Reason			
Relinquished By:	Received By:	Date	
Signature	Signature	/ /	
Printed Name	Printed Name	Time	
Company	Company		
Reason			

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