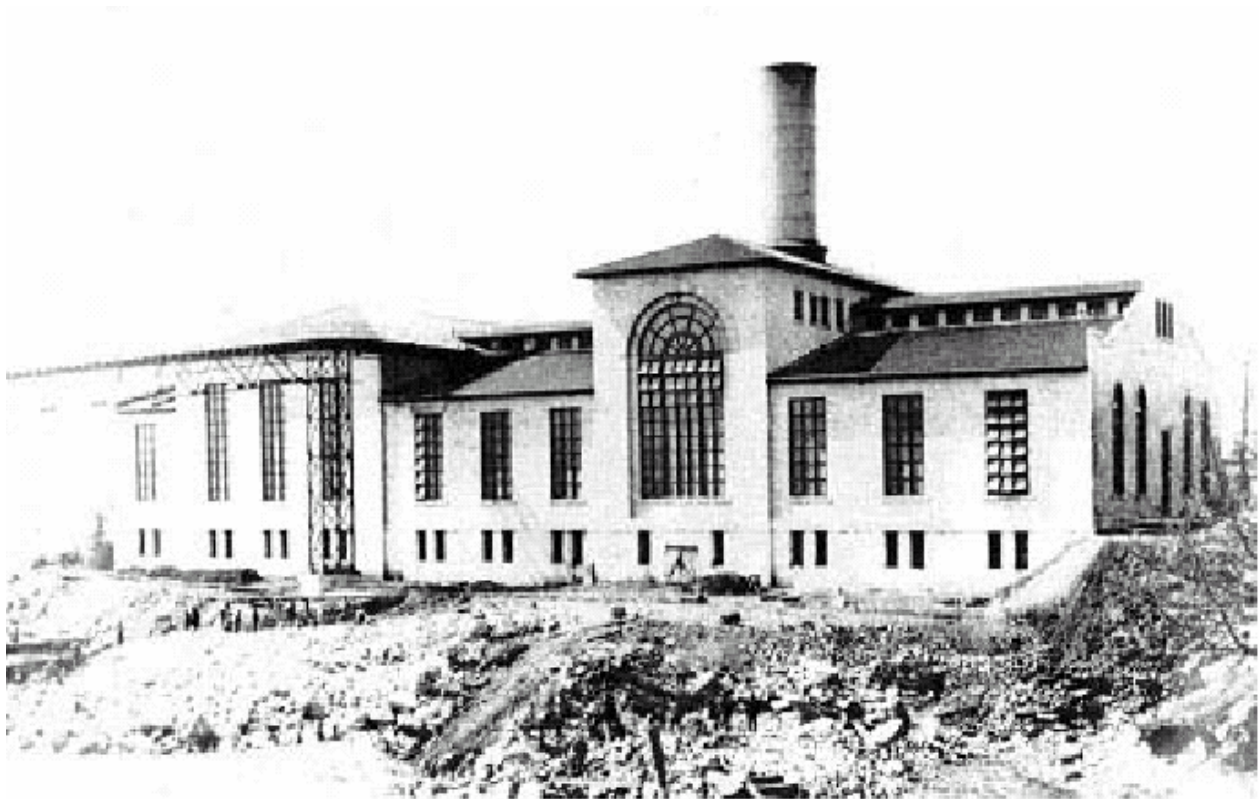




Case Study of the Triad Approach: Expedited Characterization of Petroleum Constituents and PCBs Using Test Kits and a Mobile Chromatography Laboratory at the Former Cos Cob Power Plant Site



Case Study of the Triad Approach: Expedited Characterization of Petroleum Constituents and PCBs Using Test Kits and a Mobile Chromatography Laboratory at the Former Cos Cob Power Plant Site

Prepared by:

U.S. Environmental Protection Agency
Office of Superfund Remediation and Technology Innovation
Brownfields Technology Support Center
Washington D.C. 20460



In cooperation with:

U.S. Environmental Protection Agency Region 1 and Metcalf & Eddy



Notice

This material has been funded wholly by the United States Environmental Protection Agency (EPA) under Contract Number 68-W-02-034. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Copies of this report are available free of charge from the National Service Center for Environmental Publications (NSCEP, P.O. Box 42419, Cincinnati, OH 45242-2419; telephone (800) 490-9198 or (513) 489-8190 (voice) or (513) 489-8695 (facsimile). Refer to document EPA 542-R-04-008. This document can also be obtained electronically through EPA's Clean Up Information (CLU-IN) System on the World Wide Web at <http://clu.in.org>.

Comments or questions about this report may be directed to Dan Powell, EPA, Office of Superfund Remediation and Technology Innovation (5102G), 1200 Pennsylvania Avenue NW, Washington, D.C. 20460; telephone (703) 603-7196.

Foreword

This case study is one in a series designed to provide cost and performance information for innovative tools that are available to support less costly and more representative site characterizations. Case studies developed by the EPA Office of Superfund Remediation and Technology Innovation Office (OSRTI) are designed to introduce project managers and technical team leaders the use of new technologies and novel applications of familiar tools or processes. Case studies such as this one include detailed information about the technologies and strategies used in this Triad project. Briefer project profiles for this and other types of projects that exemplify how the concepts of the Triad approach have been used can be found at www.triadcentral.org.

Acknowledgments

Special acknowledgement is given to U.S. EPA Region 1 and to the staff of Metcalf & Eddy for their thoughtful suggestions and support in preparing this case study.

Table of Contents

Notice.....	ii
Foreword.....	iii
Acknowledgements.....	iii
CASE STUDY ABSTRACT.....	ix
TECHNOLOGY QUICK REFERENCE SHEETS	
Total Petroleum Hydrocarbons (TPH) and Polynuclear Aromatic Hydrocarbons (PAH) By Ultraviolet Fluorescence (UVF).....	xi
Polychlorinated Biphenyls (PCB) By Gas Chromatography/Electron Capture Detector	xii
EXECUTIVE SUMMARY	1
SITE INFORMATION	4
SITE LOCATION AND DESCRIPTION	4
SITE HISTORY AND USE.....	5
PROPERTY REUSE SCENARIO.....	6
CONCEPTUAL SITE MODEL.....	6
Initial Site Investigations	7
Current Site Use.....	10
Site and Regional Geology	10
MEDIA OF CONCERN	11
CONTAMINANTS OF POTENTIAL CONCERN.....	11
EXPOSURE ROUTES AND RECEPTORS	13
WORK PLAN DEVELOPMENT	14
INITIAL WORK PLAN	14
Site-Specific Objectives for Initial Work Plan.....	14
Development of the Original Sampling Approach.....	15
Original Sampling Rationale.....	15
SYSTEMATIC PLANNING	16
The New Sampling Approach.....	17
Analytical Options	18
Developing Decision Logic	19
DEMONSTRATION OF METHODS APPLICABILITY	22
Initial Field Sampling Event Conducted in Support of the Demonstration of Methods Applicability Study	23
FIELD INVESTIGATION	28
SAMPLE COLLECTION.....	28
SAMPLE ANALYSIS	29
SITELAB® UVF TEST KITS.....	29
EPA Region 1 Mobile Laboratory Polychlorinated Biphenyl Analyses.....	30
EPA Region 1 Mobile Laboratory XRF	31

TABLE OF CONTENTS (Continued)

<u>Section</u>	<u>Page</u>
ARSENIC RESULTS	32
PAH RESULTS	33
Correlating Field PAH Results with the Connecticut Residential Direct Exposure Criterion	34
Understanding Field-based Results for PAHs by Reviewing Sample Chromatograms.....	35
Summary of Findings for Field-generated PAH Data.....	35
TPH RESULTS.....	36
Correlating Field-based Results for TPH with the Residential Connecticut Direct Exposure Criterion	36
Understanding Field-based Results for TPH by Reviewing Sample Chromatograms.....	38
Summary of Findings for TPH.....	38
PCB RESULTS.....	38
LESSONS LEARNED	40
COST COMPARISON	42
BIBLIOGRAPHY	44

TABLES

Tables

1	PATHWAY RECEPTOR DIAGRAM
2	LIST OF CONTAMINANTS OF POTENTIAL CONCERN
3	SUMMARY OF ORIGINALLY PROPOSED SAMPLES
4	SUMMARY OF ANALYTICAL DATA FROM THE DEMONSTRATION OF METHODS APPLICABILITY STUDY
5	COST COMPARISON BETWEEN A TRADITIONAL AND A TRIAD APPROACH

FIGURES

Figure

- 1 SITE LOCATION MAP
- 2 CONCEPTUAL SITE MODEL DIAGRAM
- 3 HISTORICAL AND INITIALLY PROPOSED SAMPLING LOCATIONS
- 4 PROPOSED SAMPLING LOCATIONS (TRIAD APPROACH)
- 5 SAMPLING LOCATIONS, FEBRUARY 2003
- 6 LOGIC DIAGRAM 1 – ARSENIC IN FLY ASH INVESTIGATION
- 7 LOGIC DIAGRAM 2 – TPH, PAH, AND PCB INVESTIGATION
- 8 ARSENIC RESULTS SUMMARY, EPA SW-846 METHOD 6010B
- 9 FIXED LABORATORY TOTAL CARCINOGENIC PAHs vs. FIELD TEST KIT TOTAL PAHs
- 9A DEVELOPMENT OF A FIELD BASED ACTION LEVEL FOR CARCINOGENIC PAHs
WHEN NO HISTORICAL DATA IS AVAILABLE
- 10 TOTAL PAH RESULTS SUMMARY, SITE LAB FIELD TEST KITS
- 11 FIXED LABORATORY TPH vs. FIELD TEST KIT TPH
- 11A DEVELOPMENT OF A FIELD BASED ACTION LEVEL FOR TPH WHEN NO
HISTORICAL DATA IS AVAILABLE
- 12 TPH RESULTS SUMMARY, SITE LAB FIELD TEST KITS
- 13 PCB RESULTS SUMMARY, FIELD AND FIXED LABORATORY RESULTS
- 14 TOTAL PCB RESULTS SUMMARY, FIELD AND FIXED LABORATORY RESULTS

ENCLOSURES

Enclosures

- 1 SOME METHOD VALIDATION ISSUES FOR THE RCRA PROGRAM: THE FORMAL
VALIDATION PROCESS FOR NEW METHODS DEVELOPMENT AND
DEMONSTRATION OF METHOD APPLICABILITY FOR A SPECIFIC PROJECT
- 2 STATISTICAL PLOTS AND SUMMARY STATISTICS FOR PROJECT TARGET
ANALYTES
- 3 SELECTED CHROMATOGRAMS FOR SAMPLES USED TO DEVELOP FIELD-BASED
ACTION LEVELS

ACRONYMS AND ABBREVIATIONS

95LCL	95 percent lower confidence level
95UCL	95 percent upper confidence level
ACM	Asbestos-containing material
bgs	Below ground surface
BTSC	Brownfields Technology Support Center
CLP	EPA Contract Laboratory Program
COPC	Contaminant of potential concern
cPAH	Carcinogenic polynuclear aromatic hydrocarbon
CSM	Conceptual site model
CTDEP	Connecticut Department of Environmental Protection
CTDPH	Connecticut Department of Public Health
DMA	Demonstration of methods applicability
DEC	Residential direct exposure criterion
EA	Environmental assessment
ECD	Electron capture detector
EDRO	Extended Diesel-Range Organics
EPTOX	Extraction procedure toxicity test
EPA	U.S. Environmental Protection Agency
ETPH	Extractable total petroleum hydrocarbon
GC/ECD	Gas chromatography method using an electron capture detection system
GC/FID	Gas chromatograph/flame ionization detector
GC/MS	Gas chromatography/mass spectrometry
GPS	Global positioning system
ICAP	Inductively coupled argon plasma
IOC	Inorganic carbon
M&E	Metcalf & Eddy
μL	Microliter
μg/kg	Micrograms per kilogram
mfl	Million fibers per liter
mL	Milliliters
mg/kg	Milligram per kilogram
OEME	Office of Environmental Measurement and Evaluation
OVA	Organic vapor analyzer
PAH	Polynuclear aromatic hydrocarbon
PCB	Polychlorinated biphenyl
ppb	Part per billion
ppm	Part per million

ACRONYMS AND ABBREVIATIONS (Continued)

QC	Quality control
RAS	Routine analytical services
SIM	Selected ion monitoring
SOP	Standard operating procedure
SPLP	Synthetic precipitation leaching procedure
SVOC	Semivolatile organic compound
TBA	Targeted brownfields assessment
TCLP	Toxicity characteristic leaching procedure
TPH	Total petroleum hydrocarbons
TRC	TRC Environmental Consultants
UV	Ultraviolet
UVF	Ultraviolet fluorescence
VOC	Volatile organic compound
WAM	Work assignment manager
XRF	X-ray fluorescence

CASE STUDY ABSTRACT

Cos Cob Power Plant Site Greenwich, Connecticut

Site Name and Location: Cos Cob Power Plant 22 Sound Shore Drive Greenwich, CT 06830	Sampling and Analytical Technologies: <ul style="list-style-type: none"> • Systematic planning process • Dynamic work strategies • Direct push soil sampling • Field measurements of total polynuclear aromatic hydrocarbons (PAH) by ultraviolet fluorescence spectrophotometry • Field measurements of total petroleum hydrocarbons (TPH) by ultraviolet fluorescence spectrophotometry. • Field measurements for polychlorinated biphenyls (PCBs) by gas chromatograph/electron capture detector (ECD). 	CERCLIS #: None
Period of Operation: 1907- mid 1960s Operable Unit: The property where the former Cos Cob power plant was located is approximately 9 acres in size.		Current Site Activities: The Town of Greenwich, Department of Public Works has recently used the property for storage of construction materials. The town of Greenwich Connecticut is also evaluating re-use and remediation alternatives for the property.
Points of Contact: Denise M. Savageau Town of Greenwich 101 Fields Point Road Greenwich, CT 06830 203-622-6461 James P. Byrne EPA Region 1 1 Congress St., Ste. 1100 Boston, MA 02114-2023 617-918-1389 Kathleen M. Yager EPA Technology Innovation Program 11 Technology Drive North Chelmsford, MA 01863 617-918-8362	Media and Contaminants: <i>Surface and subsurface soil site wide:</i> <ul style="list-style-type: none"> • Soil may be affected by TPH and PAHs from petroleum spills on site. • Contaminants associated with on-site disposal of coal ash, including fly ash and slag. Chemicals of potential concern (COPCs) include PAHs and arsenic. • Site soil may be affected by PCBs associated with storage and use of transformers. Known spills have occurred on the property. • Asbestos is a COPC based on historical occurrence and previous assessments but is not addressed in this case study. <i>Groundwater:</i> <ul style="list-style-type: none"> • Groundwater was sampled in 1988, and no contamination was found. Based on the lack of water use and tidal influences in the area, groundwater is not considered a medium of potential concern at this time. 	Technology Demonstrator: siteLAB [®] ultraviolet fluorescence kits for PAHs and TPH. The EPA Region 1 laboratory provided single column GC/ECD analyses in the field for PCBs and screening for metals using XRF. <i>See Technology Quick Reference Sheets for additional information.</i>
Number of Samples Analyzed During the Investigation: A total of 112 samples were collected and analyzed at an off-site laboratory for arsenic. A total of 93 samples were collected and analyzed in the field for PAHs and TPH. Of the 93 samples, 23 were sent for comparative analysis for PAHs and 17 samples were sent for comparative analysis for TPH at an off-site laboratory. A total of 103 samples were also analyzed for PCBs on-site using a single column GC/ECD. Fifteen of these samples were also sent for off-site analyses of PCBs by a dual column GC/ECD method.		
Cost and Time Savings: Use of the Triad approach for site characterization resulted in an estimated cost savings of approximately 35 percent when compared with a traditional approach, assumed to involve two mobilizations and fixed laboratory analytical methods. In addition to saving costs, use of the Triad approach increased the size and quality of the data set used to make decisions about the site. Site characterization was achieved in a single mobilization lasting 1 week. Sufficient data necessary to make site decisions was collected in a single Brownfield's funding cycle (1 year). Site characterization following a traditional approach would have required multiple mobilizations taking place over 2 Brownfield's funding cycles (2 years).		

Results:

The project was completed successfully and cost-effectively. The relatively high data density for the site allowed regulators and stakeholders to make decisions with a high degree of certainty. Members of the project team were very satisfied with the time and cost savings achieved following the principles of the Triad approach.

Description:

The Cos Cob Power Plant case study is an example of how site investigation can be streamlined using systematic planning, dynamic work strategies, and field-based measurements. Work originally planned to be conducted over a two-year period was compressed into a single 1-week mobilization. Data needed by the town of Greenwich, Connecticut was collected in a single event. A preliminary conceptual site (CSM) model was evolved to near-maturity in real-time through field-based decision making, providing stakeholders with the data they needed in a fraction of the time required when using a traditional phased approach. Significant time and cost savings were realized when compared to a traditional multi-phased approach.

The Cos Cob Power Plant site was accepted by the U.S. Environmental Protection Agency (EPA) for the Targeted Brownfields Assessment (TBA) program in June 2002. Metcalf & Eddy, Inc. (M&E) was retained in the fall of 2002 to carry out the work, which was estimated to cost \$75,000 for the field effort. The 9-acre waterfront property is the location of the former Cos Cob Power Plant, which was a coal-fired trunk-line electrical generation facility. Operations were terminated in the 1960s. Historical industrial activities have resulted in the potential increase of contamination such as asbestos, coal, ash, transformer fluids and slag on site.

The plant was decommissioned in 1986; in 1987, the site was deeded to the town by the Connecticut Department of Environmental Protection (CTDEP) with the understanding that the property would eventually be open to all residents of the state. Since 2000, the Town of Greenwich, Department of Public Works has used the property for storage of construction materials.

The Town of Greenwich has established a Cos Cob Power Plant Committee made up of citizens interested in redevelopment of the site. Public interest is high and support is overwhelming for restoration of the property as a public recreational site. Restoring the site will provide public access to important coastal resources and protect important fisheries and wildlife habitat associated with the Cos Cob Harbor, Mianus River, and Long Island Sound. Proposed developments for the property include a waterfront public park with walking trails, playing fields, picnic areas, and a boating facility. The site is located in an area where most shoreline is privately owned; which limits public access to coastal resources. As a public site, public access and recreational opportunities would be provided.

Based on a review of historical aerial photographs and conversations with town representatives, the area south of the former powerhouse is almost entirely composed of fly ash from the former power plant. It is estimated that 22 to 35 feet of fly ash material exists on and beneath this portion of the property. It is also estimated that 30 feet of fill material made up of coal, slag, and ash is present beneath the northeastern portion of the site.

Remediation costs for the site will be included in the town's capital budget. Redevelopment will be financed through public and private partnerships. The town faces some challenges in reaching closure, however. For example, the results obtained during the February 2003 Triad-based TBA site investigation indicate that contamination from total petroleum hydrocarbons (TPH), polynuclear aromatic hydrocarbons (PAHs), and arsenic was found at levels that generally exceed Connecticut residential direct exposure criteria (DEC) to a depth of possibly 30 feet. Although elevated concentrations of TPH and PAH appear to be mainly associated with releases of fuels and other hydrocarbons, lower concentrations of these constituents are also widespread at the site at depths well below ground surface. As a result of the arsenic, PAH, and TPH contamination, reuse alternatives and potential closure requirements may be revised because removal of soil necessary to meet residential DEC for these contaminants would not be cost effective. Some viable alternatives for closure in support of reuse might include emplacement of fill material over portions of the site or development of alternative closure standards based on a risk assessment and more realistic exposure assumptions.

TECHNOLOGY QUICK REFERENCE SHEET #1

Total Petroleum Hydrocarbons (TPH) And Polynuclear Aromatic Hydrocarbons (PAH) By Ultraviolet Fluorescence (UVF)

Summary of Project-Specific Performance Information			
Project Role: Provide real time results to guide dynamic sampling activities for a Triad investigation. Test kit concentrations were correlated to fixed laboratory concentrations to develop field-based action levels.	Analytical Information Provided: A total of 93 samples were collected, extracted, and analyzed for Total Polynuclear Aromatic Hydrocarbons (PAHs) (C11-C22 Aromatics) using a UV3100 fluorescence detector. Raw fluorescence results were used in conjunction with the Total Petroleum Hydrocarbon (TPH) forecasting guide to generate TPH Extended Diesel Range Organics (TPH-EDRO) results. Ultraviolet Fluorescence (UVF) results for total PAHs in 23 samples were compared to fixed laboratory results using SW-846 method 8270 operated in the selected ion monitoring (SIM) mode. UVF results for TPH in 16 samples were compared to fixed laboratory results using SW-846 method 8015M.		
Project Cost and Time Savings			
Total Cost (includes instrument rental, consumables, and labor): \$7,300		Total Cost Per Sample (includes instrument rental, consumables, and labor): \$78	
Instrument Cost: UV3100 Purchase Price: \$12,500 Rental: \$300/day \$600/3 days \$ 900/week \$2,500/month	Consumables Cost: Extraction Kits (20 samples)= \$300 5 kits used= \$1,500 Calibration Kit=\$200 2 kits used= \$400	Labor Cost: \$48/ Sample	Time Savings: 1 Year Site characterization was achieved in a single mobilization lasting 1 week. Sufficient data necessary to make site decisions was collected in a single Brownfield’s funding cycle (1 year). Site characterization following a traditional approach would have required multiple mobilizations taking place over 2 Brownfield’s funding cycles (2 years).
		Waste Disposal Cost: Not available. Disposal cost for small amounts of methanol and extract are assumed to be minimal.	
Site-Specific Precision and Accuracy Achieved: Relative Percent Difference $RPD = \frac{ A- B }{(A+ B) / 2} \times 100$ Comparability= (UVF result/fixed lab result) x 100 <div><div>Total PAHs (C11-C22 Aromatics)</div><div>TPH</div></div> <div>Duplicate RPDs:9% to 10%8% to 10%</div> <div>Split Sample Comparability:Not Applicable43% to 186%</div>			Throughput Achieved: 93 samples

TECHNOLOGY QUICK REFERENCE SHEET #1 (continued)

Total Petroleum Hydrocarbons (TPH) And Polynuclear Aromatic Hydrocarbons (PAH) By Ultraviolet Fluorescence (UVF)

General Commercial Information (Information valid as of October 2003)		
Vendor Contact: Steve Greason 978-363-2299	Vendor Information: siteLAB® Corporation 4 Crane Neck Street, West Newbury, MA 01985 877-748-3522 www.site-lab.com	Limitations on Performance: The test kit reports total PAHs as opposed to specific PAH compounds. TPH values are estimated as diesel-range organics based on the raw sample fluorescence. The shelf life of the calibration kits is 3 months after purchase.
Principle of Analytical Operation: This test is based on the excitation of aromatic compounds, such as benzene, toluene, ethylbenzene, and xylenes (BTEX) and PAHs, in petroleum hydrocarbons exposed to ultraviolet (UV) light. The compounds both absorb and emit (fluoresce) energy at specific wavelengths, so an energy filter is used to allow only wavelengths specifically absorbed by aromatic compounds to reach the cuvette containing the sample (or sample extract). Fluorescence emissions from the sample are then passed through another filter to reach a photomultiplier detector. The result is a total PAH, TPH, or BTEX concentration for each sample, depending on how the instrument is calibrated. Sample results are quantitated based on a 5-point calibration curve generated using certified standards of interest (PAH, TPH, BTEX, or a combination) for a given project. Water samples are analyzed directly after a simple 10X or 100X dilution. Soil samples are extracted by shaking for 2 minutes in methanol; then, the extract is filtered and diluted for analysis.		Availability/Rates: Test kits are commercially available as off-the-shelf products. Associated extraction kits and UV fluorescence detectors are available for purchase or rental from the manufacturer.
		Power Requirements: 120 volts of AC power is required for the UV3100 fluorescence detector. The unit can be operated using a vehicle cigarette lighter or portable generator.
		Instrument Weight and/or Footprint: Approximately 5 square feet of space is required to run sample extract batches, analyze samples using the UV3100, and download information from the UV3100 to a laptop computer.
GENERAL PERFORMANCE INFORMATION		
Known or Potential Interferences: Interferences are limited because the excitation and emission filters limit fluorescence from non-target analytes. Site-specific matrices also provide ratios of PAH compounds from site contaminants. Soil with high concentrations of naturally occurring humic materials can produce low-level false positive results in rare cases.		
Applicable Media/Matrices: Soil/Water	Analytes Measurable with Expected Detection Limits: Total PAHs – 0.05 milligram/kilogram (mg/kg) Extended Diesel-Range Organics (EDRO) – 0.05 mg/kg (values are wet weight)	Other General Accuracy/Precision Information: See www.site-lab.com for technology evaluations, case studies, and detection limit studies.
Wastes Generated Requiring Special Disposal: Small volumes of methanol used for sample extraction and small volumes of sample extract.		Rate of Throughput: Samples can be prepared in batches of 10 with a batch preparation time of about 5 minutes. Analysis of individual samples can be completed in about 30 seconds.

TECHNOLOGY QUICK REFERENCE SHEET #2

Polychlorinated Biphenyls (PCBs) By Gas Chromatography/Electron Capture Detector (GC/ECD)

Summary of Project-Specific Performance Information			
Project Role: Provide real time screening results for Polychlorinated Biphenyls (PCBs). Results were used to guide step-out sampling for contaminant delineation and select samples for definitive fixed laboratory analysis.		Analytical Information Provided: 103 soil samples were collected, extracted, and analyzed for PCBs using a single-column Gas Chromatography (GC) instrument with an Electron Capture Detector (ECD) for tentative identification and semi-quantitation of PCB congeners. All field samples with tentatively identified concentrations of PCBs were sent for offsite definitive analysis using a dual column GC/ECD method. Confirmation samples were analyzed following EPA Region 1 Standard Operating Procedures (SOP) (PESTSOIL2.SOP).	
Project Cost and Time Savings			
Total Cost: EPA Region 1 provided mobile laboratory services at no cost to the project.		Total Cost Per Sample: EPA Region 1 provided mobile laboratory services at no cost to the project.	
Instrument Cost: Shimadzu GC-14 with ECD and data module. Purchase price: \$12,000 Rental costs were not available because EPA Region 1 provided mobile laboratory services at no cost to the project.	Consumables Cost: Not available	Labor Cost: EPA Region 1 provided the mobile laboratory at no cost to the project.	Time Savings: 1 Year Site characterization was achieved in a single mobilization lasting 1 week. Sufficient data necessary to make site decisions was collected in a single Brownfield’s funding cycle (1 year). Site characterization following a traditional approach would have required multiple mobilizations taking place over 2 Brownfield’s funding cycles (2 years).
		Waste Disposal Cost: Not available. Disposal cost for small amounts of methanol, hexane, water, and extract are assumed to be minimal.	
Site-Specific Precision and Accuracy Achieved: Relative Percent Difference $RPD = \frac{ A- B }{(A+ B) / 2} \times 100$ Comparability= (Mobile lab result/fixed lab result) x 100 <div><div>Duplicate RPDs: Split Sample Comparability:</div><div><div>Total PCBs</div><div>14% to 21%^a 13% to 130%^a</div></div> Notes: ^a (mobile laboratory results in wet weight/ fixed laboratory results in dry weight)</div>			Throughput Achieved: 103 samples

TECHNOLOGY QUICK REFERENCE SHEET #2 (continued)

Polychlorinated Biphenyls (PCBs) By Gas Chromatography/Electron Capture Detector (GC/ECD)

General Commercial Information (Information valid as of October 2003)		
Vendor Contact: U.S. EPA Region I Mobile Laboratory Scott Clifford/ Dick Siscanaw 617-918-8327	Vendor Information: U.S. EPA Region I Laboratory USEPA New England Office of Environmental Measurement and Evaluation (OEME) 11 Technology Drive N. Chelmsford, MA 01863-2431	Limitations on Performance: Analyses were performed on a single-column GC/ECD instrument for tentative identification and semi-quantitation of PCB congeners. Detections by the single-column method can be false positives, and all detections found using the mobile field laboratory were confirmed by off-site analysis using a dual-column method. Confirmation samples were analyzed following EPA Region 1 Standard Operating Procedures (SOP) (PESTSOIL2.SOP).
Principle of Analytical Operation: This analysis is based on a micro-extraction of a soil sample and analysis of the extract by GC/ECD. Approximately 1 gram of each sample aliquot was weighed in a 4-milliliter vial and a mixture of methanol, hexane, and reagent-grade water was added to perform the extraction. Each sample was placed on a vortex for approximately 1 minute and then centrifuged. A portion of the resulting extract was injected directly onto the gas chromatograph column, and results were graphed by the ECD. Concentrations were evaluated using an external standard technique. Dilutions were made as necessary to samples that exceeded the calibration range.		Availability/Rates: The EPA Region I mobile laboratory is available to assist in analysis of samples for investigations at Brownfield's sites. Requests should be submitted to the EPA Region I Laboratory. The Region I Mobile Laboratory is also available to support Superfund site cleanups.
		Power Requirements: The mobile laboratory provides all of its own power and is completely self-contained. The mobile laboratory comes complete with all reagents and tools to perform extraction and a Shimadzu model GC with ECD was used for analysis.
		Instrument Weight and/or Footprint: Bench-top GCs generally weigh between 100 and 200 pounds, but can be less than 100 pounds. Laboratory space required is controlled by the need for sample preparation and extraction. Documentation can also increase the need for additional space in the laboratory.
GENERAL PERFORMANCE INFORMATION		
Known or Potential Interferences: Interferences are limited, but false positives can occur. All samples with potential PCB detections identified from the mobile laboratory were sent for confirmation analysis using a dual-column GC/ECD method according to EPA Region 1 SOP (PESTSOIL2.SOP), which is based on EPA SW-846 Method 8082.		
Applicable Media/Matrices: Soil/Water	Analytes Measurable with Expected Detection Limits: PCBs – 1 milligram per kilogram (mg/kg) wet weight	Other General Accuracy/Precision Information: Soil samples were analyzed for PCBs following EPA Region I SOP "PCBs Field Testing for Soil and Sediment Samples" (EIA-FLDPCB2.SOP)
Wastes Generated Requiring Special Disposal: Small volumes of methanol and hexane used for sample extraction and small volumes of sample extract.		Rate of Throughput: Sample preparation is about 3 to 5 minutes per sample. Analysis of individual samples can be completed in 10 minutes.

EXECUTIVE SUMMARY

The following case study was prepared by the Brownfields Technology Support Center (BTSC), within the U.S. Environmental Protection Agency's (EPA) Office of Superfund Remediation and Technology Innovation (OSRTI). The case study was developed as part of EPA's ongoing initiative to promote the use of an integrated Triad approach to limit decision uncertainty at hazardous waste sites through the use of sound science. The Triad approach, which consists of systematic planning, dynamic work strategies, and real-time measurement technologies that include field-based analyses, is being promoted by OSRTI and its partners as a viable method for streamlining site investigations.

The Cos Cob Power Plant site is located in the southeastern corner of Connecticut, and is adjacent to Cos Cob Harbor. The site was the location of a former power plant, which has since been demolished. The current owner of the site is the Town of Greenwich, Connecticut. The town plans to reuse the site and has received a Targeted Brownfields Assessment (TBA) grant to assess potential reuse options. Reuse alternatives proposed for the site include creation of a walking trail and wetlands and a series of playing fields. EPA Region 1 requested assistance from the BTSC in an attempt to maximize the efficiency of the TBA by applying the Triad approach. A scoping meeting was held between EPA Region 1 and the BTSC during November of 2002. This initial planning meeting discussed a revised approach to site characterization that would rely on the use of field-based measurement technologies and the Triad approach.

A preliminary conceptual site model (CSM) was developed based on a review of existing data from previous investigations. The CSM indicated that potential threats to human health and the environment were essentially limited to those posed by direct contact with contaminated surface soil and sediment. Contaminants of potential concern included asbestos, petroleum-related substances, polychlorinated biphenyls (PCBs), and arsenic. A review of past use and analytical results showed that contamination could extend to some depth beneath the site and that the distribution mechanism was known to be related to placement of coal ash as fill across the site, petroleum spills, or to storage of transformers that contained PCBs. It was agreed that a primarily field-based approach could be used to expand sampling and analytical coverage at the site and that a dynamic work strategy would likely be beneficial to assist in further delineation of contaminants at the site, particularly for PCBs.

The initial work plan developed by Metcalf & Eddy (M&E) (2002) called for limited authoritative sampling and analysis, using a fixed off-site laboratory, at locations where historical releases were expected. A second phase of work would have been required under the original project plan. A revised "dynamic" sampling strategy based on the Triad approach was proposed by the BTSC that called for use

of test kits, field methods and a grid sampling approach to affordably expand the extent and density of information available to support decision-making. The revised work plan, developed by M&E (2003), in cooperation with the BTSC and the EPA Region 1 laboratory, called for the use of ultraviolet fluorescence test kits for analysis of total petroleum hydrocarbons (TPH) and polynuclear aromatic hydrocarbons (PAH) and a field-based single column gas chromatography (GC) method using an electron capture detection system for analysis of PCBs. To meet project sensitivity requirements, samples were analyzed for arsenic at an off-site laboratory using trace inductively coupled argon plasma (ICAP) atomic emission spectrometry. Analysis at a fixed laboratory was used to confirm field-based results for PCBs for samples with positive detections. A modified GC/mass spectrometry method using the instrument in the selected ion-monitoring mode was also to be used to refine the correlation between results for PAHs from the field test kits. Assumptions concerning the appropriateness of limiting metals analysis to a single analyte (arsenic) were confirmed by analyzing a percentage of the total soil samples collected for a full suite of metals using an off-site ICAP method.

The field effort was completed in one week. Direct-push methods were used to collect soil samples from 1-foot intervals across the site. Initially, samples from only the top two 1-foot depth intervals were analyzed in the field, and a small percentage of the samples collected were sent for off-site comparative analyses. Deeper sampled intervals were analyzed selectively based on the presence of PCBs. EPA Region 1's mobile laboratory performed the field analyses for PCBs that were used to guide the investigation. All samples that tentatively identified the presence of PCBs were sent for comparative analysis at an off-site laboratory.

The town was interested in evaluating the potential need for remediation based on a comparison between contaminant concentrations measured at the site and a residential reuse scenario. In Connecticut, residential reuse criteria are generally applied to recreational reuse scenarios. Results obtained during the investigation indicated that the top 2 to 3 feet of soil contained concentrations of TPH, PAHs, arsenic, and PCBs that consistently exceed the residential reuse criteria. (Connecticut defines surface soil as 0 to 4 feet below ground surface [bgs].) A review of past disposal practices at the site suggested that the same conditions could extend to as deep as 30 feet bgs, thereby rendering excavation and disposal of contaminated material to meet residential standards cost prohibitive. Concentrations of contaminants of potential concern (COPCs) are relatively low given the planned reuse for the site, suggesting that modification of the reuse alternative or establishment of reasonable and protective action levels could facilitate reuse with only minor amounts of cleanup required for hot spots that contain PCBs.

Field-based technologies and unaligned grid sampling were employed to increase site coverage and limit decision uncertainty. A dynamic work strategy was used to further delineate PCB contamination, focusing on areas where positive detections were above the DEC and some additional characterization

was warranted to support estimating the cost of remediation. Estimated cost savings as compared with the use of a more traditional, phased approach were calculated at approximately 35 percent. Time was also saved in that the project was completed in a single investigation and TBA funding cycle.

SITE INFORMATION

The Cos Cob Power Plant site is located in the southeastern corner of Connecticut and is adjacent to Cos Cob Harbor. The site was the location of a former power plant, which has since been demolished. The current owner of the site is the Town of Greenwich, Connecticut. The town is planning for reuse of the site and has received a Targeted Brownfields Assessment (TBA) grant to assess potential reuse options. The U.S. Environmental Protection Agency (EPA) Region 1 requested assistance from the Brownfields Technology Support Center (BTSC) to increase the efficiency of the TBA by applying the Triad approach, an integrated method to limit decision uncertainty at hazardous waste sites through sound science using systematic planning, dynamic work strategies, and real-time measurement technologies that include field-based analyses.

Site description and background information presented in this section were summarized from reports provided by the Town of Greenwich, and from conversations and a site visit with town representatives and Metcalf & Eddy (M&E), contractor to EPA Region 1, held on July 31, 2002. Limited information was also drawn from an environmental database search and Sanborn map review (Environmental Data Resources 2002), and a search of files at the Connecticut Department of Environmental Protection (CTDEP).

SITE LOCATION AND DESCRIPTION

The former Cos Cob Power Plant site is located at 22 Sound Shore Drive in the Cos Cob section of the Town of Greenwich, Connecticut, on the west bank of the Mianus River just south of the I-95 bridge and east of the Cost Cob Metro North train station (Figure 1). The portion of the former plant property owned by the town is approximately 9 acres and is bordered to the north by Metro North transformer yards, to the west by an electrical substation and transformer yard owned by Connecticut Light and Power Company, to the southwest by a condominium complex, and to the east and south by Cos Cob Harbor (Mianus River). The property was deeded to the town by the CTDEP in 1987, with the understanding that the property would ultimately be open to all residents of the state.

An aerial photograph of the site provided by the Town of Greenwich predates demolition of the power plant and was used to prepare figures for this report and to identify locations of structures that were formerly present at the site. Demolition of the power plant began in 1999 and was completed in 2000. The power plant, metal frame building, water towers, and aboveground oil tank have all been removed.

No structures on the property are owned by the town, but the town public works department uses the property to store construction materials. A large pile of soil currently occupies the area of the former powerhouse. The town property is otherwise unused. Access to the property is limited to town employees and is restricted by a fence along the northern and western boundaries.

SITE HISTORY AND USE

The Cos Cob Power Plant was built in 1907 by the New York, New Haven, and Hartford Railroad to provide power for electrification of the railroad. The coal-fired plant operated in this capacity until the 1960s. The plant was a multi-level concrete and metal building that housed boilers, transformers (known to contain polychlorinated biphenyls [PCBs]), and other electrical generation and distribution equipment. Ash and slag from power generation were disposed of on the grounds surrounding the plant; a large aboveground oil storage tank was also formerly located on the site. The type of oil stored in the tank has not been identified, however. Several additions were made to the building over the years before its use was discontinued in the 1960s. In 1986, the idled plant was decommissioned by the Connecticut Department of Transportation, and the property was transferred to the Town of Greenwich the following year. Plant equipment, such as transformers and boilers, were left intact. The plant, which had been essentially vacant for 20 years, continued to deteriorate and was the target of vandalism. One case of vandalism resulted in the release of transformer oils to the ground. The town reported the spill to the CTDEP, and contracted with Marin Environmental (Marin) to remediate the release area and to conduct a limited investigation of site soils in 1998 (Marin 1998a). The town also retained Marin Environmental to complete an inventory of transformers and breakers within the plant and sample oil within the equipment to determine its PCB content (Marin 1997). Further information regarding the work by Marin is presented below under initial site investigation. Transformer oils were subsequently sampled again by Osprey Environmental in 1998 to support a request for bids issued by the town for removal and disposal of the oils (Osprey 1998). These latter samples were analyzed for parameters other than PCBs that were needed to estimate costs for off-site disposal, namely Resource Conservation and Recovery Act metals, British thermal unit content, percent water, and total halogens.

In 1999, the town and CTDEP became increasingly concerned about the potential for releases of asbestos-containing materials (ACM) from the deteriorating main building and smaller metal buildings. An inspection of the main building in 1999 by Osprey Environmental, on behalf of the town, found ACM both inside and outside the building. The types of ACM identified ranged from nonfriable transite, galbestos, and roofing products, to boiler gasket materials and thermal insulation. Osprey Environmental

evaluated the potential for a release of ACM to the environment and concluded that releases had likely occurred from several areas.

On behalf of the town, Osprey Environmental notified EPA, CTDEP, and the Connecticut Department of Public Health (CTDPH) of the likely releases. Osprey recommended the removal of ACM, with the concurrence of the CTDPH. The ACM was removed, and the main building and smaller metal buildings were demolished during 1999 and 2000.

PROPERTY REUSE SCENARIO

Reuse scenarios are not yet well established for the site. The property currently has deed restrictions resulting from the agreement when the town received the property from the state of Connecticut. Restrictions include: the property must be maintained as open space and accessible to all state residents. Although some additional re-use scenarios have been suggested, the town has been unable to consider re-use scenarios that do not meet the deed restriction criteria.

Currently, the town intends to redevelop the property as a waterfront public park. Possible uses of the park that the town is considering include walking trails, playing fields, picnic areas, and a shoreside boating facility. The town has formed a committee that has actively sought community input regarding redevelopment of the property. Responses to a town-wide questionnaire distributed in 2001 indicate that the majority of residents prefer passive recreational uses such as walking trails and picnic areas.

CONCEPTUAL SITE MODEL

A CSM is a description of everything that is known about a site that is relevant to the decisions to be made in support of proposed reuse alternatives. At the Cos Cob site, existing environmental sampling data, geologic information, and preliminary reuse plans were reviewed to develop a preliminary CSM diagram (shown on Figure 2). A more detailed review of existing chemical and historical information is presented in the draft field task work plan (M&E 2003a). A brief description of the results of previous investigations and the materials compiled in development of the preliminary CSM for the site is presented below.

Initial Site Investigations

TRC Environmental Consultants (TRC) conducted an environmental assessment (EA) of the site for the Town of Greenwich in 1988 (TRC 1988). Surface and subsurface soil samples, limited samples of surface water and sediment, and groundwater samples were collected, as follows:

- Ten surface soil samples and 19 soil boring samples were collected from nine locations at 0 to 12 inches bgs. Split spoon samples were collected at 2-foot intervals to 6 feet bgs, and at every 5 feet or change in strata throughout the depth of the borehole. A minimum of two samples were taken from each borehole and samples were analyzed for PAHs, extraction procedure (EP) toxicity metals, and PCBs. Samples from three locations were also analyzed for volatile organic compounds (VOC) because of the proximity to potential fuel oil contamination.
- Six subsurface test borings and three monitoring well borings were drilled on the property. Test borings were advanced until no visible sign of contamination or waste material was observed.
- Three groundwater samples were collected from the three monitoring wells installed during the EA. Samples were analyzed for metals, common leachate indicator parameters, metals, PAHs, and VOCs. The wells are no longer in existence at the property.
- Two surface water and four sediment samples were collected from two locations bordering the site as well as from two on-site locations. Samples were analyzed for metals, PCBs, inorganic carbon, PAHs, and VOCs.

Soil was analyzed for extractable metals using the EP toxicity procedure, an acid-leach procedure that has been superseded by the toxicity characteristic leaching procedure (TCLP). The use of EP toxicity was consistent with CTDEP guidelines at that time (1988). Four metals were detected in EP toxicity samples: arsenic, barium, lead, and silver. Based on the guidelines of that time, results did not suggest a need to remove or remediate site soils. Key observations, as noted in the TRC report, are quoted from the EA report document as follows:

“...approximately 22 to 35 feet of fly ash fill material exists in the southern portion of the site, and approximately 30 feet of coal/slag/ash fill material exists in the northeastern portion of the site. At two other areas on the site, namely at test borings B-1 and B-3 (Figures 3 and 4), signs of fuel oil soil contamination were observed, both visually and olfactory (i.e., oily appearance and odor) and through elevated readings with a portable Organic Vapor Analyzer (OVA).” (TRC 1988).

Only one soil sample contained detectable levels of VOCs. TRC did not compare detected concentrations of PAHs with current Connecticut residential direct exposure criterion (DECs), because none were in place when the investigation was performed in 1988. Tables in Appendix B of the draft field task work plan (M&E 2003a) compare the TRC results for soil samples to the current DEC. Surface soil samples

SS-3, SS-5, B-2, and B-3 (Figure 3) exhibited concentrations of PAHs that exceed the current DEC's. Concentrations of PAHs reported by TRC for subsurface soil samples did not exceed the currently used DEC's.

Of the three groundwater samples collected, the concentration of zinc reported in two of the samples exceeded the surface water protection criterion of 123 parts per billion (ppb). This suggested the potential need for at least some surface water control measures as part of any remedy. No VOCs or PAHs were detected, and no other metals were detected at levels that exceeded the DEC's.

The TRC report prompted later concerns with respect to direct exposure to surface soils (PAHs in some samples exceeded the residential DEC's later established by CTDEP). Results for metals were not conclusive because data for total metals in soils were not obtained, and EP toxicity results are not directly comparable to DEC. The widespread presence of ash noted by TRC indicated that soils were likely to contain levels of metals that exceed DEC. In addition, TRC noted fuel oil odors in some locations (B-1 and B-3), suggesting the possibility of petroleum releases. At these two locations, PAHs were also detected in the soils.

Marin Transformer Inventory, 1997. The town retained Marin in 1997 to conduct a transformer survey and PCB evaluation at the site (Marin 1997). The purpose was to identify the number and volume of electrical transformers and aboveground storage containers within the plant. Seventy-four transformers were identified on the site; 54 disconnect switches/circuit breakers were located within the power plant building, and 11 aboveground storage containers (tanks, drums, and others) were found within the power plant building. A total of 91 oil samples were collected from selected transformers, switches, circuit breakers, and storage containers, and then analyzed for PCBs. Aroclor 1260, a common commercial PCB mixture, was detected in five of the 91 oil samples at concentrations ranging from 2.2 to 12.0 parts per million (ppm). Most of these detections were located in the area called "former transformer/breaker area" shown on Figures 3 and 4. Others were from transformers located on the main level of the power plant building in the northwestern corner of the site, in an equipment maintenance area. The EA report recommended that fluids within the equipment at the site be removed and disposed of off site because the equipment did not have secondary containment and thus did not comply with CTDEP aboveground storage regulations.

Marin Limited Soils Investigation, 1998. The town also retained Marin to conduct an investigation of soil in selected site locations, as requested by CTDEP in a letter from Ms. Lori Saliby dated November

25, 1997. The CTDEP had received an anonymous report of historical disposal of dielectric fluid and had also been notified by the town of a spill from a transformer that had apparently been overturned by vandals.

The main areas of concern were: (1) an area in the basement of the building where the transformer was overturned and soil staining was evident (the transformer spill area, identified on Figures 3 and 4 as the remediated basement oil-stained area), and (2) several outdoor areas alleged to have been subject to historical disposal of fluids (the A-, B-, and D-series Marin borings on Figures 3 and 4). An area "C" was also identified (north of the Cos Cob plant, around one of the cinder block buildings), but was eliminated from the investigation because it was not on the town's property. Shallow soil samples were collected in the A, B, and D areas (depth range of 6 inches to 1.5 feet below ground surface [bgs]) and analyzed for PCBs by EPA Method 8080 and for TPH by EPA Method 418.1 (Marin 1998a). No PCBs were detected in any of the soil samples collected. TPH was detected in samples collected at locations A-1, A-2, B-2, B-3, and D-3 at levels exceeding the Connecticut DEC for residential exposure under the Remediation Standard Regulations of 500 ppm (that is, 500 milligrams per kilogram [mg/kg]). Marin recommended that these areas be further investigated as part of a comprehensive site assessment, before the appropriate course of action could be selected.

Marin's investigation of the transformer spill area confirmed the presence of TPH in excess of the DEC in shallow soils in the basement. Samples were collected from the surface of the basement dirt floor to a depth of 6 inches. PCBs were detected in one of five soil samples collected, at a concentration of 1.9 mg/kg. PCBs were not detected in the other four soil samples (the reporting limit for these samples was 1.0 mg/kg). The Marin report recommended that the transformer spill area be remediated by excavating the contaminated soil. Marin completed remediation for the town in April 1998. A letter from Marin to CTDEP dated July 6, 1998, documented the remediation and presented the results of confirmation soil sampling. The depth of the excavation ranged from 12 to 18 inches, and approximately 15 cubic yards of soil was removed and disposed of off site (Marin 1998b).

Osprey, 1999: Asbestos was found at levels that constitute a "release." Types of ACM identified included nonfriable transite to galsbestos. The ACM was removed, and the buildings were demolished in 1999 and 2000.

Current Site Use

The Department of Public Works has used the town's portion of the property to store construction materials since the plant was demolished in 2000. Multiple piles of segregated construction materials (gravel, soil, and piping) are located within the site boundaries. There are no structures on the site. The topography is relatively flat, except near the stone and concrete sea walls or where piles of clean soil are present and the ground surface slopes steeply up and then back down to Cos Cob Harbor. Most of the site is vegetated only by grass or consists of vegetation free tightly compacted fill, except for the area along the southern sea wall and the slag ash area, where trees are present.

Site and Regional Geology

Cos Cob Harbor is located in Greenwich, Connecticut, along the southwestern region of the state. The regional bedrock is primarily composed of Harrison Gneiss. The Harrison Gneiss is characterized by interlayered dark and light gray layers of medium grain size crystalline material with a strong foliation. The major geological units which make up the Long Island Sound include bedrock, buried coastal-plain sediments, continental glacier moraines, glacial-lake deposits, and marine delta sequences. Crystalline bedrock and deltaic deposits associated with glacial Lake Connecticut, influence sedimentation in the northern and western regions of the sound. Data from boring logs indicate black silt with little sand and trace gravel to a depth of 30 to 35 feet below ground surface at the site. A gray marine silt is present at depths below 35 feet (Figure 2).

Historic aerial photographs and information gathered from conversations with town representatives revealed that the southernmost portion of the site, south of the former powerhouse, is almost entirely composed of fly ash from the former power plant (Figures 3 and 4). This area was slowly filled in over the years with ash from the power plant. Previous site investigations document the presence of ash to a depth of near 30 feet bgs in this area. As shown on Figure 3, two distinct areas of ash cover the site. The area northeast of the former power house is composed of slag ash derived from coal ash that remains in the boiler, while the debris to the south is composed almost entirely of fly ash that was collected from the plant's exhaust stacks.

MEDIA OF CONCERN

Table 1 provides a pathway receptor diagram developed by the project team that shows the primary sources and potential receptors for the Cos Cob site. This table shows that surface soil and solids present a potential risk to human health and the environment and represent the primary media of interest at the site. Surface water and sediment are not considered media of interest because remediation under the reuse scenario would likely involve PCB hot spot removal, along with capping and drainage improvements for remaining arsenic, PAH, and TPH contamination. Groundwater at the Cos Cob site is considered brackish and nonpotable; therefore, groundwater is not designated as a medium of concern in this evaluation. Contaminant concentrations in groundwater are expected to be relatively low and constituents immobile. Therefore, impacts from groundwater beneath the site to the harbor are considered unlikely.

CONTAMINANTS OF POTENTIAL CONCERN

The contaminants of potential concern (COPC) at the site were identified through historical information and documentation from previous investigations as petroleum hydrocarbons and related PAHs, metals (primarily low levels of arsenic related to fly ash), and PCBs in locations where transformers had been stored. In addition, asbestos near former buildings was identified as a potential concern. Table 2 provides a summary of COPCs at the site and their related DEC.

Metals. Metals, particularly arsenic, are contaminants of concern because of their presence in coal ash and the documented use of ash as fill on the site. The DEC for arsenic is low (10 mg/kg), and arsenic is commonly present in soils affected by coal ash at concentrations that exceed this level. During the EA conducted at the site, soil samples were collected for analysis of metals by the EP toxicity procedure, a leaching test that has since been superseded by the toxicity characteristic leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP). The EP toxicity procedure (EPTOX) does not give a measurement of the total concentrations of particular metals in soil; consequently, the available historical results are not directly comparable to the Connecticut DEC's and additional analyses would be required to meet project objectives.

PAHs. PAHs are also of potential concern, due to their presence in coal ash, as well as their presence in petroleum oils. Previous assessments (TRC 1988) revealed low levels of PAHs (but that exceeded DEC) in some surface soil samples. It is not known whether the PAHs are from coal, coal ash, petroleum releases, nor is it known whether their presence is widespread or localized.

Petroleum Hydrocarbons. Marin surface soil samples at locations A-1, A-2, B-2, B-3, and D-3 (Figure 3) exhibited concentrations of TPH at levels greater than DEC (Marin 1998a). These samples were collected in areas suspected of being affected by a release. These areas were investigated by M&E on December 9, 2002, during a field event designed to collect site-specific soil samples for a “demonstration of methods applicability” study designed to constrain the use of a siteLab[®] test kit. No odor or visual evidence of petroleum hydrocarbons was noted in the samples. It is considered likely that PAHs represent the principle petroleum-related COPCs present in site soil. The DEC for carcinogenic PAHs (cPAH) are much lower than that for TPH.

PCBs. The Marin letter report documents remediation of a PCB spill in the basement of the former powerhouse (Marin 1998b). Although TRC’s soil samples collected during the EA for PCB analysis did not exhibit detectable levels of PCBs (TRC 1988), the EA was limited in extent and PCBs are suspected to be present over at least the northern two-thirds of the site.

Asbestos. The likelihood that surface soil is affected by ACM is considered moderate, based on the evaluation conducted by Osprey Environmental in 1998. Releases of ACM to the environment are likely to have occurred before the ACM was abated and the buildings were demolished in 2000 (Osprey 1998).

Areas and contaminants of potential concern are summarized in the following list.

Site Area	Media of Potential Concern
Sitewide surface and subsurface soils	<p>Soils throughout the site may be affected by contaminants associated with on-site disposal of coal ash (both fly ash and slag or bottom ash) from the power plant. Contaminants commonly found in areas where ash is used as fill include metals (particularly arsenic) and PAHs. Ash extends to depths of up to 30 feet across portions of the site.</p> <p>Asbestos containing material (ACM) may also be mixed with site soils as a result of possible releases from the deteriorated power plant buildings before they were demolished in 2000.</p>
Surface and subsurface soils in areas where contaminants were previously encountered (Marin investigations)	Previous investigations detected petroleum hydrocarbons in several locations (A-, B-, and D-series borings), and recommended further investigation of these areas. Anecdotal evidence suggests the potential for PCB contamination as well, although PCBs were detected in only one location previously, and that location has since been remediated.

Site Area	Media of Potential Concern
Groundwater	Groundwater was sampled by TRC in 1988, and no contamination was encountered. Groundwater is not considered a concern based on the TRC results. However, because the TRC samples were collected more than 10 years ago, before the power plant was demolished, it may be worthwhile to conduct a limited groundwater sampling event at some future time, particularly if construction that will require dewatering is contemplated.

EXPOSURE ROUTES AND RECEPTORS

A complete exposure pathway consists of four fundamental components: (1) a source and mechanism of chemical release, (2) an affected environmental medium and a probable chemical migration process, (3) an exposure point, and (4) an exposure route by which humans come into direct contact with the chemical. If any of these components is missing, then the exposure pathway is incomplete and no exposure can occur.

Results of the previous investigations indicate that human receptors are the risk drivers for the former Cos Cob Power Plant. Potential exposure pathways for the site were selected based on current land use and most probable future activities at the site, as well as an evaluation of potential transport or uptake pathways.

Future adult and child recreational users may be exposed to COPCs in surface soil. Exposure to the recreational user is limited to surface soil because planned recreational use of the area is not likely to require disturbance of deeper (subsurface) soils. Potential surface soil exposure pathways for the future recreational user are incidental ingestion of soil, dermal contact with soil, and inhalation of particulates released from soil (Table 1). The surface water exposure pathway is considered incomplete for this study because no surface water bodies or direct contact between ash and surface water are anticipated; this pathway may need to be addressed further as site reuse is planned and implemented, however.

WORK PLAN DEVELOPMENT

The BTSC became involved with this project in the fall of 2002, when the EPA project manager and the EPA Region 1 Technology Innovation Office (TIO) representative identified the site as a good candidate for application of the Triad approach. The EPA Region 1 project manager arranged for assistance to be provided by the BTSC and further directed M&E to develop a draft work plan for the TBA at the Cos Cob site. The draft work plan was developed to provide a summary of existing site information and present an example for a “traditional” approach to site assessment under a TBA. Subsequent to a review of that work plan and other site information, a project meeting was held at EPA Region 1 offices in November 2002. As a result of that meeting, the work plan was revised to incorporate the use of field-based analytical technologies, statistical sampling, and accelerated decision-making consistent with the principles of the Triad approach. The initial work plan was never completed or formally submitted for EPA review because it was decided early on to abandon it and move toward a plan based on the Triad approach.

The objective for the BTSC was to work with EPA Region 1 and M&E to develop a revised work plan and approach for the Cos Cob site that incorporated elements of the Triad approach. The Triad approach, a framework for efficiently managing decision uncertainty, can be applied to reach project objectives faster and in as few mobilizations as possible. The Triad approach is well suited to Brownfields projects such as Cos Cob where budget and schedule are crucial to successful project completion. Further information about the Triad approach is available on line at the Triad Resource Center website at <http://www.triadcentral.org>, and in “*Using the Triad Approach to Streamline Brownfields Site Investigation and Cleanup*” (EPA 542-B-03-002; June 2003).

INITIAL WORK PLAN

This section describes the activities originally identified under the TBA using a traditional phased approach and fixed laboratory analyses. The original technical approach for this site was based on EPA’s statement of work, and clarifications and modifications to the scope were discussed at two scoping meetings held between EPA and M&E (November 9, 1998, and March 26, 1999).

Site-Specific Objectives for Initial Work Plan

The original objective for this site was to conduct a site investigation to assess the nature and extent of soil contamination, sufficient to allow development of a conceptual remedial plan and planning-level cost

estimate for site remediation, consistent with the town's plans for site reuse as a recreational area. In general, the original proposed site investigation would have focused on known or suspected areas where contaminants of concern were anticipated to have been released. Field observations and analytical data were to be collected to provide information on surface and subsurface conditions and to support development of further assessment procedures and potential cleanup alternatives, if necessary. The goal was to identify the presence or absence of potential hot spots; delineation was to be left to later phases of the project.

Development of the Original Sampling Approach

The original sampling plan called for collection of authoritative, judgmental samples to confirm the presence or absence of contamination at locations where previous reports had implied potential source areas. Contamination was primarily suspected to be related to two primary source types: (1) surface spills of petroleum and PCBs that were expected to decrease with depth and, (2) coal fly ash containing low levels of metals and spent petroleum hydrocarbons to a depth of nearly 30 feet bgs on some portions of the site. The primary objectives of the original TBA for the former Cos Cob Power Plant property were:

- Visually observe surface and subsurface soil conditions (particularly noting the presence of ash).
- Use “field-based” methods (headspace and x-ray fluorescence [XRF]) to help identify possible “hot spots” of petroleum or heavy metals contamination, and to select samples for laboratory analyses.
- Characterize site surface soil via off-site laboratory analyses for the identified COPCs.
- Compare analytical results for soil with DEC in a screening-level risk assessment.
- Develop additional assessment procedures and potential cleanup options, if warranted.

Original Sampling Rationale

The original sampling rationale called for collection of authoritative, judgmental soil samples at 20 locations (Figure 3). The rationale for each sample location and the off-site laboratory analytical suite proposed for each location are presented in Table 3. The original sampling rationale was based on off-site laboratory analysis only.

SYSTEMATIC PLANNING

Comprehensive, up-front planning is essential to effectively complete any environmental project. Proper planning will promote collection of data that will lead to defensible decisions. The residential DEC's were used as the cleanup goals and in selection of the appropriate analytical methods. By understanding the questions that need to be answered project managers and team personnel can use systematic planning as a tool to develop a roadmap to success.

In order to streamline the site characterization activities, project goals were examined and potential design modifications identified before entering the field. Project objectives identified by the core technical team for the site are provided in the box below.

Overall Project Objectives

- 1) Estimate the nature and extent of contaminants of potential concern (COPCs) at the site above the state of Connecticut residential direct exposure criterion (Table 2).
- 2) Accomplish the above mentioned objective in a single mobilization to facilitate reuse planning activities, while staying within budgetary constraints.

After a review of the project objectives, the project team provided input on potential design modifications to the originally proposed work plan regarding the following site activities:

- Redesign of the sampling and analysis program to increase the sampling coverage and incorporate the use of appropriate field-based analytical technologies.
- Design and implementation of a “demonstration of methods applicability” study to optimize method performance and develop preliminary field-based decision criteria.
- Focus the collection of QC samples where results would yield the highest value relative to limiting decision errors.
- Implementation of the field program.
- Data processing and refinement of decision criterion.

The BTSC project team participated during the project startup to assure integration of activities elemental to the Triad approach. Activities discussed included evaluation of field method performance and completeness of documentation. The BTSC team suggested that audits of mobile and fixed-labs during startup be conducted by an outside party not directly responsible for data collection. A third party review such as that conducted by the BTSC for this project was found to be helpful. Alternatively, for other projects, it would be helpful to have a project chemist on site during startup/implementation.

Detailed decision rules and focused quality control requirements were developed in cooperation with the BTSC during the systematic planning process. The core technical team worked in conjunction with the vendors of field-based analytical tools and other stakeholders to develop the final approach used at the site. The following sections describe the results of the core technical team's efforts to revise the proposed sampling and analysis approach for the site.

The New Sampling Approach

A random or non-nodal systematic grid-sampling program was developed to replace the original authoritative sampling plan. Some aspects of the original plan were preserved such as sampling locations selected based on historical information. Preserving aspects of the original sampling program and increasing data density across the site using a random systematic grid, provided a larger number of samples improving site coverage. Field-based sampling technologies were proposed to allow for this increased sample density at no additional cost. By using field-based methods, a larger number of samples could be collected and analyzed in a single mobilization.

The grid sampling approach used was developed based on an exposure area of 5,000 square feet. In the project teams opinion this size was thought to be consistent with the typical size of an average residential lot. Based on the size of the exposure area (5,000 square feet) and available project resources, a total of 72 grids were sampled during the project. The plan called for further delineation where PCB contamination was found within any one of the grid sectors. At these grids, a "step out" sampling approach was planned where the original location would be surrounded by 4 additional direct push sampling locations 10 feet to the north, south, east, and west. Initial sampling points within each grid were identified using a random sample locator program. Non-nodal grid sampling schemes, also known as random systematic sampling, combines the benefits of both random (a sampling scheme best employed when historical knowledge of contaminant distribution is limited) and systematic (a sampling scheme used to locate and delineate "hot spots") sampling methods.

A track-mounted Geoprobe was proposed as the sampling platform to drive sample cores from 0 to 4 feet bgs at each sampling location, and field analytical options were evaluated by BTSC staff and EPA Region 1 Mobile Laboratory personnel. The State of Connecticut considers the upper 4 feet of soil to be surficial and where DEC action levels are applicable to the site.

Analytical Options

The Triad approach encourages project teams to make maximum use of real-time measurements to support decision-making on site. The use of field-based analytical technologies allows for the investigation to focus on areas of elevated contamination detected in real time and helps to direct additional field analyses and fixed lab comparison analyses in a single mobilization.

Connecticut DEC's shown in Table 2 were used when selecting suitable field-based analytical methods for the project. For example, the low DEC for arsenic of 10 milligrams per kilogram (mg/kg) was considered when the project team decided that field-based XRF methods might not be sufficiently sensitive.

Typically XRF detection limits range from 10 to 100 mg/kg for most metals. It is generally considered acceptable when reporting limits or practical quantitation limits for analytical methods are at least 2 to 3 times lower than potentially applicable regulatory threshold limit values. This assures the utility of results for decision-making purposes. Arsenic is known to be present in the fly ash, at relatively low concentrations near the regulatory threshold of 10 mg/kg making it a potential risk driver. As a result, the team agreed that off-site analysis for arsenic would be the preferred option using an ICAP atomic emission spectroscopy method that has reporting limit of 1 mg/kg or less. The EPA Region 1 Mobile Laboratory planned to take a portable XRF unit into the field to confirm the assumption that arsenic was the primary metal of potential concern at the site and to rule out the presence of other metals that have regulatory threshold limit values well within the working range of sensitivity for field portable XRF.

In addition to XRF for metals, options for analyzing TPH and PAHs in the field included various immunoassay kits, ultraviolet fluorescence (UVF), gravimetric, and turbidometric methods. A single-column gas chromatograph equipped with an electron capture detector (GC/ECD) was identified for use by the EPA Region 1 Mobile Laboratory to evaluate the presence of PCBs. The EPA Region 1 Laboratory later identified the siteLAB[®] test kits, a UVF system, as the preferred method for TPH and PAH analyses based on costs, ease of application, and successes at other sites with petroleum product contamination.

The project team concluded that a demonstration of methods applicability (DMA) was needed for the UVF method to assure the reliability of the method for application at the site. The DMA would also be used to establish preliminary field-based action levels. The results of the DMA study are further discussed in the Section titled Demonstration of Methods Applicability. A detailed description of the methods as they were applied for the investigation is presented in the Section titled Sample Analysis.

Developing Decision Logic

When decision logic is developed for sites where actions will be based primarily on the use of field-based measurement technologies, it is often necessary to consider many factors, such as:

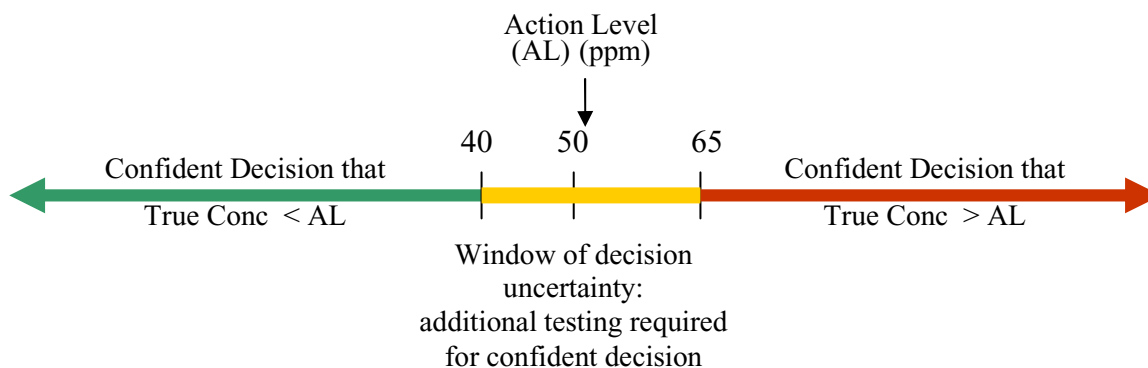
- Field observations or other data may suggest that there is the potential for similar, yet different, analytes to yield similar responses when a test kit or other screening analytical method is used. This issue can be identified and sometimes resolved through application of the DMA.
- If a significant bias is expected in the field analytical results, one strategy is to collect sufficient comparison data (for example, splitting well-homogenized samples for analysis by both the field and traditional methods) during a DMA, in early sampling events, or both. If a predictive relationship can be identified between the field measurements on an analyte-specific basis, this relationship can be used to guide decision making using the field based methods.

When data distribution characteristics are normal or lognormal, a predictive relationship can be established and field-based action levels developed (Enclosure 2). Statistical plots like those provided in Enclosure 2 should be used initially to establish that the use of a particular field-based technology is viable. The reliability of the preliminary field-based action levels developed during a DMA need to be refined as more data is collected. Field-based action levels are initially selected based on a comparison between more selective fixed lab results and those generated using a selective field-based method. Safety factors are usually applied to assure the reliability of site decisions.

As work progresses, a sufficiently large comparison data set usually becomes available allowing action levels to be revised and improved.

Depending on the nature of project decisions, two or three decision intervals or safety factors are commonly identified based on the results of the DMA. The most common breakdown is into three intervals, as shown in the diagram on the following page: (1) an interval where it is judged that the field data can be trusted to confidently declare areas “clean” (where no further action is needed), shown on left side of the line; (2) an interval where field results can be trusted to confidently declare an area “dirty” (where remedial action is needed), shown on the right side of the line); and (3) an interval where the field results are considered ambiguous, and a confident decision of “clean” or “dirty” would require more data to manage the decision uncertainty, shown in yellow in the central area of the line. Reasons for this uncertainty may stem from sampling variability or from analytical uncertainty (imprecision or bias in the field method), or both. When only two intervals are desired or, a single limit is proposed: data values less than this value allow the area to be declared “clean,” and data values greater than the limit are accepted as indicating that the area is “dirty”. In this case, a safety factor is applied. For example, in the

figure below, the field-based action level with a safety factor built in might be set at 40 ppm when deciding that the site is clean. Below this level sample results would be considered clean while results above this level would be considered dirty.



Setting these limits is a judgment call that must balance several considerations: (1) the “quality” of the predictive relationship (that is, how many comparison points are available to build confidence that decisions can be made correctly, and how much scatter is present around the predictive line); (2) how well the range of variables that affect the performance of the two analytical systems (for example, potential analytical interferences, different matrix characteristics, and low versus high levels of contaminants) was captured in the comparison data set; and (3) the cost or consequences of making a decision error (that is, declaring an area “clean” when it actually is not, or declaring an area “dirty” when it actually is not) versus the costs or consequences of collecting the additional data needed to address excessive decision error, as discussed below.

Weighing sampling costs versus potential decision errors further involves the following considerations:

- Estimating the cost of collecting additional data should consider not only the expense of collecting and analyzing additional samples, but the repercussions of any delays to the project schedule that may be incurred as well. (If the project work plan is based on a dynamic approach, the cost to budget and schedule may be minimal.)
- Estimating the cost of a “false action” decision error (that is, incorrectly declaring an area “dirty” so that follow-up action is required) requires considering whether the cost of the false action would be minor or major. The cost may be minor if it is known that a soil treatment system or institutional control will be built anyway, or if the ramification of this false action decision will add only an incremental amount of soil to the volume already slated for treatment; for example, to add additional fencing to isolate 11 acres instead of 10 acres. On the other hand, a false action decision could be costly if the entire decision on whether a treatment system or institutional control is needed hinges on a faulty conclusion. The costs of false action decision errors also should factor in any social, redevelopment, or community ramifications from declaring an area “dirty.”

- Estimating the cost of a “false inaction” decision error (that is, incorrectly declaring an area “clean” so that no further action is needed) must consider the ramifications to human and ecological health of potential exposure to excessive contamination, as well as the social and political costs that will be incurred when the error is discovered or suspected. It is often more important to protect public and environmental health from potentially harmful health effects and to error on the side of caution. On the other hand, this approach can be costly. Nonetheless, since it can be prohibitively expensive in some scenarios to gather all the information needed to ensure that decisions are entirely correct, it is possible to structure the decision-making process so that substantial costs can be saved by judiciously deciding when relatively small errors on the side of caution can be accommodated. These decisions can be thought of as a kind of “safety factor” that supports using field measurements and other types of nontraditional tools to achieve significant cost savings while decisions remain protective of human health and the environment.

Managing decision uncertainty that stems from sampling variability can require collection of grab or composite samples to obtain a more confident estimate of the mean concentration for the decision unit or a more confident estimate of the boundaries of contamination. Managing decision uncertainty that stems from analytical uncertainty requires first that sampling variability has been managed (so the representativeness of samples is known). Then, samples that represent critical decision points are selected for processing by more rigorous analytical methods to produce analyte-specific data, or data free of excessive analytical bias or imprecision.

Usually, a DMA study as defined by EPA’s Office of Solid Waste Methods Team, which manages the SW-846 methods manual (see Enclosure 1) is designed and implemented initially to begin the process of evaluating potential sampling and analytical method issues, as well as the comparability of the various sampling and analytical methods under consideration. The results of the study are used to compute appropriate safety factors and preliminary uncertainty limits for decision-making that should be applied at a site. Differing safety factors may need to be developed for a specific monitoring and measurement technology and type of decision. Uncertainty limits to support decision-making are used to establish concentrations where stakeholders feel comfortable that a correct decision is being made.

A DMA is usually designed to evaluate the ability of a method to meet project-specific data needs (that is, the specific contaminants and media of concern at a given site). The study considers the precision, sensitivity, and bias of the field-based instrument technology so that an adequate safety factor can be built into the overall decision uncertainty limits. Internal method quality control results, along with investigative, replicate, and spiked samples analyzed in the field as well as off-site methods, are generally used collaboratively to estimate the total uncertainty associated with a measurement such that realistic safety factors can be developed. Uncertainty management measures or focused QC to support refinement of decision criteria at the Cos Cob site included the following:

- Focusing collection of comparative analyses on a concentration range where fixed lab results would be of the greatest benefit for managing decision uncertainty (i.e., in and around the field-based action levels)

- Comparative analysis for PAHs using off-site GC/mass spectrometry (MS) and selective-ion monitoring (SIM)
- Comparative analysis for PCBs using off-site dual-column GC/ECD whenever positive field screening results indicated the potential presence of PCBs

The number of data points is typically limited when a DMA is performed, making rigorous statistical analysis less powerful. Judgment is therefore used to evaluate the comparison data used to construct preliminary safety factors so that intolerable decision errors are avoided. As more is learned about a site and the contaminant distributions more clearly defined, the preliminary safety factors can usually be reduced as the standard deviation for results becomes smaller.

DEMONSTRATION OF METHODS APPLICABILITY

The project team and the BTSC discussed potential options for implementing the field program for the Cos Cob site and developing decision criteria for field-based analytical methods. Decision logic diagrams were developed for arsenic (Figure 6) as well as for TPH, PAH, and PCBs (Figure 7) and circulated to the team for further refinement. A conservative initial action level of 100 ppm for TPH was identified based on a comparison between field test kit and fixed laboratory results concerning when TPH concentrations might exceed the DEC of 500 ppm. Another field-based action level of 50 ppm was established for PAHs using the test kit-based on the professional judgment of the project chemist, given that the test kits report total PAH and the lowest DEC for an individual cPAH compound is 1 ppm. Test kit concentrations of TPH between 100 and 500 ppm, and of PAHs between 50 ppm and 500 ppm, were identified as regions of analytical uncertainty had the highest potential for impacting decision-making. In these concentration ranges, the project team decided to collect additional samples for off-site comparative analyses to refine the decision criteria. Samples with concentrations below or above these ranges were considered “clean” or “dirty”, respectively, and only limited comparative analyses were deemed necessary.

EPA Region 1 Mobile Laboratory personnel indicated that the laboratory had the capacity to analyze all samples in the 0- to 1- and the 1- to 2-foot intervals for PCBs. Consequently, the EPA Region 1 Mobile Laboratory analyzed all grid samples for PCBs and sent samples for comparative analyses to an off-site laboratory when results indicated the presence of PCBs. This approach alleviated the need for field-based decision criteria or a DMA for PCBs.

As noted previously, off-site analysis of arsenic samples was selected to provide the best reporting limits and data most appropriate for making project decisions. Therefore, no field-based decision criteria were established for metals, and a DMA was not required. The off-site analyses were conducted following

EPA SW-846 Methods 3050B/6010B. Nonetheless, the EPA Region 1 Mobile Laboratory still used XRF to screen soil samples and evaluate the potential for metals other than arsenic to be present at concentrations that might exceed the potentially applicable DEC's. It was thought that the additional data provided by the on-site XRF would be useful in evaluating other metals and identifying sample locations with higher arsenic values. The XRF results were also used to identify samples for a full suite of analyses for metals to confirm the assumption that arsenic was the primary inorganic constituent of potential concern.

With PCBs and metals excluded, the DMA study was designed to assess the applicability of the siteLAB[®] UVF test kits and to refine the TPH and PAH decision criteria for use during the field investigation. M&E developed a technical memorandum that summarized the proposed approach detailing sampling locations and procedures to support the study (M&E 2003b). The field-based analytical technology vendor (siteLAB[®]) participated in a day of analytical training for the samples collected during the study. Samples used to conduct the DMA were collected in a single day from areas where contamination was suspected to be present. The objective of the training session was not only to train the project team in the use of the kit, but also to analyze the samples collected from the site and submit them for analysis at the off-site laboratory to establish a correlation between the field-based and fixed laboratory methods.

Initial Field Sampling Event Conducted in Support of the Demonstration of Methods Applicability Study

Soil borings were advanced using a Geoprobe 5410 drilling rig on December 9, 2002. Soil samples were collected continuously at each location using direct-push techniques. The soil borings were logged and described, including any evidence of impact by oil and hazardous materials. Soil boring locations are shown on Figure 5.

Seventeen soil borings (T-1 through T-17) were completed from 0 to 4 feet bgs. Borings T-1 through T-11 were advanced in the fly ash area located in the southern portion of the site (Figure 5), where samples (A-1 and A-2) collected by Marin in 1998 indicated elevated TPH contamination. Borings T-12 through T-17 were advanced in the slag ash area located in the northeastern portion of the site (Figure 5), where a sample (D-3) collected by Marin in 1998 indicated high TPH contamination. All samples except T-17 were divided into a 0- to 2-feet bgs interval and a 2- to 4-feet bgs interval. Each sample interval was homogenized and placed into a sealed labeled Ziploc bag.

While advancing boring T-17, M&E personnel observed a distinct layer of ash at the 2- to 3-foot bgs interval. Sampling personnel homogenized the 2 to 3 feet bgs interval as one sample and the 0 to 2 feet

bgs and 3 to 4 feet bgs intervals as the second sample. Samples for analysis by the siteLAB[®] test kits were selected based on the presence of visible staining. Coal and ash was present in the majority of samples. Field personnel attempted to select samples that covered a range of contamination in the coal and ash. Selecting samples across a range in concentration can provide a more robust data set for supporting preliminary correlations. The 2 to 3 feet bgs sample from boring T-17 was also selected since it was composed primarily of ash. In addition, two samples that did not contain any coal or ash were selected. A total of eight samples were selected for analysis by the siteLAB[®] test kits.

Test Kit Training Session and Sample Analysis

On December 12, 2002, a half-day training session was held at EPA's Office of Environmental Measurement and Evaluation (OEME) laboratory in Chelmsford, Massachusetts. In attendance were the EPA project manager, the M&E project manager, two M&E staff members scheduled to participate in the main February field event to be conducted at the Cos Cob site, the OEME quality assurance chemist, the OEME mobile laboratory chemist, and several others interested in learning about the kits. The training was conducted by Mr. Stephen Greason, technical support manager, siteLAB[®] Corporation. Mr. Greason provided an overview of the siteLAB[®] UVF methods, how they work, and hands-on instruction to the M&E representatives. After the training, the eight samples brought back from the site were analyzed using the UVF test kit. Mr. Greason summarized the results and transmitted them via e-mail to session participants.

Laboratory Results

The eight samples selected for test kit analysis were also submitted to fixed laboratories for extractable total petroleum hydrocarbons (ETPH) analysis using the CTDEP approved version of SW-846 method 8015, and for semi-volatile organic compounds (SVOC) analysis using the EPA Contract Laboratory Program – Routine Analytical Services (CLP-RAS). Woods Hole Group conducted the ETPH analyses and Ceimic conducted the CLP-RAS analyses. The results for ETPH and the target analyte PAHs are presented in Table 4, along with the test kit results.

CLP-RAS Results. For the eight samples submitted, the laboratory diluted the extracts prior to analysis based on sample pre-screening that indicated high concentrations of hydrocarbons that exceeded the CLP-RAS method calibration range. For a number of the samples (T-1 0-2', T-3 0-2', T-4 0-2', and T-5 0-2'), no PAHs were reported as detected, but reporting limits exceeded the DEC regulatory threshold limit values because of over dilutions of the samples by the fixed laboratory. The detection limits were lower

for the remaining samples (T-5 2-4', T-13 0-2', T-13 2-4', and T-17 2-3'), but they still exceeded the DEC's. After discussion among project team members, samples T-1 0-2', T-3 0-2', T-4 0-2', and T-5 0-2' were reanalyzed using EPA SW-846 method 8270C operated in the selected ion monitoring (SIM) mode to obtain lower reporting limits. The Connecticut residential DEC's were not exceeded in the reanalyzed samples where PAH concentrations were reported.

Results of the methods applicability study indicated at least two differing PAH data populations. Field-based results for PAHs in one population, represented by samples T-1 and T-3, were between 700 and 850 ppm (Table 4). Individual PAH concentrations in these samples were at the DEC's for benzo(b)fluoranthene and benzo(a)pyrene (1.0 ppm), according to the EPA Region 1 laboratory analysis. Field-based results for the second distinct population were near 50 ppm with some PAH concentrations near the DEC in samples T-13 and T-17, according to the EPA Region 1 laboratory results. The benzo(b)fluoranthene concentrations from the laboratory analyses in these samples ranged as high as 0.5 ppm. Results for the two samples at T-13 and the sample at T-17 were consistent with each other (55 ppm, 53 ppm, and 52 ppm). Taken as a whole, the results indicated that, for test kit total PAH concentrations less than or equal to 50 ppm, it was unlikely that any individual PAH compound would exceed its DEC. Therefore the preliminary decision criteria seemed to hold up under the initial empirical test.

ETPH Results. For the eight samples analyzed, the test kit results were equivalent to or higher than the ETPH results from the fixed laboratory, except for sample T-5 (0- to 2-foot depth). As observed for the PAHs, two distinctly different sample types were identified. The correlation between the results for the test kits and the laboratory were close for the five samples where the laboratory identified the petroleum as "similar to fuel oil #6; absence of straight chain aliphatics indicated the product present was weathered" (Table 4). Examples of chromatograms from these samples (T-4 0-2', T-13 0-2', and T-17 2-3') are presented in Enclosure 3. It is considered probable that, for these samples, ETPH is dominated by PAHs, and the PAHs are likely from coal and coal ash.

For three other samples (T-1, T-3, T-5 areas), the laboratory identified the petroleum product evidenced in the sample chromatograms as "similar to high molecular weight components in the lube-oil range." The chromatograms from these samples are presented in Enclosure 3. The test kits exhibited a high bias for two of these samples (T-1 and T-3), reporting field-based concentrations of 3,300 to 4,000 ppm versus laboratory results of 1,500 and 1,400 ppm. The reported laboratory concentration for Sample T-5, taken from 0 to 2 feet bgs, was 760 ppm TPH, while the field-based method result was only 138 ppm (Table 4). These three samples were located in an area of the site where previous investigations had reported

elevated TPH concentrations. It is considered possible that this area of the site may be contaminated by multiple petroleum releases as well as by coal ash suggesting to the project technical team that correlation of cPAHs to the total PAH results of the test kits could be problematic. When numerous sources of petroleum products are present various ratios and relative concentrations for cPAH should be anticipated.

Refining the Preliminary Decision Criteria

The DMA confirmed that samples with a total PAH concentration less than 50 ppm as reported from the siteLAB® test kits would not be likely to exceed the individual DEC's for any cPAH compounds. Based on the trial results, samples with test kit total PAH concentrations on the order of 800 ppm began to have individual cPAHs that exceeded DEC's (Table 4). However, in light of the complexity of the PAH data observed during the DMA, the project team incorporated a safety factor where additional confirmation data would be collected in an attempt to continue to refine decision criteria while the major field effort was under way. The safety factor effectively increased the upper limit of the uncertainty range to 500 ppm, so that the range of between 50 ppm to 500 ppm total PAH was identified as being of greatest interest for submission of comparative fixed laboratory analysis during the main field investigation at the site. Although the majority of comparative samples would be collected in this range of concentration, several samples would also be collected for concentrations greater than 500 ppm and less than 50 ppm for completeness.

For TPH, where the field test kit and fixed laboratory results had better correlations, the anticipated decision criterion of 500 ppm was confirmed; it appeared that test kit values greater than 500 ppm TPH would begin to exceed the DEC. Additionally, the DMA results indicated that, for test kit results between 100 and 500 ppm, comparative analyses should be performed during the investigation to refine the correlation between field-based and fixed laboratory results. Although the test kit result was close to or higher than the laboratory result for all but one sample (T-5, 0-2 feet bgs), this result seemed to suggest that a false decision could be made based on test kit results below 500 ppm, (A subsequent data review after the investigation suggested that the result for sample T-5, 0-2 from the fixed laboratory could have been biased high by contaminant carryover from a previously run sample).

To summarize, the DMA study helped the project team define a window of decision uncertainty between 50 to 500 ppm for PAH and 100 to 500 ppm for TPH for the siteLAB® test kits. Comparative analyses would therefore be submitted at greater frequencies in these concentration ranges during the main field investigation. The study also found that there were two separate populations of results for both PAH and TPH, indicating two basic different types of contaminated soil media at the site. The sample population

containing the highest total PAH concentrations (more than 700 ppm) also contained the higher TPH concentrations that were classified in the “lube oil” range (sample locations T-1 and T-3). The other population contained total PAH concentrations near 50 ppm and TPH concentrations less than 500 ppm that were classified as hydrocarbons in the weathered “fuel oil #6” range.

Reporting limit study documentation provided by siteLAB[®], and the successful analysis of samples within the kit’s default calibration range (0.05 to 1.5 ppm for PAH, 0.1 to 5 ppm for TPH) in the DMA, indicated that the reporting limits provided by the field test kits were easily sufficient to meet project decision objectives.

FIELD INVESTIGATION

The main field sampling program of the TBA, which included on-site analysis using test kits and a mobile laboratory, as well as collection of samples for off-site laboratory analysis, was conducted from February 3, 2003, through February 7, 2003. Personnel from M&E, the EPA Region 1 Mobile Laboratory, and the BTSC were on site to conduct or observe field activities and to provide input into decisions about when to send samples for off-site comparative testing.

Several of the field activities included a dynamic component that allowed data to be analyzed and interpreted in the field to guide the investigation in real time. These types of field activities are an integral part of the Triad approach. Before the team mobilized for site activities, a grid spacing network was developed that would allow for a reasonably dense sampling design over the site given logistical considerations such as layout and area. The result was an overlay that segregated the site into 72 grids that were approximately 70 feet by 70 feet. A random location generator was then used to select sampling locations within each grid (Figure 5) except where historical data and or visual observations suggested an alternative location might be more representative of the presence of contamination.

SAMPLE COLLECTION

Samples collected during the field activities were obtained using a small track-mounted Geoprobe to drive sample cores from 0 to 4 feet bgs. The Geoprobe was moved to the appropriate grid and the approximate sampling location was identified by the location generator as necessary. Some sampling locations were adjusted to account for steep slopes, debris, vegetation, or soil piles within each grid. Within some grids, soil piles of clean soil prevented the collection of a representative sample. Sampling locations were marked using stakes and were mapped on the last day of the field effort using global positioning system (GPS) equipment.

When samples were collected, the cores were visually inspected, logged, and segregated into 1-foot homogenized sample aliquots. Samples were then analyzed for TPH and PAHs using field test kits. The on-site laboratory also conducted field analyses for PCBs and screened samples for metals using XRF. Various PCB “hot spots” were delineated horizontally as they were identified by surrounding the point location with four “step out” samples at a distance of 10 feet. Particular attention was paid to locations where PCBs or high concentrations of PAHs were detected, and these “hot spots” were delineated as time and resources allowed.

Some sample locations were also sampled for ACM, but those results are not further discussed in this case study.

SAMPLE ANALYSIS

With the exception of arsenic analyses which were analyzed at the off-site laboratory by EPA SW-846 method 3050B/6010B, the soil samples were analyzed in real time (that is, as the samples were collected) in the field and samples were sent off site for fixed laboratory comparative analysis in accordance with the focused quality control plan developed during the DMA. The use of field analyses allowed the project team to collect more data points within the time and budget allotted under the TBA. Additional sample collection in areas where PCB “hot spots” were found could also be delineated. Field analytical techniques for the UVF test kits (TPH and PAH), GC/ECD (PCBs), and XRF (metals) are discussed in the following sections.

siteLAB® UVF Test Kits

The siteLAB® test kits used a simple extraction technique where 5 grams of the homogenized sample were placed into a small extraction jars and 10 milliliters (mL) of methanol added. The cap of the extraction jar was tightened firmly and the samples were vigorously shaken for 2 minutes and allowed to settle for an additional 2 minutes. The extract was forced through a 0.45-micron filter to remove solids and a small portion (100 microliters [μL]) of the extract was diluted with methanol to 100X. The 100 times dilution factor is recommended by the manufacturer to avoid saturating the UVF detector, an effect known as “quenching.”

After the sample was prepared, the diluted extract was placed in a cuvette and analyzed using the UVF-3100 analyzer. The UVF-3100 uses a powerful lamp from which light is passed through an excitation filter, producing specific wavelengths that are absorbed by aromatic hydrocarbons such as the PAHs present in fuels and other petroleum mixtures. The wavelengths pass through the cuvette that contains the sample and excite the PAH molecules, producing fluorescence in the sample. The resulting fluorescence wavelengths are passed through an emission filter specific to PAHs, allowing only those PAH-specific wavelengths to pass through to the photomultiplier/detector.

Concentrations of total PAHs were recorded on the UVF-3100, and the results were transferred to a laptop spreadsheet. Using the raw fluorescence emitted from the sample, the UVF-3100 software also

generated a value for extended diesel-range organics (EDRO) for transfer to the spreadsheet. The values were corrected for dilution factors and reported in ppm.

A PAH-specific calibration solution was used to create five standards used during the calibration process to analyze samples for total PAHs using the UVF-3100. The five standards used during the calibration process contained concentrations of total PAHs at 0.05, 0.1, 0.5, 1.0, and 1.5 ppm. The resulting fluorescence from each standard was recorded against the standard concentration to develop a 5-point calibration curve. Samples analyzed that exhibited concentrations outside of the calibration curve were diluted until the results were within the range of concentration covered by the calibration standards (0.05 to 1.5 ppm). The corresponding result was then multiplied by the dilution factor to calculate the concentration in ppm. Field results for total PAH and TPH were reported on a wet-weight basis.

EPA Region 1 Mobile Laboratory Polychlorinated Biphenyl Analyses

Historical results for the Cos Cob site include a number of detections for PCBs. Twenty-seven sampling locations were identified for PCB analysis based on historical data. The EPA Region 1 Mobile Laboratory analyzed all samples collected from the 0- to 1- and 1- to 2-foot intervals for PCBs as samples were collected. If any PCBs were detected, then subsequent deeper intervals at the location were sampled up to a total depth of 4 feet bgs. Additional samples were also analyzed as time permitted and at the discretion of the M&E field team leader.

Soil was analyzed for PCBs in the field using the EPA Region 1 standard operating procedures (SOP) for field analysis of soil and sediment samples (EIA-FLDPCB2.SOP). Approximately 1 gram of soil was weighed and placed in a 4 mL vial for micro-extraction. Next, 200 μ L of reagent-grade water, 800 μ L of methanol, and 1,000 μ L of hexane were added to the vial. The sample was then held on a vortex to vigorously shake the sample and reagents for 1 minute as part of the sample extraction step, and the vial was then placed in a centrifuge to separate the liquid extract from any residual solids. A portion of the extract was removed from the centrifuged sample and injected directly into a Shimadzu GC-14A gas chromatograph equipped with an electron capture detector (GC/ECD). The Shimadzu GC-14A uses a steel silica coated column (Restek MXT-5) with a 30-meter length and 0.53 millimeter diameter.

Before samples were analyzed each day, a number of Aroclor standards were run, including Aroclor 1242, Aroclor 1248, Aroclor 1254, and Aroclor 1260. The resulting chromatograms were then used as external standards for comparison to chromatograms from soil samples collected during the Cos Cob investigation. Based on the comparison of the external standards to actual sample chromatograms, PCBs

in soil samples were tentatively identified. When the field GC/ECD indicated the presence of any PCB congeners, the samples were sent for off-site comparative analysis by the EPA Region 1 laboratory using the internal SOP (PESTSOIL2.SOP). The method used is based on EPA Method 8082 and employed a high-resolution Hewlett Packard 5890 GC equipped with a dual-column ECD.

Reporting limits using the Shimadzu GC-14A in the field and following EPA Region 1 SOP were adequate to support project decision-making. The residential DEC for total PCBs (1.0 ppm) compared well with GC-14A reporting limits for Aroclors 1260 and 1254 of 0.5 ppm each, while the reporting limit for Aroclors 1242 and 1248 were 1.0 ppm. Therefore, the single column GC/ECD used in the field could identify the presence or absence of any PCB congener of potential interest to levels at or below the DEC. Based on historical site use information, samples from the southern most portion of the site were not analyzed for the presence of PCBs because no record of transformer storage was evidenced. Field results for PCBs were reported on a wet-weight basis. Drying of the samples was not deemed necessary, because correction would have simply resulted in an increase in the apparent concentration. Since all positive results were to be sent for comparative off-site analyses sample drying was not preformed, saving time and money in performing the field analyses for the PCBs.

EPA Region 1 Mobile Laboratory XRF

In addition to sending samples from the 0- to 1-foot and 1- to 2-foot intervals to an off-site laboratory for analysis of arsenic by EPA SW-846 Method 3050B/6010B, the EPA Region 1 Mobile Laboratory also analyzed samples for metals using XRF technology. Results were reported on a wet-weight basis for lead, arsenic, zinc, copper, and nickel.

Soil samples from the 0- to 1-foot interval were analyzed using a Niton 732 XRF instrument, equipped with a cadmium-109 radioactive source and a silicon pin detector. Samples were collected in 1-gallon Ziploc bags and thoroughly homogenized by manual kneading. Additional sample preparation steps such as drying or sieving were not employed. After homogenization, a portion of the sample was placed in an XRF cup and pressed firmly against the Mylar film placed over the sample cup. Accurate XRF results are best achieved when the sample cup is filled and the sample is in good contact with the film that covers the cup. The XRF probe window then can be placed in direct contact with the sample cup for the most accurate readings.

The XRF reporting limit for arsenic (60 mg/kg) exceeded the DEC of 10 mg/kg, and reporting limits for the other metals were relatively elevated. A reporting limit of 40 mg/kg was used for lead, 70 mg/kg for

zinc, 150 mg/kg for copper, and 200 mg/kg for nickel. Results were based on wet weight and provided good screening information to help identify arsenic hot spots and indicate whether additional metals were present at levels near the residential DEC. Select samples were sent for off-site analysis for a full suite of metals. Because XRF reporting limits for several metals exceeded the DEC, the instrument was not used to make any decisions in the field.

ARSENIC RESULTS

Arsenic is believed to be the metal that presents the greatest potential risk to human health and the environment at the Cos Cob site based on past site use and disposal practices. A total of 112 samples (excluding duplicates) were collected for arsenic analysis during the field effort in February 2003. Fifty-six of the 72 grids were sampled successfully, and samples analyzed for the presence of arsenic for the 0- to 1-foot and 1- to 2-foot intervals at each location. Laboratory analytical results for arsenic are provided on a dry-weight basis in Figure 8. Individual sampling grids are color coded to display areas where: (1) samples could not be collected, (2) the maximum arsenic result in samples collected from the top 2 feet was reported as less than the DEC, (3) the maximum arsenic result in samples collected from the top 2 feet exceeds the residential DEC, and (4) the maximum arsenic result in samples collected from the top 2 feet exceeds two times the DEC. Regardless of the calculated 95 percent upper confidence limit (95UCL) for a specific analyte in a sample data set, CTDEP requires that any area with a sample result greater than two times the DEC be remediated to limit exposure.

Elevated levels of arsenic were found commonly at two times the DEC in the top 2 feet of soil across the site, with higher concentrations generally reported from the southern “fly ash” area. Further review of the data also reveals that 55 of the 112 total results (49 percent) for arsenic exceeded the DEC of 10 mg/kg. In addition, concentrations from 32 of the 112 results (29 percent) were greater than two times the DEC.

Summary statistics and statistical plots for arsenic are included in Enclosure 2. The summary statistics include the detection frequency, mean, median, geometric mean, minimum detected result, maximum detected result, standard deviation, variance, and the 95UCL. Probability plots, histograms, and box-and-whisker-plots for both the untransformed and log-transformed data are also provided in Enclosure 2. Review of the probability plots indicates that the arsenic results visually approximate a single lognormal distribution.

The 95UCL for arsenic is approximately 30 ppm across the site. This concentration for arsenic is relatively low considering the planned reuse for the property (recreational), but greater than residential

risk-based criteria. This type of contamination is likely present to a depth of almost 30 feet bgs at the site based on the CSM (the known distribution of coal and or fly ash at the site).

PAH RESULTS

Samples from the 0- to 1-foot bgs interval at each sample location were analyzed for PAH and TPH using siteLAB[®] Test Kits. Based on the test kit results, a subpopulation of these samples was submitted for off-site analysis for PAHs using a GC/MS method operated in the SIM mode. Samples from deeper intervals were collected from (1 to 2 foot, 2 to 3 foot, and 3 to 4 foot intervals) at locations where total PAH concentrations were found to be elevated. Analysis of the samples from the deeper intervals was completed as time allowed and at the discretion of the M&E field team leader.

Given the limited resources for comparison analyses, off-site analysis of samples with total PAH results less than 50 ppm or greater than 500 ppm was limited to two samples below and two samples above these levels of concentration. Results found between 50 ppm and 500 ppm were considered to be in the range of concentration where it was most important to continue to refine the relationship between results from the field test kit and the off-site laboratory. Fifteen samples with total PAH results in this range were sent for off-site analysis. Therefore, a total of 19 comparison sample pairs were collected and sent for off-site analysis during the February 2003 sampling event. Comparison samples were chosen to represent a range of values within the 50 ppm to 500 ppm window and from across the site to improve the spatial representativeness of the comparison data set.

Summary statistics and statistical plots for the PAH results are provided in Enclosure 2. Usable data points from the methods applicability study conducted in December 2002 have been included in the data sets for PAHs. Specifically, PAH results for samples T-1 0-2', T-3 0-2', T-4 0-2', and T-5 0-2' from December 2002 were included in the PAH data set.

Statistics and plots for PAHs were divided into two different categories: a summary of the results from the siteLAB[®] field test kit for total PAHs, and a summary of the results for total cPAHs from the off-site comparison analysis by EPA Method 8270C operated in the SIM mode. The summary statistics for both PAH categories include the detection frequency, mean, median, geometric mean, minimum detected result, maximum detected result, standard deviation, variance, and the 95UCL. Probability plots, histograms, and box-and-whisker plots for both the untransformed and log-transformed data are provided in Enclosure 2.

Correlating Field PAH Results with the Connecticut Residential Direct Exposure Criterion

Field results did not appear to have a simple relationship to the DEC for cPAHs. This finding is not surprising or unusual, considering the complexity of the hydrocarbon chemistry present at the site as evidenced by the distinctly differing TPH patterns observed across the site. To better understand the relationship between results from the test kit and laboratory, results for cPAHs from the fixed laboratory were plotted in two-dimensional scatter plots for comparison with field-based results (Figure 9). Total cPAH values were calculated by adding the sum of the five carcinogenic PAH compounds (benz[a]anthracene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene) for results reported from the fixed laboratory analyses.

Results for the 19 comparison samples collected in February 2003 and the four reanalyzed sample results from the DMA study were combined to create a 23-data-point comparison (Figure 9). Results for total PAHs from the siteLAB[®] field test kits were plotted on the y-axis, and results for cPAHs were plotted on the x-axis. Correlations were poor for several samples (J-9 2-3', T-1 0-2', T-3 0-2', F-8 0-1', and A-3 0-1'), but review of the sample chromatograms indicated some potential explanations for the observed discrepancies. These issues are discussed in more detail later in this case study.

After the analytical results for cPAHs had been reviewed, it was determined that the lowest total cPAH result where an individual cPAH compound exceeded the DEC was found in sample F-8 3-4'. The total cPAH result for this sample was 4.03 ppm, while individual cPAH results for benz(a)anthracene (1.3 ppm) and benzo(a)pyrene (1.1 ppm) exceeded the DEC of 1.0 ppm. On this basis, a slightly more conservative value of 4.25 ppm was then plotted on a best-fit regression line where the total PAH result from the siteLAB[®] test kits was the dependent variable and the total cPAH result from the fixed laboratory was the independent variable (Figure 9A). According to the best-fit line, a value of 4.25 ppm for total cPAH corresponded to a siteLAB[®] field test kit value of 510 ppm. An additional 20-percent safety factor was built into the kit value, and 400 ppm was estimated as the kit value where corresponding cPAH compounds may begin to exceed the DEC of 1.0 ppm.

Field-based decision criteria for data from the siteLAB[®] field test kits was then applied to the results of the February 2003 sampling event and used to prepare a map that displays locations of soil samples where concentrations were expected to exceed the DEC. Figure 10 provides an overview of the site sampling grids and indicates locations where total PAH values from the siteLAB[®] field test kits exceeded 400 ppm. Elevated levels of total PAHs are indicated in the top several feet of soil across the site, with higher concentrations found in the southern “fly ash” area. Further review of the data also reveals that of the 93

total PAH results from the siteLAB[®] field test kits, 14 (15 percent) exceeded the DEC of 400 ppm, and two of the 93 results (2 percent) exceeded two-times the decision criteria. In addition, of the 23 comparison samples, seven results from the siteLAB[®] test kit exceeded 400 ppm, while individual cPAH values in nine samples exceeded the DEC of 1.0 ppm.

Understanding Field-based Results for PAHs by Reviewing Sample Chromatograms

A review of Figure 9 indicates a reasonable degree of correlation between the field and laboratory PAH results for most of the samples, particularly those samples where the chromatograms indicate the presence of weathered lubricating oil range hydrocarbons. There are, however, several exceptions to the good correlation between field-based and laboratory results. In the case of sample J-9 2-3', for example, the siteLAB[®] test kit indicated an elevated total PAH value, while the laboratory results indicated relatively lower values for cPAHs. For samples F-8 0-1' and A-3 0-1', the siteLAB[®] field test kit indicated low total PAH values and laboratory results indicated relatively higher values for cPAHs. In these cases, a review of the sample chromatograms from the fixed laboratory GC analysis indicates a diversity of lighter fuel-range hydrocarbons with varying concentrations of PAHs (see Enclosure 3). When the lighter fuel-range hydrocarbons are present, the response of the field test kit for total PAHs appears less reliable (given the kit calibration scheme used).

Summary of Findings for Field-generated PAH Data

Overall, the PAH data generated in the field using the siteLAB[®] test kit appear adequate for the decision making purposes of this project, despite the difficult matrix. The reliability of any correlation between field and laboratory results is complicated by the variety of hydrocarbon sources present at the site and the complexity of hydrocarbon chemistry in general concerning cPAHs and their related action levels. Although the highest concentrations of PAHs may be associated with releases of fuels and other petroleum products (as opposed to the fly ash), the wide distribution of relatively low levels of cPAHs across the southern portion of the property suggests that contamination levels that exceed the DEC for cPAHs could persist well below ground surface in the southern portion of the site. As with arsenic, this suggests that removal of soil to meet residential standards may not be feasible at the site and perhaps alternative standards or modifying reuse alternatives should be considered.

TPH RESULTS

TPH analyses were conducted along with the PAH analyses for the 0 to 1-foot interval for each sampling location using a siteLAB[®] test kit. Based on the test kit results, a subpopulation of these samples was submitted for off-site analysis of TPH using a gas chromatograph/flame ionization detector (GC/FID) method (EPA Method 8015). Samples from deeper intervals (1 to 2 feet, 2 to 3 feet, and 3 to 4 feet) were analyzed at locations where total TPH concentrations were found to be elevated. Analysis of the samples from deeper depth intervals using siteLAB[®] instrumentation was completed as time allowed and at the discretion of the M&E field team leader.

Given the limited resources for comparison testing, off-site analysis of samples for TPH field results less than 100 ppm or greater than 500 ppm (the two decision criteria) were limited with two samples below and two samples above these levels. Results found between 100 ppm and 500 ppm were considered to be in the range of concentration where it was most important to continue to refine the relationship between the results from the field test kit and the fixed laboratory. Five samples with total TPH results in this range were sent for off-site analysis. Therefore, a total of nine comparison sample pairs were collected and sent for off-site analysis during the February 2003 sampling event. Comparison samples were chosen to represent a range of values within the 100 ppm to 500 ppm window and from across the site to improve the spatial representativeness of the collaborative data set.

Summary statistics and statistical plots for the TPH results are provided in Enclosure 2. Usable data points from the methods applicability study conducted in December 2002 have been included in the data sets for TPH. Specifically, results for samples T-1 0-2', T-3 0-2', T-4 0-2', T-5 0-2', T-5 2-4', T-13 0-2', T-13 2-4', and T-17 2-3' from December 2002 were included in the TPH data set. TPH statistics and plots were divided into two categories: a summary of the results from the siteLAB[®] field test kit for TPH, and a summary of the TPH results from the off-site analyses by EPA Method 8015. In general, direct statistical comparisons are only valid if identical methods for quantification are used.

The summary statistics for the two TPH categories include the detection frequency, mean, median, geometric mean, minimum detected result, maximum detected result, standard deviation, variance, and the 95UCL. Probability plots, histograms, and box-and-whisker plots for both the untransformed and log-transformed data are provided in Enclosure 2.

Correlating Field-based Results for TPH with the Residential Connecticut Direct Exposure Criterion

In addition to the standard summary statistics and statistical plots, TPH results from the siteLAB[®] field test kit and from the fixed laboratory were plotted in two-dimensional scatterplots for comparison. Results for eight of the comparison sample pairs collected in February 2003 (no field analysis was completed for sample KK-2 0-1') and the eight sample pairs from the methods applicability study conducted in December 2002 were combined to create a 16-data-point comparison (Figure 11). TPH results from the siteLAB[®] field test kits were plotted on the y-axis, while results for TPH from the fixed laboratory analyses were plotted on the x-axis. Correlations for several samples were poor, with some kit values over-predicting the laboratory result (T-1 0-2', T-3 0-2'), while others tended to underestimate the result from the fixed laboratory (T-5 0-2', and G-9 0-1'). Review of the sample chromatograms indicates the reason for the discrepancies. Sample chromatograms are discussed in more detail later in this case study.

After the analytical results for TPH had been reviewed, it was determined that the lowest field result for total TPH where the corresponding fixed laboratory result exceeded the CTDEP residential DEC of 500 mg/kg was found in sample T-5 0-2'. Problems were found both for this sample and sample G-9 0-1' associated with quantitation of the TPH results from the fixed laboratory. Problems associated with quantitation of samples T-5 0-2' and G-9 0-1' are discussed below. Issues associated with the quantitation of the results for these samples were, however, considered to be inconsequential relative to constructing a best fit line and field-based action level. The DEC (500 ppm) was plotted as the fixed laboratory value on the linear regression curve (Figure 11A) and a corresponding field TPH value computed. The best-fit line indicated that the corresponding value from the siteLAB[®] field test kit for TPH was 668 ppm. Given the good correlation ($R = 0.77$) between the fixed and field results for the majority of the samples, an additional 10 percent safety factor was built into the kit value, and a value of 600 mg/kg was estimated as the field test kit value where the corresponding result for TPH from the fixed laboratory may begin to exceed the DEC of 500 mg/kg.

Based on the field data collected using the siteLAB[®] field test kits, a map was prepared showing the estimated distribution of TPH results that exceeded the DEC (Figure 12). Figure 12 provides an overview of the site sampling grids and indicates locations where TPH values from the siteLAB[®] field test kits exceed the field action level of 600 mg/kg. Elevated levels of TPH are distributed across the site, with higher concentrations found in the southern "fly ash" area. Further review of the data also reveals that, of the 93 total TPH results from the siteLAB[®] field test kits, 32 (34 percent) exceeded the field-based decision criterion of 600 mg/kg, and 21 of the 93 results (23 percent) exceeded two-times the field

decision criteria. In addition, of the 16 comparison sample pairs, results for four from the siteLAB[®] test kit exceeded 600 mg/kg, while fixed laboratory values for six samples exceeded the DEC of 500 mg/kg.

Understanding Field-based Results for TPH by Reviewing Sample Chromatograms

A review of Figure 11 indicates a good correlation among the majority of the samples. Chromatograms for these samples generally indicated the presence of weathered lubricating oil-range hydrocarbons. There are, however, a few exceptions to the good correlation, including samples T-1 0-2', T-3 0-2', T-5 0-2' and G-9 0-1'. These outliers were also classified as lubricating oil-range hydrocarbons by the laboratory (see Enclosure 3). These outliers likely reflect random variation in hydrocarbon composition at the site, as well as uncertainties in analyte identification and quantitation by the field and fixed laboratory methods. The difference in results could also be a function of high sub-sample heterogeneity commonly referred to as the nugget effect. While this is a common occurrence at hazardous waste sites and must be addressed where the decisions being made in the field may be in support of an excavation or other treatment activity, at the Cos Cob site this was not the case. These excursions from the norm were noted, but no action was deemed necessary because sufficient data that fit the linear regression were available such that a general decision concerning nature and extent of TPH contamination could be made. Under different circumstances such as those mentioned above corrective action might have been needed to be considered. There are several ways to limit the impact of contaminant heterogeneity commonly associated with the nugget effect on sample results. Project teams may need to consider increasing sample volumes, conducting sample processing/homogenization, collecting composite samples, and other sampling alternatives when the nugget effect is pronounced and site decisions require a higher degree of certainty.

Summary of Findings for TPH

Results for TPH are similar to those reported for PAHs, as might be anticipated, although contamination levels that exceed the residential DEC appear to be even more wide spread (Figure 12). TPH concentrations suggest that removal of soil to meet residential standards across the site would be cost prohibitive and that other alternative reuse plans or cleanup options should be considered.

PCB RESULTS

Samples were collected for analysis of PCBs in 32 grids that were also sampled for the other target parameters. Additional "step-out" samples were collected where PCBs were tentatively identified by the

mobile laboratory, as possible, to further assess the lateral and vertical extent of PCB contamination within the schedule and budget constraints of the field program. Sample locations, depths, and results are displayed in Figures 13 and 14.

Samples from 21 grids where aliquots were analyzed for arsenic, PAHs, and TPH were not subsequently analyzed for PCBs. Samples were not analyzed for PCBs from grids: K3, K5, J3, J4, and J5, located at the site entrance, nor in grids D6, D7, C2, C3, C4, C5, C6, C7, B2, B3 B5, B6, A2, A3, A4, and A5, in the southern portion of the site. Samples for analysis of PCBs were not collected in these grids because no evidence of transformer storage in these areas was indicated based on historical use records. In some areas, PCB contamination could not be adequately delineated due to budget and time limitations. Those areas where data gaps remain include (grids F8, F9, and G11) shown on Figure 14. Additional sampling will likely be required in these areas should PCB contamination require remediation at the site.

The majority of PCB detections were tentatively identified as Aroclor 1260 by the mobile laboratory, however, results for comparative fixed laboratory analyses, indicated the presence of Aroclor 1242, Aroclor 1262, and Aroclor 1268 as well. Detections of Aroclor 1260 in samples from three locations (sample G-11 1-2' and step-out samples F9N 0-1' and F9NW 1-2') analyzed in the field were significant (10 ppm or greater). At sampling grids F8, F9, and G11 where PCBs were detected at greater than 5 ppm in the 0- to 1-foot or 1- to 2-foot intervals, the hot spots were further delineated vertically by sampling subsequent deeper 1-foot intervals until results were non-detected or the 3 to 4 feet interval was reached. The contamination was partially delineated horizontally by surrounding the location with an additional four boreholes approximately 10 feet from the original borehole. If the 10-foot step-out (horizontal) samples were analyzed and PCBs were detected, then the 10-foot step out location with the highest concentration was surrounded with 5-foot step-out samples to further delineate the contamination. This logic continued at the discretion of the M&E field team leader as time and budget permitted in an attempt to delineate the approximate size of the identified PCB "hot spots."

Fourteen samples were sent for off-site comparative analysis for PCBs. At locations D2 0-1', D5 0-1', and J12 0-1', samples analyzed in the field indicated the presence of PCBs. Subsequent comparative analyses did not, however, detect PCBs in samples from these locations suggesting the presence of some type of matrix interference. At locations F8 0-1', F9 0-1', G9 0-1', G10 0-1', and G11 0-1, G13 0-1' and H9 0-1' and step-out samples F9N 0-1', F9NN 0-1', and F9NW 0-1', off-site analysis confirmed the results from the field laboratory for both non-detected values (submitted at a frequency of 10 percent of all samples collected for PCB analysis) and reported positive results.

LESSONS LEARNED

Using the Triad approach successfully improved site coverage and the certainty with which the town can now move forward with a reuse plan for the site within a single TBA funding cycle. The original judgmental sampling plan was revised through the cooperative development of a systematic plan, which called for the use of a dynamic work strategy and the use of field-based analytical measurements. The planning process identified key ranges of concentrations and safety factors to guide data interpretation and decision-making. Increased data density as a result of using field-based methods, enabled the project team to more aggressively manage decision uncertainties.

In general, TPH values from the field test kits had greater reliability than those obtained for PAH values primarily because of the diversity of hydrocarbon signatures found at the site. TPH results correlated very well with fixed laboratory results and could be used to make subsequent decisions for the site. Results from the field test kit for TPH provide a more powerful tool for making site decisions. Lighter fuel-range hydrocarbons proved particularly troublesome when developing a predictive relationship between the total PAH results from the siteLAB[®] field test kits and the results from the fixed laboratory for total cPAHs. Analysis of the data indicated that developing a strong linear predictive relationship for decisions based on total PAHs would be even more difficult. However, using safety factors and decision confidence intervals (as described on page 20) allowed data for both PAH and TPH to provide sufficient maturation of the CSM in relation to the potential issues related to site redevelopment.

Analytical results for arsenic in samples from the 0- to 1-foot and 1- to 2-foot intervals indicated that arsenic values consistently exceeded the DEC of 10 mg/kg. Additional sampling at greater depths is expected to provide similar results based on the uniformity of fly and slag ash fill in the southern and northern portions of the site.

Because the schedule of the field team was not sufficiently flexible to remain at the site until PCB contamination could be completely delineated, several issues with PCBs at the site may remain. Schedule and budget constraints did not allow for the mobile laboratory or the subcontract driller to remain on-site as was necessary to complete the PCB delineation. Additionally, weather conditions at the site deteriorated over the course of the investigation and a snowstorm in conjunction with schedule and budget issues converged to make it necessary to demobilize prior to completion of the PCB delineation phase.

Some additional step-out sampling may be required to more adequately define the extent of PCB contamination within grids F8, F9, and G11 (Figure 14). Future sampling strategies should employ a focused effort within these grids, where the 70- by 70-foot grids are further divided into 10-foot grid sections and additional samples collected. Using this approach, sample locations where PCBs were detected could be delineated with a higher degree of certainty, possibly using a field test kit, which might improve sample throughput. This approach may also provide the additional data necessary to support a case-by-case removal of PCB hot spots, should this approach be deemed prudent at the site. The remaining data gaps for PCBs are minor, however, and can be easily addressed at the beginning of site redevelopment rather than in a second field investigation.

Overall, the project successfully expanded the data available to the town to support decision making in a single 1-week mobilization. Sites with multiple sources of differing forms of hydrocarbons can be challenging when attempting to apply both laboratory and field-based methods for decision-making. Laboratory methods and field-based methods must be well constrained and both types of data reviewed carefully before predictive relationships are deemed adequate or sufficiently representative for making site decisions. Based on the CSM developed for the site, it is clear that removal of soil necessary to meet residential standards for arsenic, PAHs, and TPH could be cost prohibitive. PCB hot spots exceeding residential standards could be further delineated, excavated and disposed of appropriately at relatively low cost. Direct exposure to the remaining arsenic, PAH, and TPH contamination can be limited by placing a clean soil cap over portions of the site and placing deed restrictions on the property to prevent digging into the contaminated materials. Alternative reuse plans and the development of more realistic risk-based action levels should also be considered, in the BTSC's opinion, before site redevelopment proceeds.

COST COMPARISON

The TBA characterization at the Cos Cob site that was based on the Triad approach produced considerable savings when compared with more traditional characterization approaches. Table 5 provides a summary of the estimated cost of using a traditional phased approach versus the cost of the actual Triad project. Using systematic planning, dynamic work strategies, and field-based measurement technologies with limited off-site comparative analyses allowed for cost-effective site characterization with savings of approximately 35 percent over a traditional plan. Cost savings could potentially range between 20 and 40 percent depending on actual findings and the number of necessary mobilizations that would be required to sufficiently characterize the site using a traditional approach. Following the principles of the Triad approach, the site was characterized to project decision confidence using a single mobilization by providing greater data densities where needed to satisfy project goals. It is always difficult to estimate what project costs would have been if a different plan had been followed. In this case, the original work plan was abandoned in favor of a more dynamic, field-based strategy before cost scenarios for the original plan had been fully calculated. Where available, existing and estimated costs developed to support the original approach have been incorporated into this cost comparison.

This cost comparison assumed that a traditional approach would have required two mobilizations to evaluate the nature and extent of contamination at the property. The costs associated with two mobilizations would have also been accompanied by costs for developing two different work plans and two sets of analytical suites. In comparison, Table 5 shows that while planning and field preparation costs (including the DMA) under the Triad approach were higher for the first mobilization, the completeness of the resulting data set eliminated the need for a second mobilization for site characterization. A dynamic approach provided total site coverage using a fairly dense spatial grid, while allowing the field team to react to areas with samples containing elevated levels of contaminants. Under the original plan, the lower proposed sampling density may have missed areas of contamination. Any that were encountered would likely not have been identified for further delineation until after demobilization when all the analytical data had been received back from the laboratory and compiled into a report to project decision makers. Delineation efforts would then have to be deferred to a subsequent mobilization.

A dynamic work plan, field kits for TPH and PAHs, and a mobile laboratory for PCBs analysis supported rapid identification of contaminated areas for evaluating the nature and extent of the contamination, while providing analytical cost savings. Field kits also provided the data necessary to choose comparison samples that provided the best coverage of spatial variability and ranges of concentration. Resource constraints limited the number of comparison sample pairs for TPH, PAH, and PCBs, so it was important

to choose samples that would contribute most to developing correlations between field analytical and fixed laboratory analytical techniques.

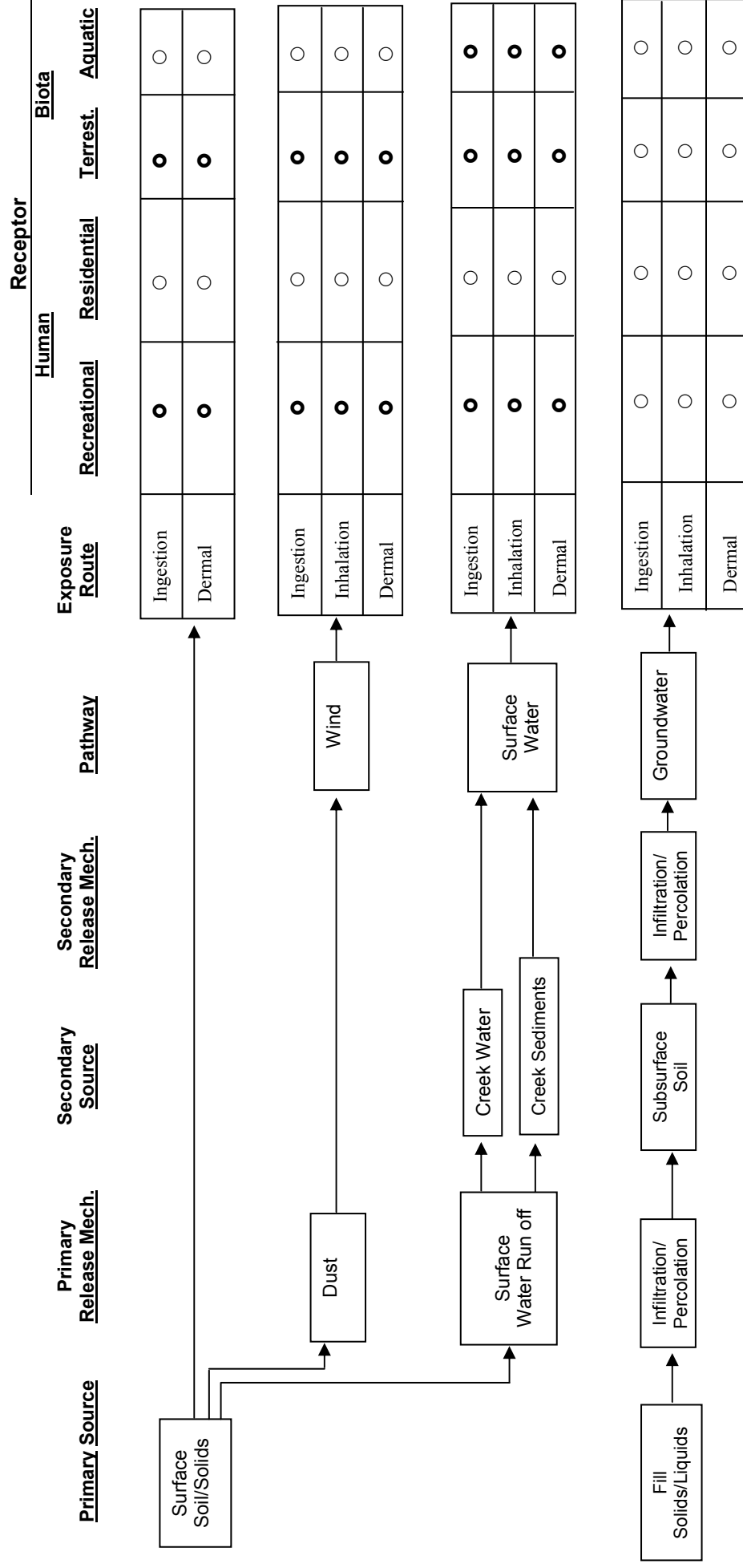
The 35 percent cost savings were realized despite the initial unfamiliarity of the project team with the Triad. Because of this lack of familiarity with Triad concepts, the project required additional meetings, consultations, and planning activities between the BTSC and the project team as the Triad approach was adopted. Table 5 shows that the hours devoted to planning activities increased from 200 hours (estimated for the planning for the original approach) to 345 actual hours. Additional consultations and reviews concerning the Triad approach, which are included as a separate line item at the end of Table 5, are estimated to have added \$18,150 in labor and other direct costs to the Cos Cob project budget. This level of planning and consultation would not be needed as project staff develop familiarity with the Triad approach, which would further increase the cost savings for future Triad projects.

BIBLIOGRAPHY

- EPA. 2000. SW-846 Test Methods For Evaluating Solid Waste, Physical/Chemical Methods. Draft Update IVB, November 2000.
- EPA. 2002. Guidance On choosing A Sampling Design For Environmental Data Collection For Use In Developing A Quality Assurance Project Plan. EPA QA/G-5S.
- EPA. 2003. "Using the Triad Approach to Streamline Brownfields Site Assessment and Cleanup." Brownfields Technology Primer Series. Technology Innovation Office, Brownfields Technology Support Center. EPA 542-B-03-002. June.
- Marin Environmental, Inc. (Marin). 1997. "Transformer/Breaker – PCB Investigation, Cos Cob Power Plant, Sound Shore Road, Greenwich, Connecticut." May.
- Marin Environmental, Inc. (Marin). 1998a. "Limited Soils Investigation, Cos Cob Power Plant, Greenwich, Connecticut." March.
- Marin Environmental, Inc. (Marin). 1998b. Letter Regarding Contaminated Soil Removal and Disposal, Cos Cob Power Plant, Greenwich, Connecticut. From Gerald M. Clark, Regional Manager, Marin. To Lori Saliby, Pesticide, PCB, UST and Marine Management Division, Connecticut Department of Environmental Protection. July 6.
- Metcalf & Eddy (M&E). 2003a. "Draft Field Task Work Plan, Former Cos Cob Power Plant, Greenwich, Connecticut. January."
- Metcalf & Eddy (M&E). 2003b. "Draft Technical Memorandum, Former Cos Cob Power Plant, Greenwich, Connecticut, Targeted Brownfields Assessment. Test Kit Trials-Investigation Summary and Suggested Approach for Use of Test Kits." January 15.
- Metcalf & Eddy (M&E). 2003c. "Targeted Brownfields Assessment, Draft Report, Former Cos Cob Power Plant, Greenwich, Connecticut." June.
- Osprey Environmental Engineering. 1998. Letter Regarding Transformer Oil Characterization-Cos Cob Power Plant, Greenwich, Connecticut. From Timothy O. Myjak, Environmental Scientist, Osprey. To Alan Monelli, Superintendent of Building Construction and Maintenance Division, Greenwich Town Hall. November 2.
- TRC Environmental Consultants (TRC). 1988. "Environmental Site Assessment Report, Cos Cob Power Plant, Greenwich, Connecticut." April 28.
- U.S. Environmental Protection Agency. 1998. "Statement of Work for the Targeted Brownfields Assessment at the Cos Cob Site."

TABLES

Table 1
Pathway Receptor Diagram
Cos Cob Power Plant, Greenwich, Connecticut



● Completed pathway
 ○ Possible complete pathway (data required)
 ○ Incomplete pathway

Table 2
List of Contaminants of Potential Concern at the Cos Cob Power Plant Site,
Greenwich, Connecticut¹

Substance	Residential Criteria in ppm
Metals	
Arsenic	10
Polynuclear Aromatic Hydrocarbons	
Acenaphthene	1000
Acenaphthylene	1000
Anthracene	1000
Benz(a)anthracene ³	1
Benzo(b)fluorathene ³	1
Benzo(k)fluoranthene	8.4
Benzo(g,h,i)perylene	1000
Benzo(a)pyrene ³	1
Chrysene	84
Dibenz(a,h)anthracene ³	1 ²
Fluoranthene	1000
Fluorene	1000
Indeno(1,2,3-cd)pyrene ³	1 ²
Naphthalene	1000
Phenanthrene	1000
Pyrene	1000
Polychlorinated Biphenyls (PCBs)	
Total PCBs	1
Total Petroleum Hydrocarbons (TPH)	
TPH	500

Notes:

ppm parts per million or milligrams per kilogram

¹ Regulatory threshold limit values were obtained from the State of Connecticut Regulation of Department of Environmental Protection. On-line Address:
<http://dep.state.ct.us/wtr/regs/remediation/rsr.pdf> Threshold limit values for residential/recreational reuse are those listed in this table.

² Criteria are based on the estimated reporting limit.

³ Carcinogenic polynuclear aromatic hydrocarbons used during the demonstration of methods applicability study to constrain test kit method performance.

Table 3: Summary of Originally¹ Proposed Samples

Location	Rationale	Analyses
1	Near former transformer and TRC sample location SS-3, where PAHs were detected in soils. Advance soil boring to 16 feet below ground. Collect samples from 0 to 4 feet (surface soil) and at water table (if encountered), or as selected based on “field screening” (<i>sic</i>) and observations, for a total of two samples for laboratory analysis. Screen each 4-foot interval using portable XRF unit (arsenic, lead) and photoionization detector (PID) headspace (petroleum). Install well only if free product (oil) contamination is observed.	PCBs, extractable TPH (ETPH), ACM (direct subcontract labs) Semi-volatile organic compounds (SVOC), metals (Contract Laboratory Program-Routine Analytical Services Labs [CLP-RAS])
2, 3, 4, 5, 6	Near Marin B and D series borings, where PAHs and/or TPH were detected in soils in excess of CTRSR soil standards. Depth and sampling protocol same as for Boring 1. Total number of samples for laboratory analysis = 10.	PCBs, ETPH, ACM (direct subcontract labs) SVOCs, metals (CLP-RAS)
7, 8	In former transformer/breaker area, where PCB-containing equipment is likely to have been located. Depth and sampling protocol same as for Boring 1. Total number of samples for laboratory analysis = 4.	PCBs, ETPH, ACM (direct subcontract labs) SVOCs, metals (CLP-RAS)
9, 10, 11	Near Marin A series borings, where TPH was detected in soils in excess of CTRSR soil standards. Depth and sampling protocol same as for Boring 1. Total number of samples for laboratory analysis = 6.	PCBs, ETPH, ACM (direct subcontract labs) SVOCs, metals (CLP-RAS)
12 through 20	Distributed evenly throughout property, making sure to include areas previously identified as containing ash. Analyze for ACM and ash-related contaminants (SVOCs, metals) only. Consider ETPH or PCBs only if oily contamination is observed during field screening. Total number of samples = 18.	ACM (direct subcontract lab) SVOCs, metals (CLP-RAS)

Notes:

¹ Prepared using information provided in the Draft Field Task Work Plan For the Former Cos Cob Power Plant, Greenwich, Connecticut (M&E 2003a) and following discussions with the M&E project manager.

Table 4

**Summary of Analytical Data From the Demonstration of Methods Applicability Study
TBA Investigation – Former Cos Cob Power Plant Property – December 2002**

LOCATION NAME SAMPLE DEPTH (ft bgs) DATE SAMPLED LUTION FACTOR FOR SVOCs COMMENTS	T-1 0 – 2 12/9/2002		T-3 0 – 2 12/9/2002		T-4 0 – 2 12/9/2002		T-5 0 – 2 12/9/2002	
	30 RAS lab	5 OEME	30 RAS lab	5 OEME	30 RAS lab	2 OEME	30 RAS lab	2 OEME
<u>PARAMETER/ANALYTE</u>								
EXTRACTABLE TOTAL PETROLEUM HYDROCARBONS – CTDEP Method (mg/kg)								
Total Petroleum Hydrocarbons	1,500	NA	1,400	NA	450	NA	760	NA
Lab's qualitative identification results (summarized from lab Form 1s):	Similar to high MW components in lube oil range		Similar to high MW components in lube oil range		Similar to fuel oil #6; absence of straight chain aliphatics indicates sample is weathered		Similar to high MW components in lube oil range	
SITELAB TPH/EDRO TEST KIT CONCENTRATION (ppm wet weight)								
TPH/EDRO	3,294		4,001		409		138	
Percent Difference, CTDEP vs. SITELAB methods for TPH								
	75		96		10		139	
SEMIVOLATILE ORGANIC COMPOUNDS (only PAH results presented below) (mg/kg)								
Naphthalene	10 U	0.043 U	10 U	0.074	12 U	0.14	12 U	0.044
2-Methylnaphthalene	10 U	NA	10 U	NA	12 U	NA	12 U	NA
Acenaphthylene	10 U	0.047	10 U	0.083	12 U	0.030	12 U	0.013 U
Acenaphthene	10 U	0.047	10 U	0.043 U	12 U	0.020 U	12 U	0.013 U
Fluorene	10 U	0.043 U	10 U	0.043 U	12 U	0.020 U	12 U	0.013 U
Phenanthrene	10 U	0.25	10 U	0.48	12 U	0.39	12 U	0.073
Anthracene	10 U	0.065	10 U	0.12	12 U	0.046	12 U	0.013 U
Fluoranthene	10 U	0.54	10 U	1.0	12 U	0.40	12 U	0.088
Pyrene	10 U	0.85	10 U	1.5	12 U	0.44	12 U	0.14
Benzo(a)anthracene	10 U	0.42	10 U	0.64	12 U	0.24	12 U	0.060
Chrysene	10 U	0.50	10 U	0.68	12 U	0.37	12 U	0.082
Benzo(b)fluoranthene	10 U	0.76	10 U	1.0	12 U	0.36	12 U	0.098
Benzo(k)fluoranthene	10 U	0.22	10 U	0.31	12 U	0.13	12 U	0.026
Benzo(a)pyrene	10 U	0.59	10 U	0.77	12 U	0.22	12 U	0.063
Indeno(1,2,3-cd)pyrene	10 U	0.42	10 U	0.50	12 U	0.18	12 U	0.048
Dibenz(a,h)anthracene	10 U	0.16	10 U	0.17	12 U	0.062	12 U	0.016
Benzo(g,h,i)perylene	10 U	0.45	10 U	0.52	12 U	0.19	12 U	0.058
Total PAHs (mg/kg)**	85	5	85	8	102	3	102	1

Table 4

**Summary of Analytical Data From the Demonstration of Methods Applicability Study
TBA Investigation – Former Cos Cob Power Plant Property – December 2002
(continued)**

LOCATION NAME SAMPLE DEPTH (ft bgs) DATE SAMPLED LUTION FACTOR FOR SVOCs COMMENTS	T-1 0 – 2 12/9/2002		T-3 0 – 2 12/9/2002		T-4 0 – 2 12/9/2002		T-5 0 – 2 12/9/2002	
	30 RAS lab	5 OEME	30 RAS lab	5 OEME	30 RAS lab	2 OEME	30 RAS lab	2 OEME
SITELAB Total PAHs TEST KIT CONCENTRATION (ppm wet weight)								
Total PAHs	700		851		83		28.7	
LAB SAMPLE ID								
ETPH-CTDEP method	0212046-01		0212046-02		0212046-03		0212046-04	
SVOCs-RAS and/or OEME	AOZ98	AA27888	AOZ99	AA27889	AOZA0	AA27890	AOZA1	AA27891
NOTES: * - RAS laboratory data have not undergone data validation. ** - Total PAHs calculated by using 1/2 the detection limit for non-detects, and adding that value to any reported values. U - analyte not detected at the listed concentration. J - analyte was detected at a concentration below the reporting limit.								

Table 4

**Summary of Analytical Data From the Demonstration of Methods Applicability Study
TBA Investigation – Former Cos Cob Power Plant Property – December 2002
(continued)**

LOCATION NAME SAMPLE DEPTH (ft bgs) DATE SAMPLED LUTION FACTOR FOR SVOCs COMMENTS	T-5 field duplicate 0 – 2 12/9/2002		T-5 2 – 4 12/9/2002 5	T-13 0 – 2 12/9/2002 10	T-13 2 – 4 12/9/2002 5	T-13 2 – 4 12/9/2002 Not submitted field duplicate	T-17 2 – 3 12/9/2002 2 Mostly fly ash	CT Residential DEC
	10 RAS lab	2 OEME						
PARAMETER/ANALYTE								
EXTRACTABLE TOTAL PETROLEUM HYDROCARBONS – CTDEP Method (mg/kg)								
Total Petroleum Hydrocarbons	Not submitted		19	300	220	350	250	500
Lab's qualitative identification results (summarized from lab Form 1s):			Not enough material for qualitative identification	Similar to fuel oil #6; absence of straight chain aliphatics indicates sample is weathered	Similar to fuel oil #6; absence of straight chain aliphatics indicates sample is weathered	Similar to fuel oil #6; absence of straight chain aliphatics indicates sample is weathered	Similar to fuel oil #6; absence of straight chain aliphatics indicates sample is weathered	
SITELAB TPH/EDRO TEST KIT CONCENTRATION (ppm wet weight)								
TPH/EDRO	Not submitted		0.4 U	271	273	Not submitted	237	
Percent Difference, CTDEP vs. SITELAB methods for TPH								
	--		192	10	22	--	5	
SEMIVOLATILE ORGANIC COMPOUNDS (only PAH results presented below) (mg/kg)								
Naphthalene	4.3U	0.042	1.8 U	0.82 J	0.30 J		0.28 J	1,000
2-Methylnaphthalene	4.3U	NA	0.86 J	2.2 J	1.3 J		0.87 J	474
Acenaphthylene	4.3U	0.015	1.8 U	3.8 U	1.8 U		0.73 U	1,000
Acenaphthene	4.3U	0.013 U	1.8 U	3.8 U	1.8 U		0.73 U	1,000
Fluorene	4.3U	0.013 U	1.8 U	3.8 U	1.8 U		0.10 J	1,000
Phenanthrene	4.3U	0.13	0.36 J	2.1 J	0.80 J		0.77	1,000
Anthracene	4.3U	0.024	1.8 U	3.8 U	1.8 U		0.73 U	1,000
Fluoranthene	4.3U	0.18	1.8 U	0.74 J	0.36 J		0.26 J	1,000
Pyrene	4.3U	0.21	1.8 U	0.62 J	0.27 J		0.25 J	1,000
Benzo(a)anthracene	4.3U	0.11	0.27 J	0.40 J	1.8 U		0.10 J	1
Chrysene	4.3U	0.10	1.8 U	1.0 J	0.79 J		0.42 J	84
Benzo(b)fluoranthene	4.3U	0.13	1.8 U	0.50 J	0.22 J		0.23 J	1
Benzo(k)fluoranthene	4.3U	0.052	1.8 U	3.8 U	1.8 U		0.73 U	8.4
Benzo(a)pyrene	4.3U	0.093	1.8 U	3.8 U	1.8 U		0.094 J	1
Indeno(1,2,3-cd)pyrene	4.3U	0.066	1.8 U	3.8 U	1.8 U		0.73 U	1
Dibenz(a,h)anthracene	4.3U	0.020	1.8 U	3.8 U	1.8 U		0.73 U	1
Benzo(g,h,i)perylene	4.3U	0.073	1.8 U	3.8 U	1.8 U		0.099 J	1,000
Total PAHs (mg/kg)**	37	1	14	25	13		5.7	

Table 4

**Summary of Analytical Data From the Demonstration of Methods Applicability Study
TBA Investigation – Former Cos Cob Power Plant Property – December 2002
(continued)**

LOCATION NAME SAMPLE DEPTH (ft bgs) DATE SAMPLED LUTION FACTOR FOR SVOCs COMMENTS	T-5 field duplicate 0 – 2 12/9/2002		T-5 2 – 4 12/9/2002 5	T-13 0 – 2 12/9/2002 10	T-13 2 – 4 12/9/2002 5	T-13 2 – 4 12/9/2002 Not submitted field duplicate	T-17 2 – 3 12/9/2002 2 Mostly fly ash	CT Residential DEC
	10 RAS lab	2 OEME						
SITELAB Total PAHs TEST KIT CONCENTRATION (ppm wet weight)								
Total PAHs	Not submitted		0.2 U	55	53	Not submitted	52	
LAB SAMPLE ID								
ETPH-CTDEP method	Not submitted		0212046-05	0212046-06	0212046-07	0212046-09	0212046-08	
SVOCs-RAS and/or OEME	AOZA6	AA27896	AOZA2	AOZA3	AOZA4	Not submitted	AOZA5	
NOTES: * - RAS laboratory data have not undergone data validation. ** - Total PAHs calculated by using 1/2 the detection limit for non-detects, and adding that value to any reported values. U - analyte not detected at the listed concentration. J - analyte was detected at a concentration below the reporting limit.								

Table 5
Cost Comparison Between a Traditional Approach
and the Triad Approach
at the Cos Cob Power Plant

Task Description	Labor Hours	Labor Costs at \$75/Hour	Subcontractor Costs	ODCs ^c	Estimated Fee Reserve at 10%	Actual Cost Using the Triad vs.
						Estimated Traditional Costs
Background review, project planning, preparation of workplan, site visit, and discussions with town officials	345	\$25,875	\$1,500	\$700	\$2,607	\$28,682
	200	\$15,000	N/A	\$200	\$1,520	\$16,720
Background review, project planning, preparation of workplan, site visit, and discussions with town officials for second mobilization	N/A	N/A	N/A	N/A	N/A	N/A
	200	\$15,000	N/A	\$200	\$1,520	\$16,720
First mobilization Field Investigation including pre-field work and post-field paperwork	373	\$27,975	\$5,500 Driller \$600 IDW	\$10,000	\$4,347 \$60	\$47,822 \$660
	248	\$18,600	\$8,000 Driller \$600 IDW	\$6,000	\$3,260 \$60	\$35,860 \$660
Second mobilization Field Investigation including pre-field work and post-field paperwork ^a	N/A	N/A	N/A	N/A	N/A	N/A
	248	\$18,600	\$8,000 Driller \$600 IDW	\$6,000	\$3,260 \$60	\$35,860 \$660
Sample analysis ^b , interaction with labs, and data validation	60	\$4,500	\$4,800 Fixed-lab As, TCLP	N/A	\$930	\$10,230
			\$4,800 Fixed- lab ETPH, PAHs	N/A	\$480	\$5,280
			\$630 Fixed lab asbestos	N/A	\$63	\$693
			\$5,000 OEME Mobile Lab PCBs, XRF metals	N/A	\$500	\$5,500
	90	\$6,750	\$22,970 OEME Fixed lab SVOC, Metals, PCB, ACM, and ETPH analyses	N/A	\$2,972	\$32,692

Table 5
Cost Comparison Between a Traditional Approach
and the Triad Approach at the Cos Cob Power Plant (continued)

Task Description	Labor Hours	Labor Costs at \$75/Hour	Subcontractor Costs	ODCs ^c	Estimated Fee Reserve at 10%	Actual Cost Using the Triad vs.
						Estimated Traditional Costs
Sample analysis, interaction with labs, and data validation for second mobilization	N/A	N/A	N/A	N/A	N/A	N/A
	90	\$6,750	\$22,970 OEME Fixed lab SVOC, Metals, PCB, ACM, and ETPH analyses	N/A	\$2,972	\$32,692
Data evaluation, TBA report preparation, and file closeout for the first mobilization	122	\$9,150	N/A	\$1,000	\$1,015	\$11,165
	180	\$13,500	N/A	\$1,000	\$1,450	\$15,950
Data evaluation, TBA report preparation, and file closeout for the second mobilization	122	\$9,150	N/A	\$1,000	\$1,015	\$11,165
	180	\$13,500	N/A	\$1,000	\$1,450	\$15,950
Consultations about use of Triad approach	200	15,000	N/A	\$1,500	\$1,650	\$18,150
	N/A	N/A	N/A	N/A	N/A	N/A
Totals	1,100	\$82,500	\$22,830	\$14,200	\$11,652	\$132,282
	1,436	\$107,700	\$63,140	\$14,400	\$18,524	\$203,764

Notes:

TRIAD

Costs associated with the Triad approach

TRADITIONAL

Estimated costs from a traditional approach

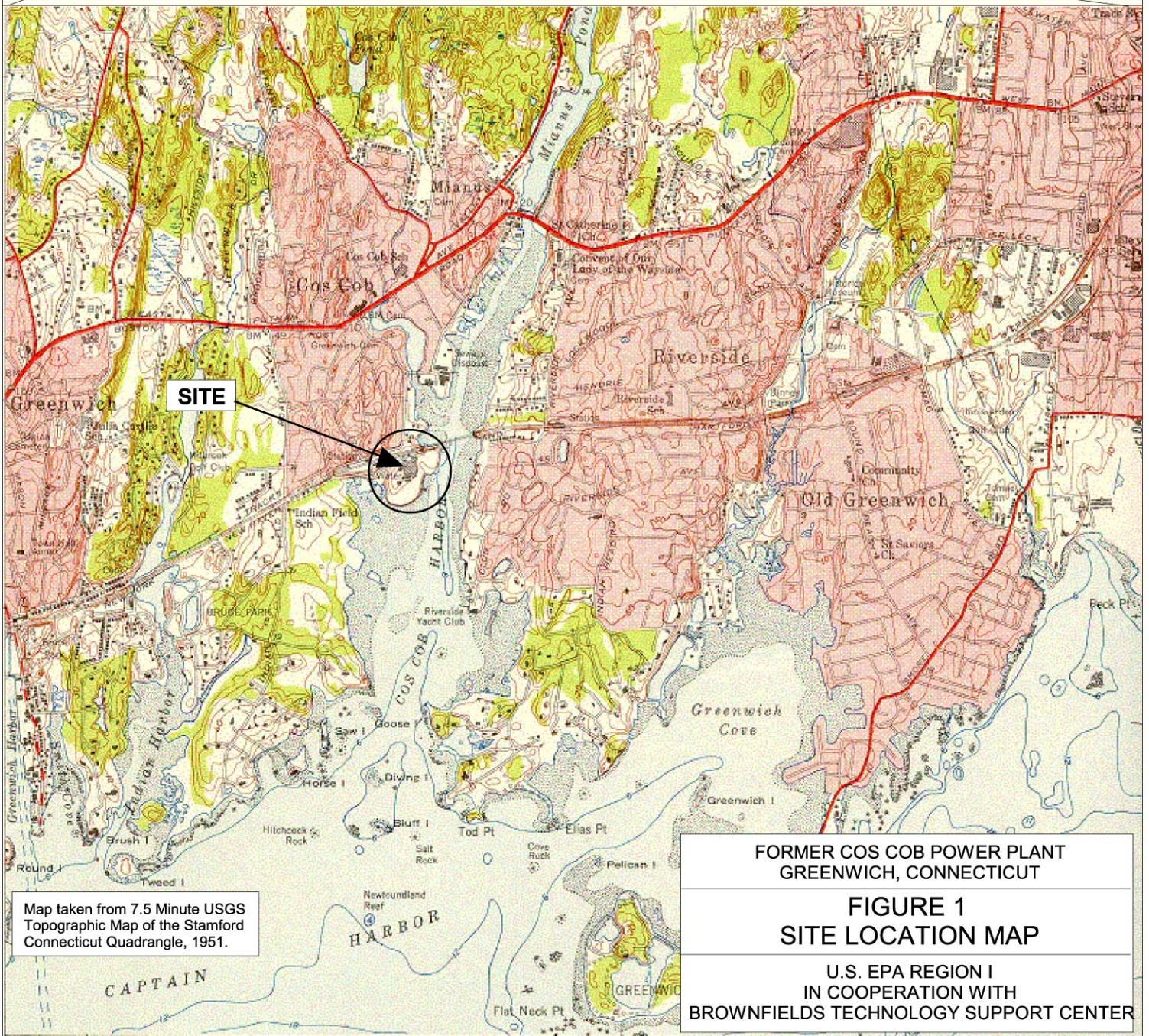
N/A Not applicable

- a A second mobilization and sampling event was assumed as a requirement under the traditional approach.
- b Field analysis of TPH and PAHs using the Sitelab field test kits is included under other direct costs (ODCs) for the first mobilization
- c ODCs: Includes copies, phone, sample shipment, computer time, field equipment rentals and supplies including test kits and fluorescence detector for TPH and PAH field analyses, travel, per diem, vehicle rental, gasoline etc.

FIGURES

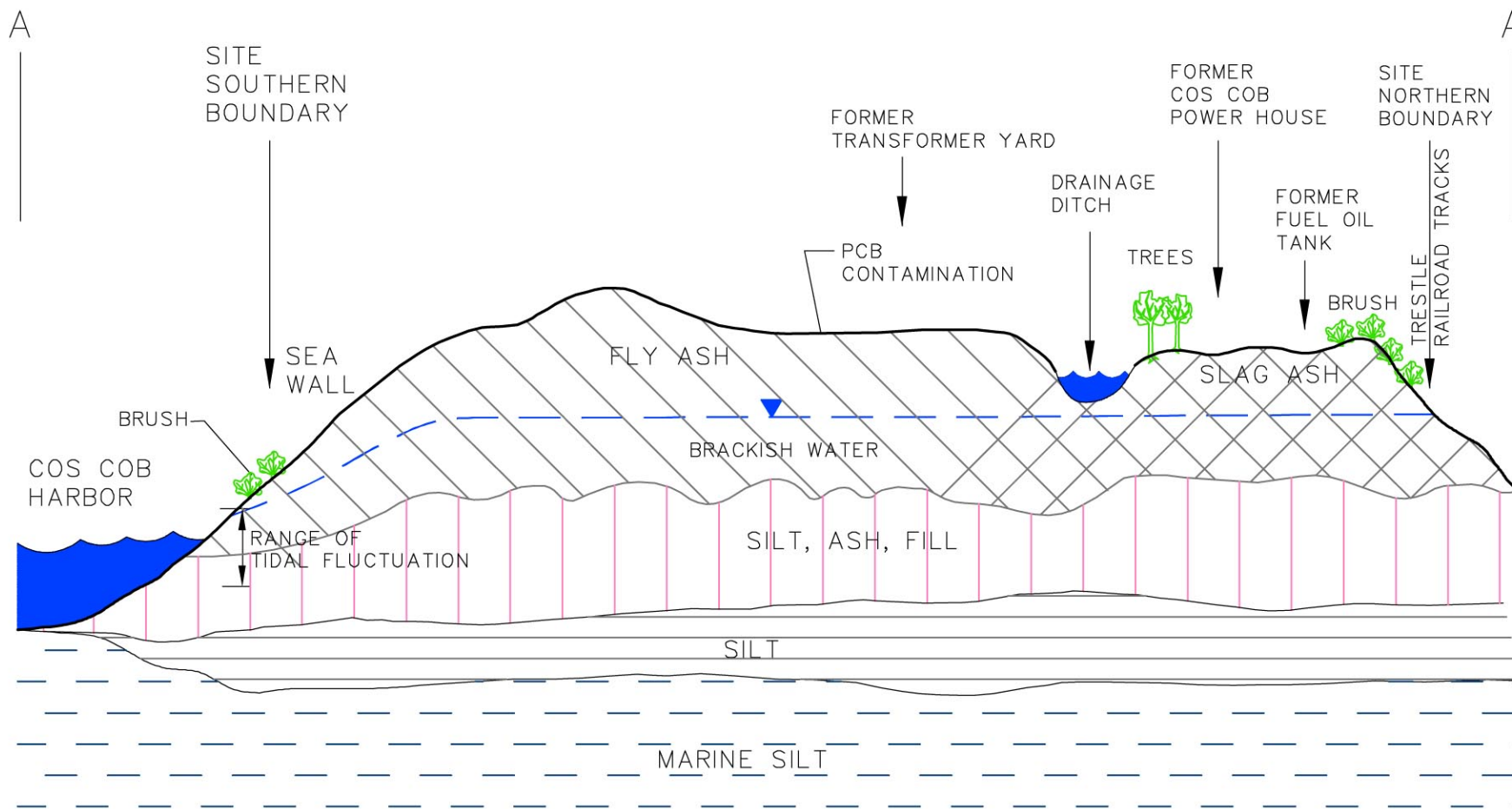


CONNECTICUT



SOUTH

NORTH

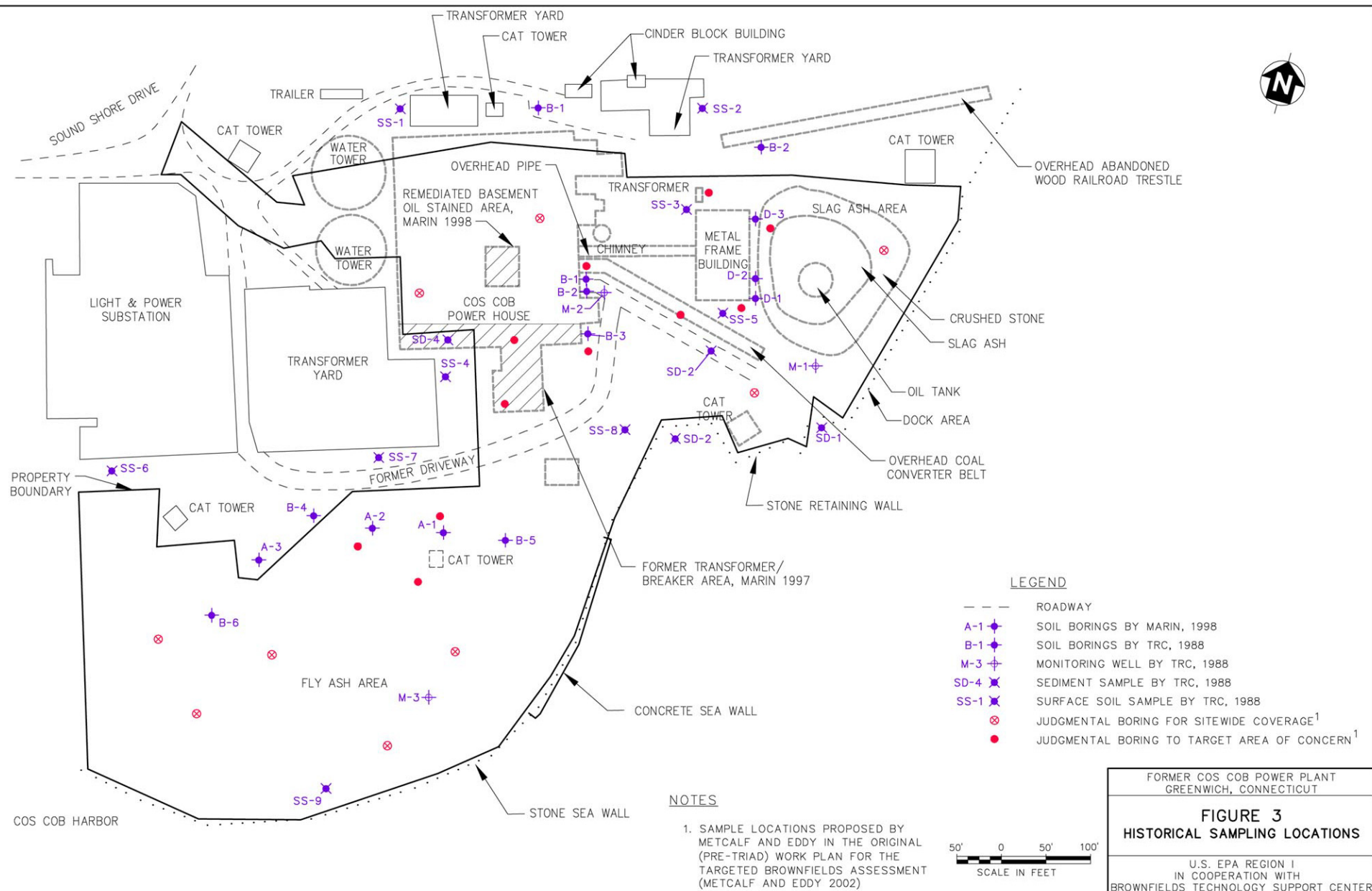


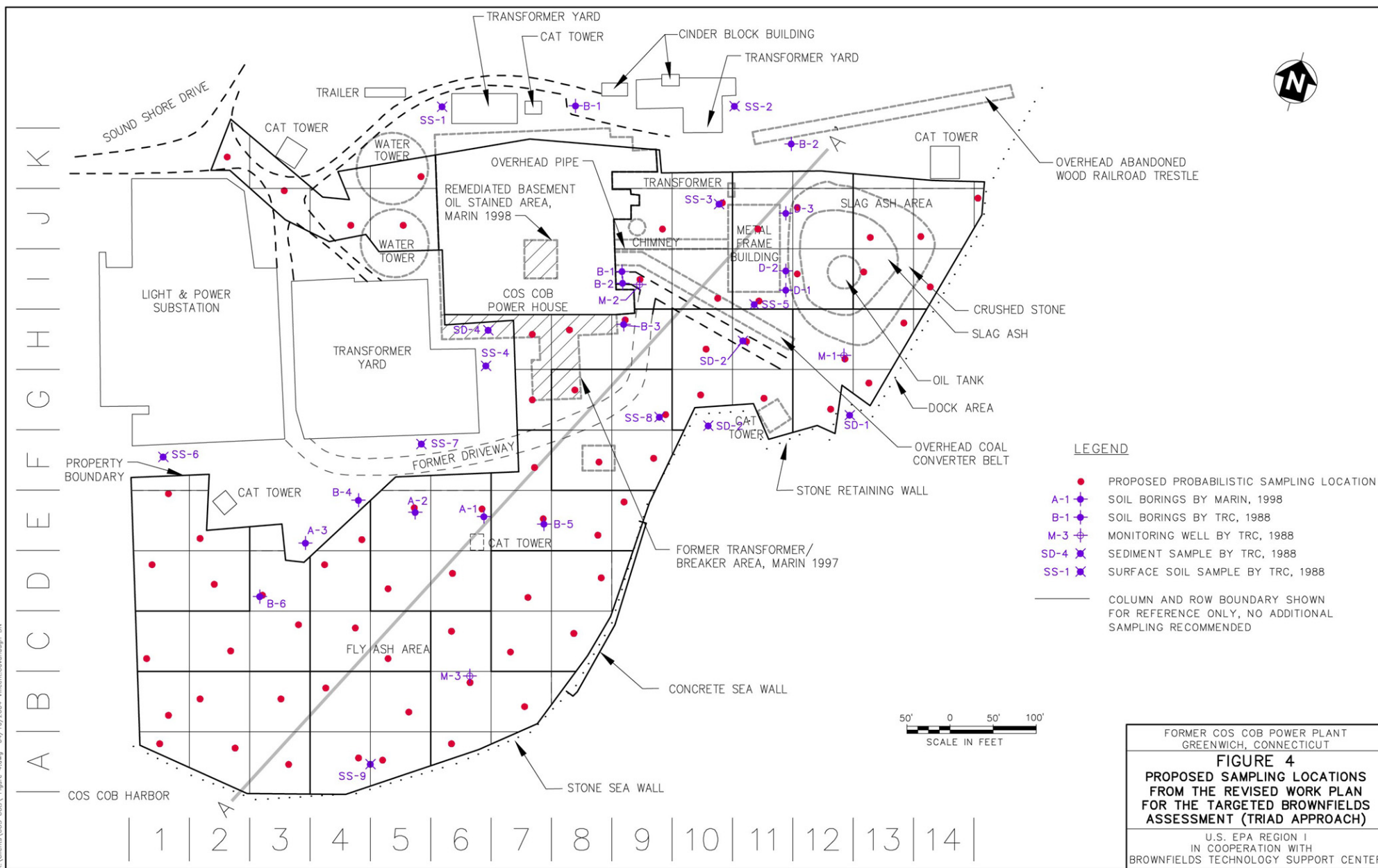
NOT TO SCALE
(VERTICALLY EXAGGERATED)

FORMER COS COB POWER PLANT
GREENWICH, CONNECTICUT

FIGURE 2
CONCEPTUAL SITE MODEL DIAGRAM

U.S. EPA REGION I
IN COOPERATION WITH
BROWNFIELDS TECHNOLOGY SUPPORT CENTER





R:\Clients\COS COB\Figure 4.dwg 04/25/2003 Vincent Covington DN

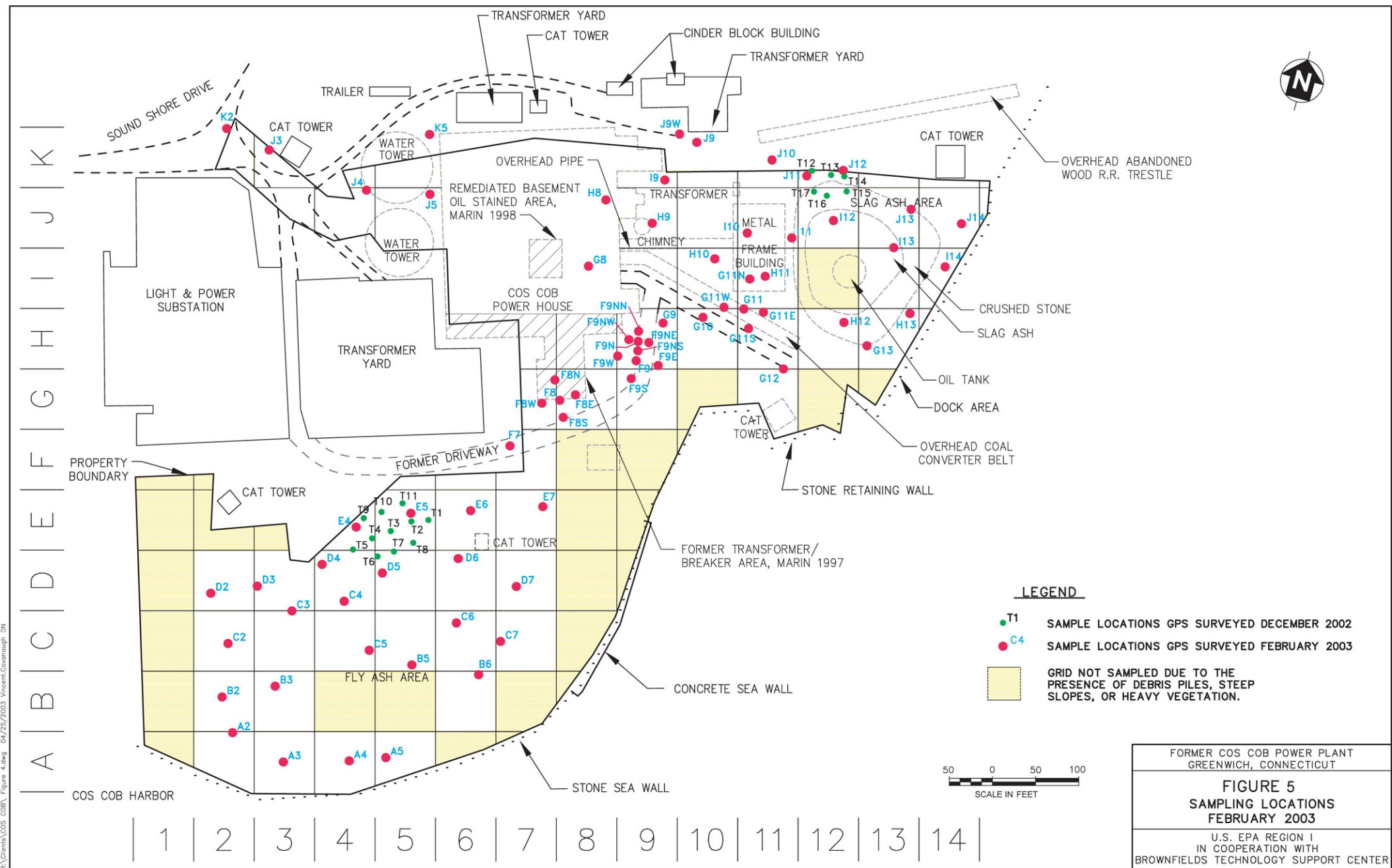


FIGURE 6

**LOGIC DIAGRAM 1:
ARSENIC IN FLY ASH INVESTIGATION
COS COB SITE**

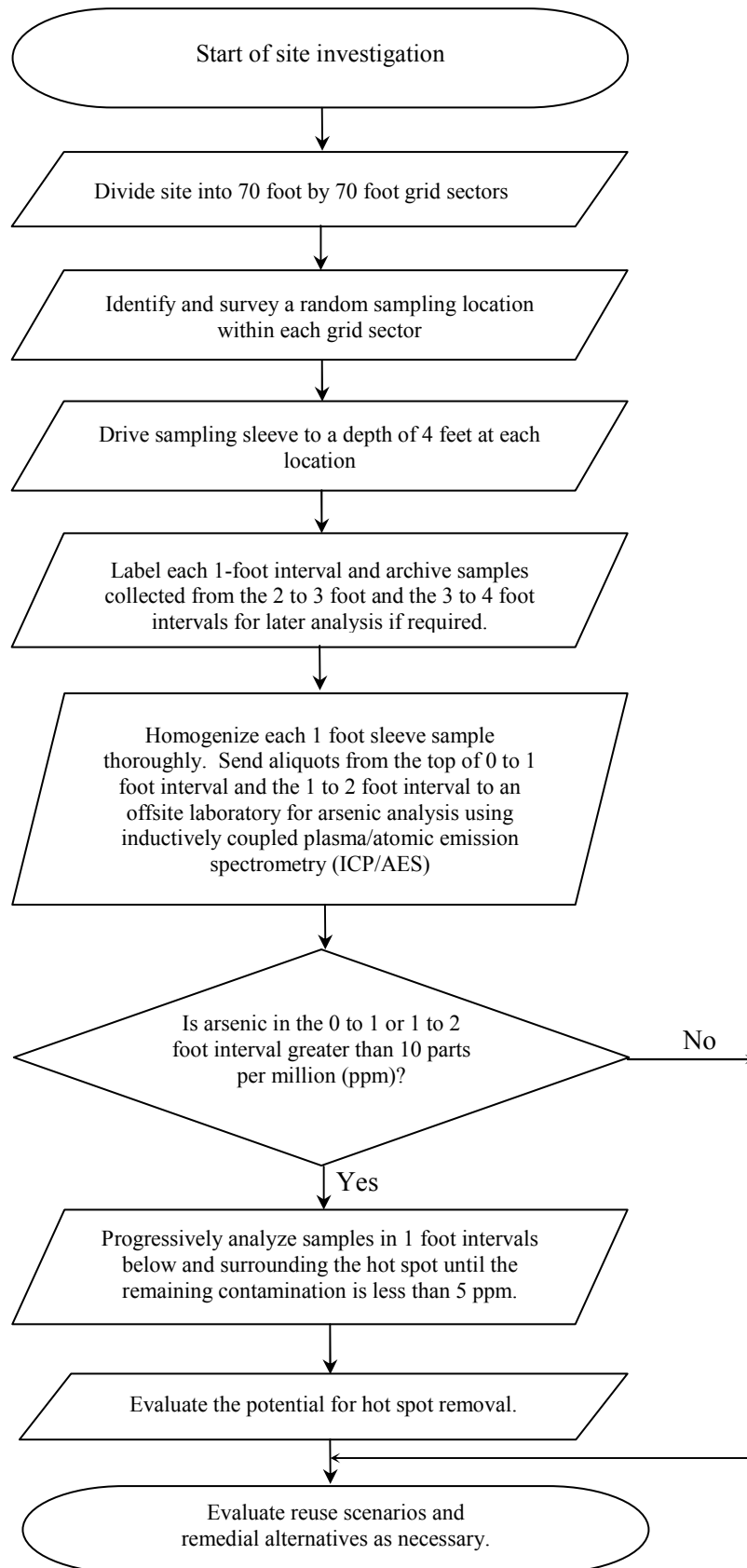
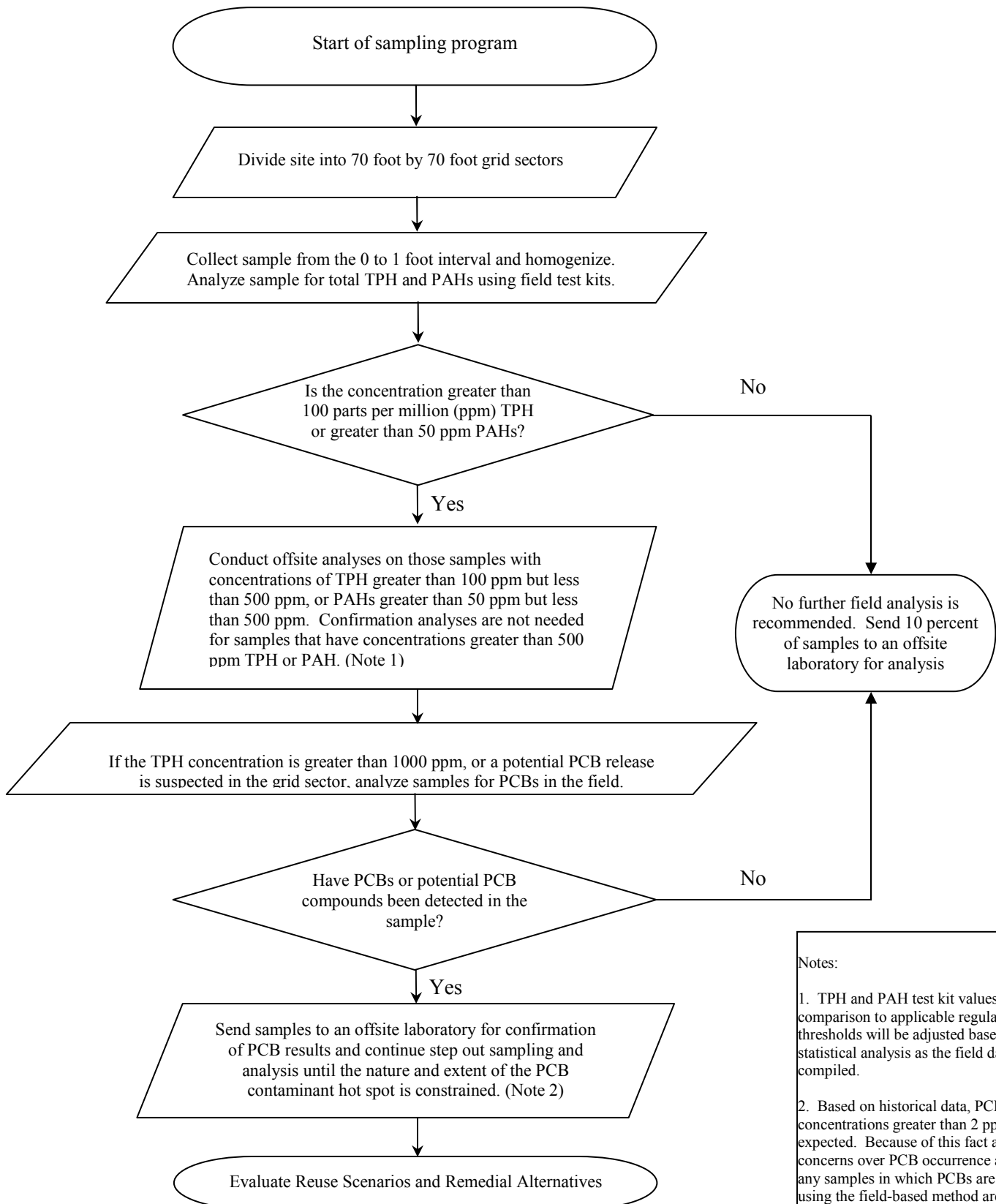


FIGURE 7

**LOGIC DIAGRAM 2:
TPH, PAH, AND PCB INVESTIGATION
COS COB SITE**



Notes:

1. TPH and PAH test kit values for comparison to applicable regulatory thresholds will be adjusted based on statistical analysis as the field data set is compiled.

2. Based on historical data, PCB concentrations greater than 2 ppm are not expected. Because of this fact and the concerns over PCB occurrence at the site, any samples in which PCBs are detected using the field-based method are recommended for further off-site laboratory analysis.

R:\Client\COS COB\proposed sample locations.dwg 08/26/2003 deborah.ford DN

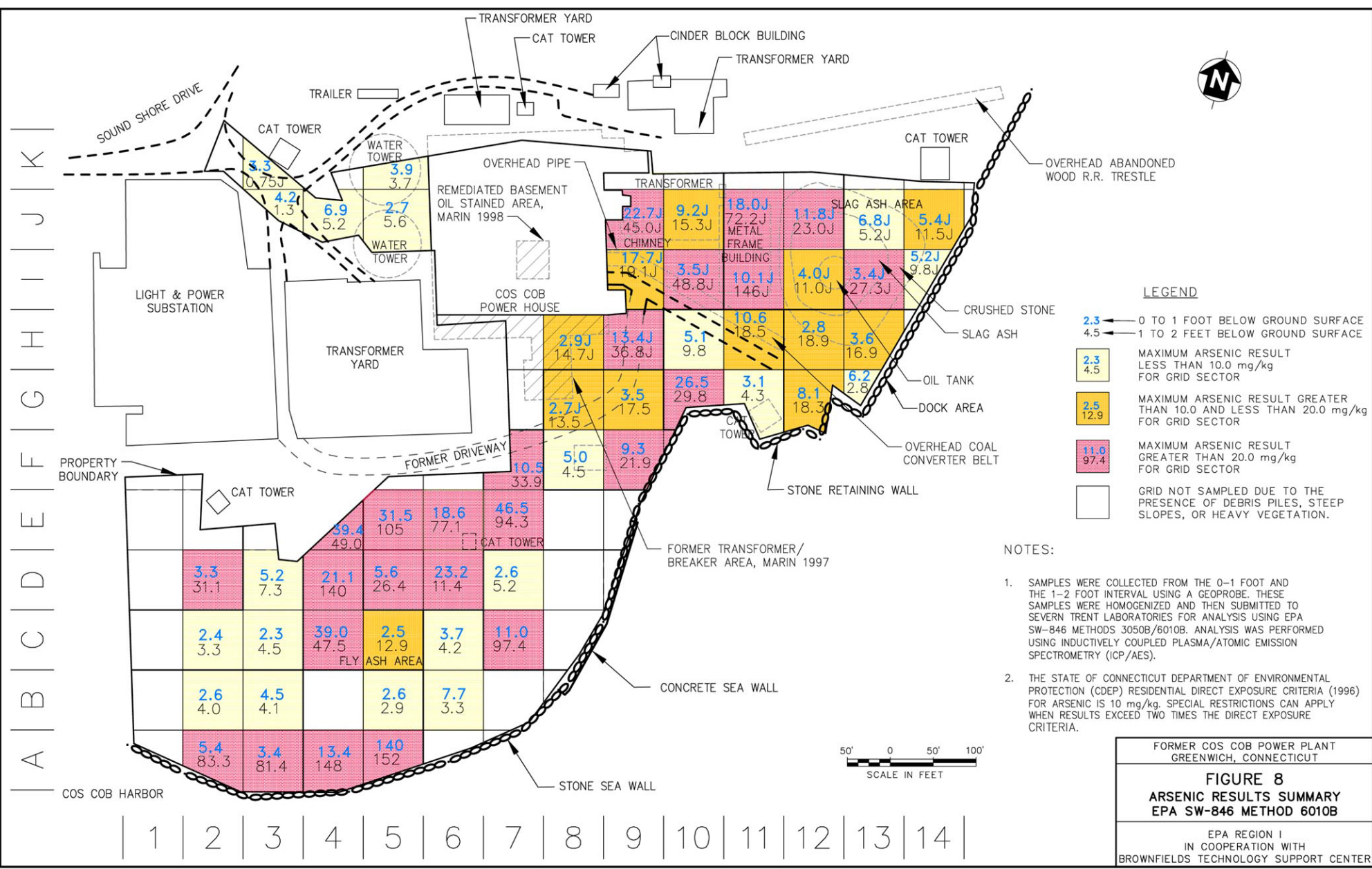


FIGURE 9

Fixed Laboratory Total Carcinogenic PAHs vs.
Field Test Kit Total PAHs
 $\text{Field} = 111.04 + 93.862 * \text{Lab}$
Correlation: $r = .38610$

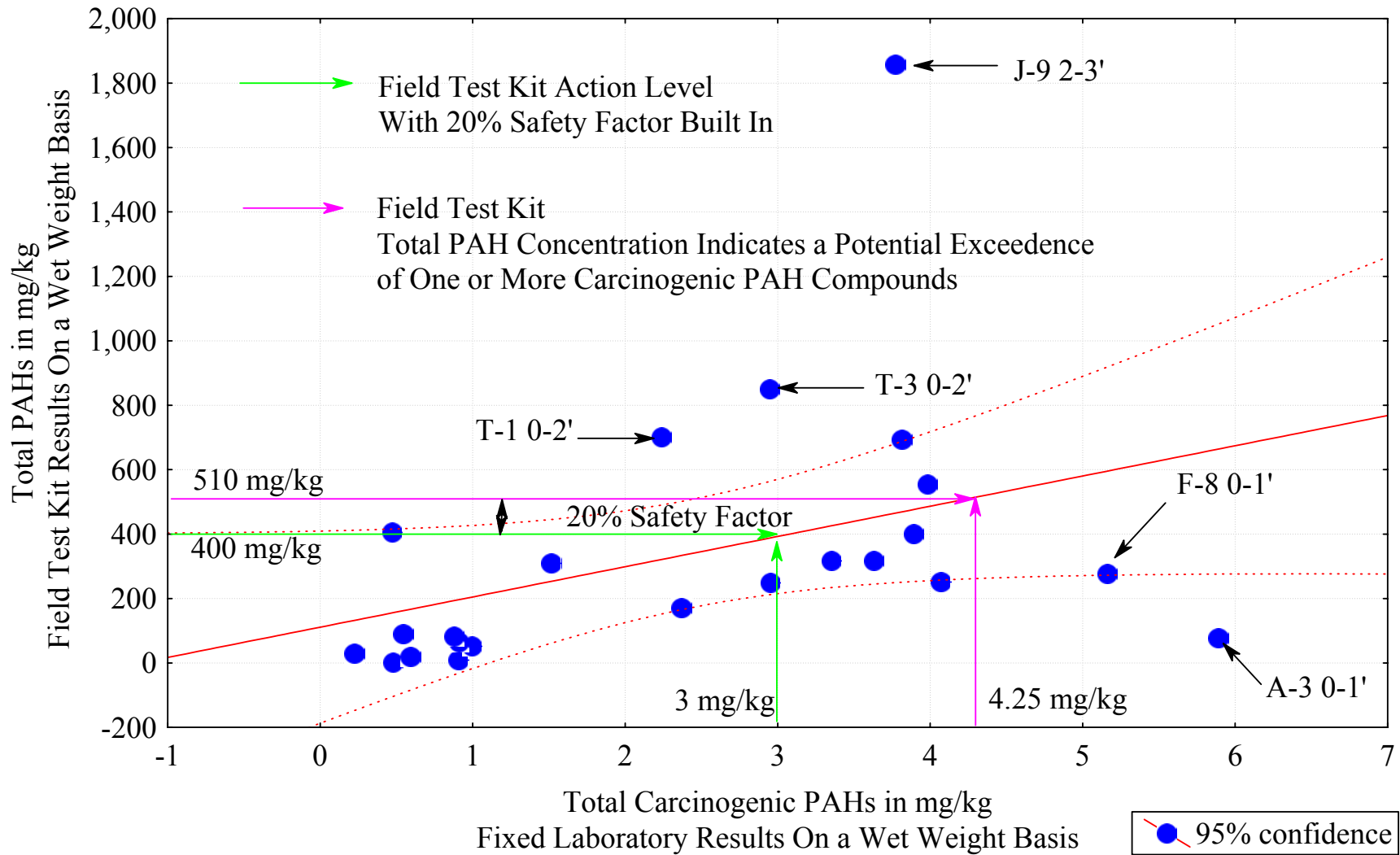
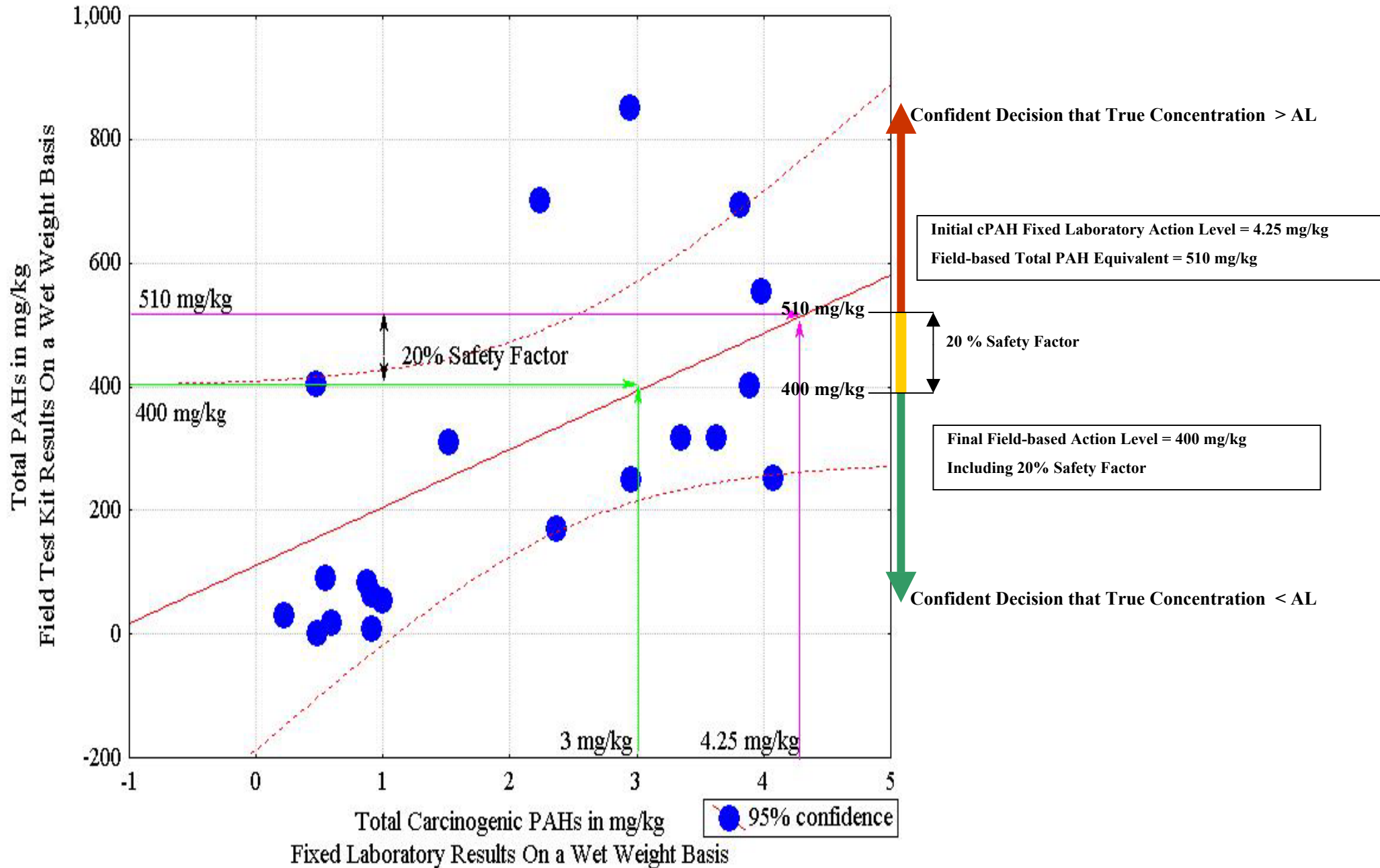


Figure 9A

Development of a Field-based Action Level for cPAHs When No Historical Data is Available



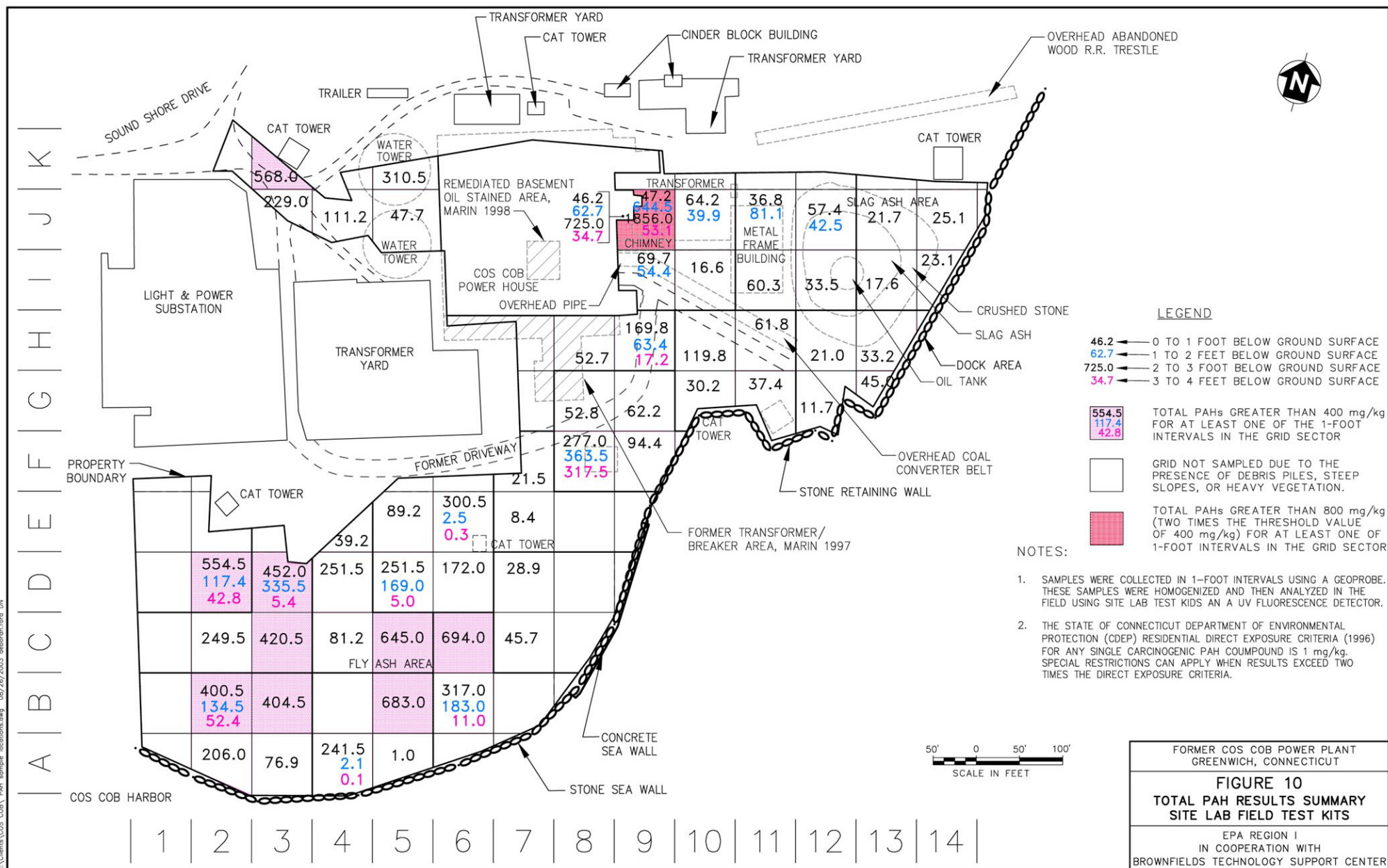


FIGURE 11

Fixed Laboratory TPH vs. Field Test Kit TPH
Wet Weight

$$\text{Field} = 32.741 + 1.2706 * \text{Lab}$$

Correlation: $r = .76815$

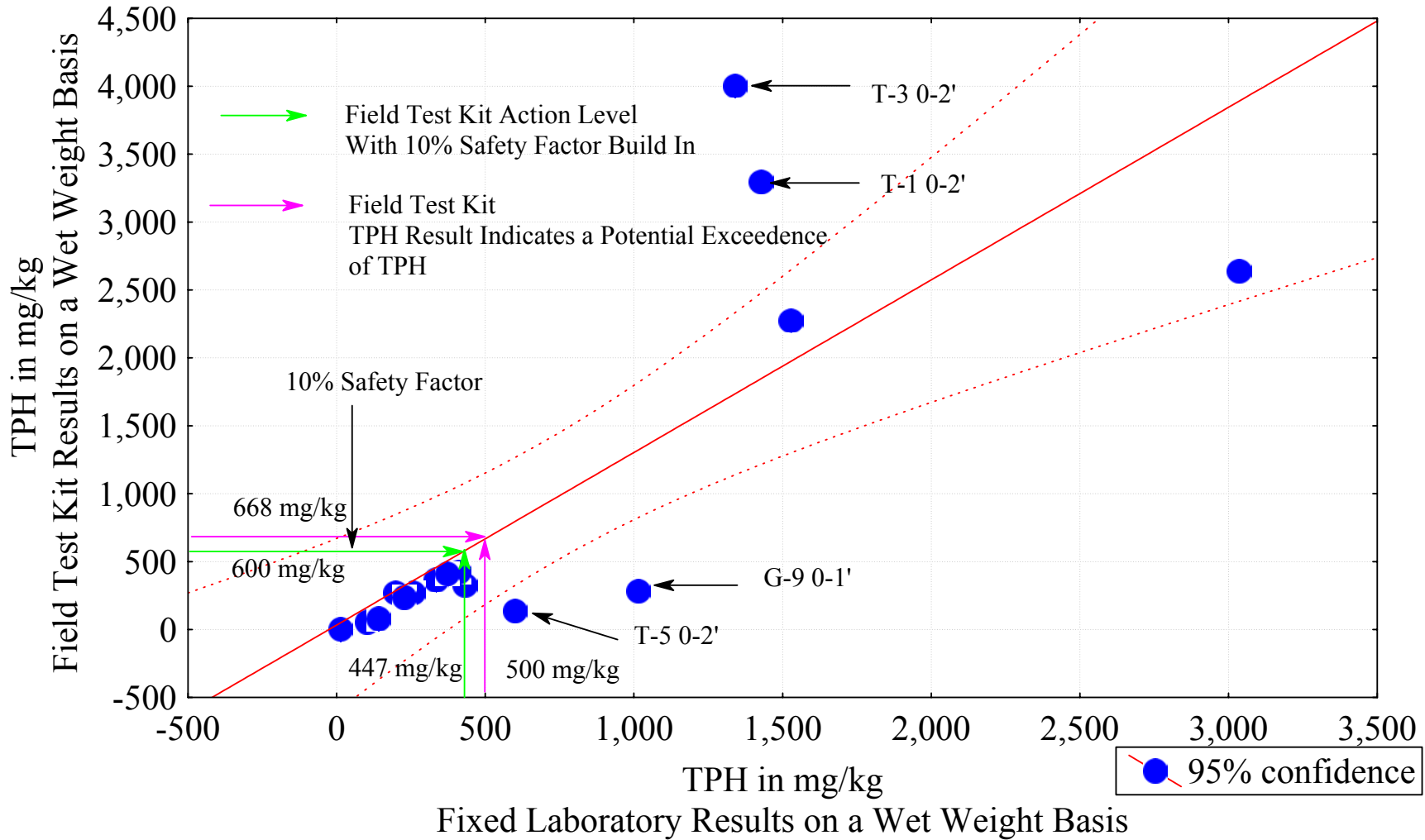
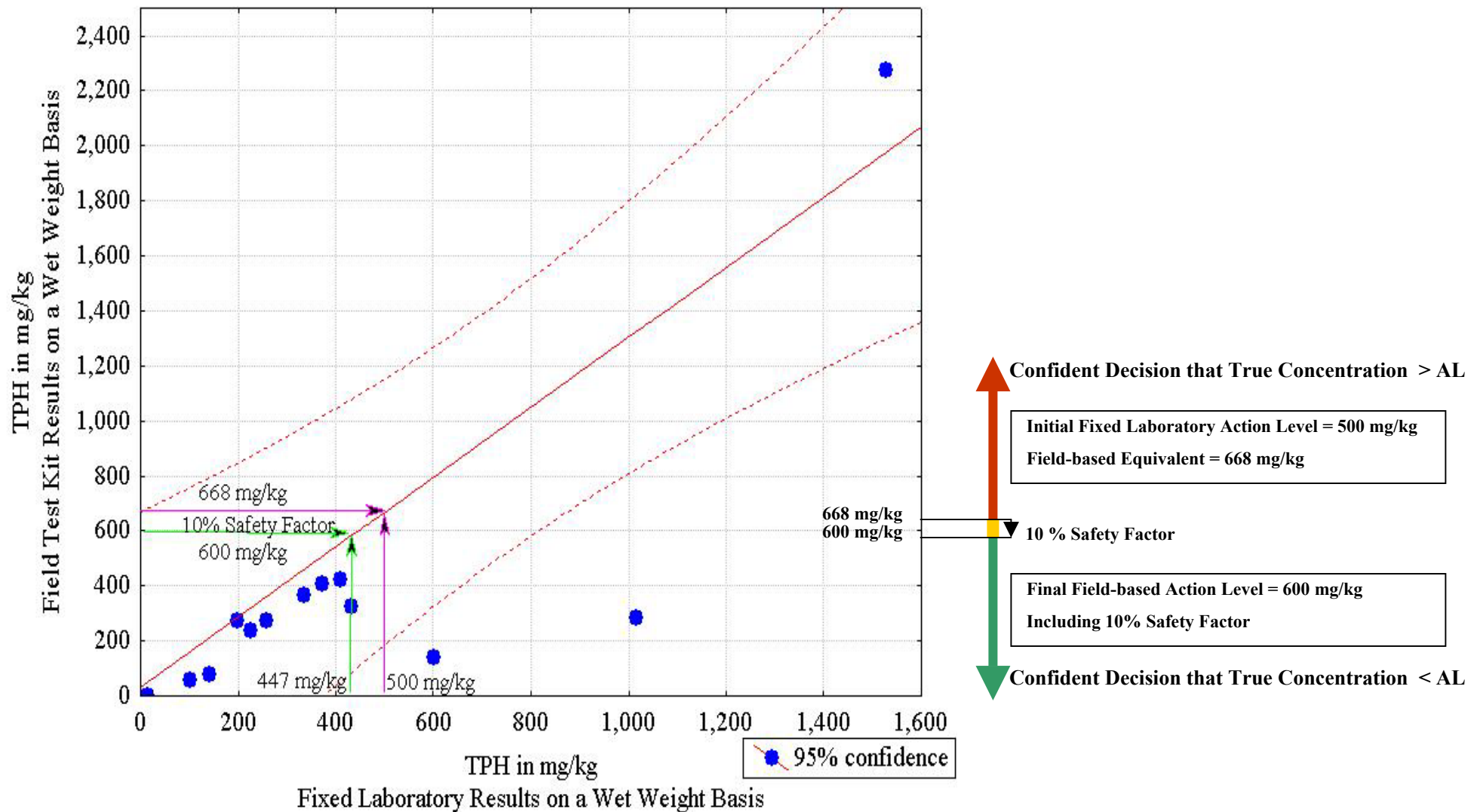
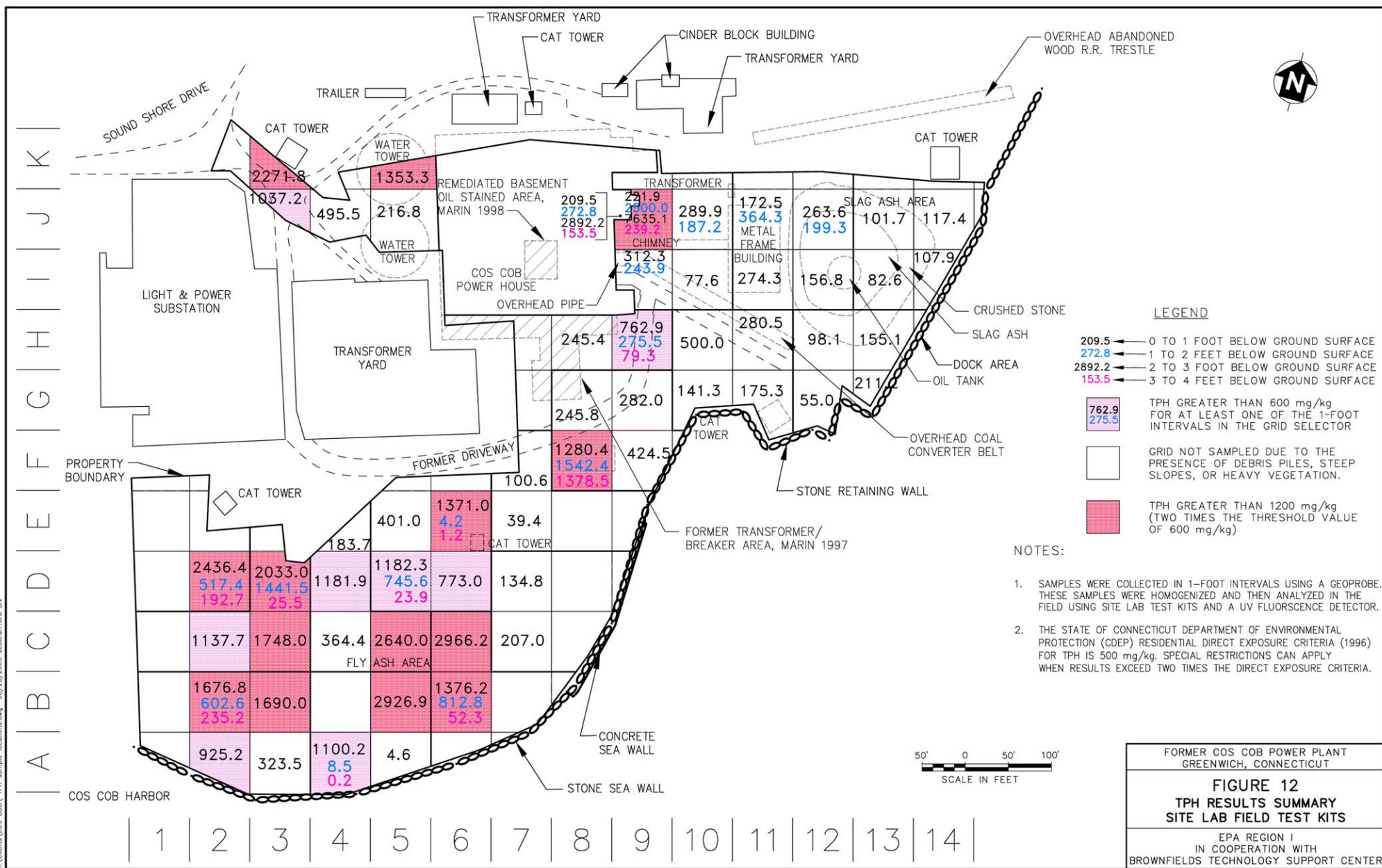
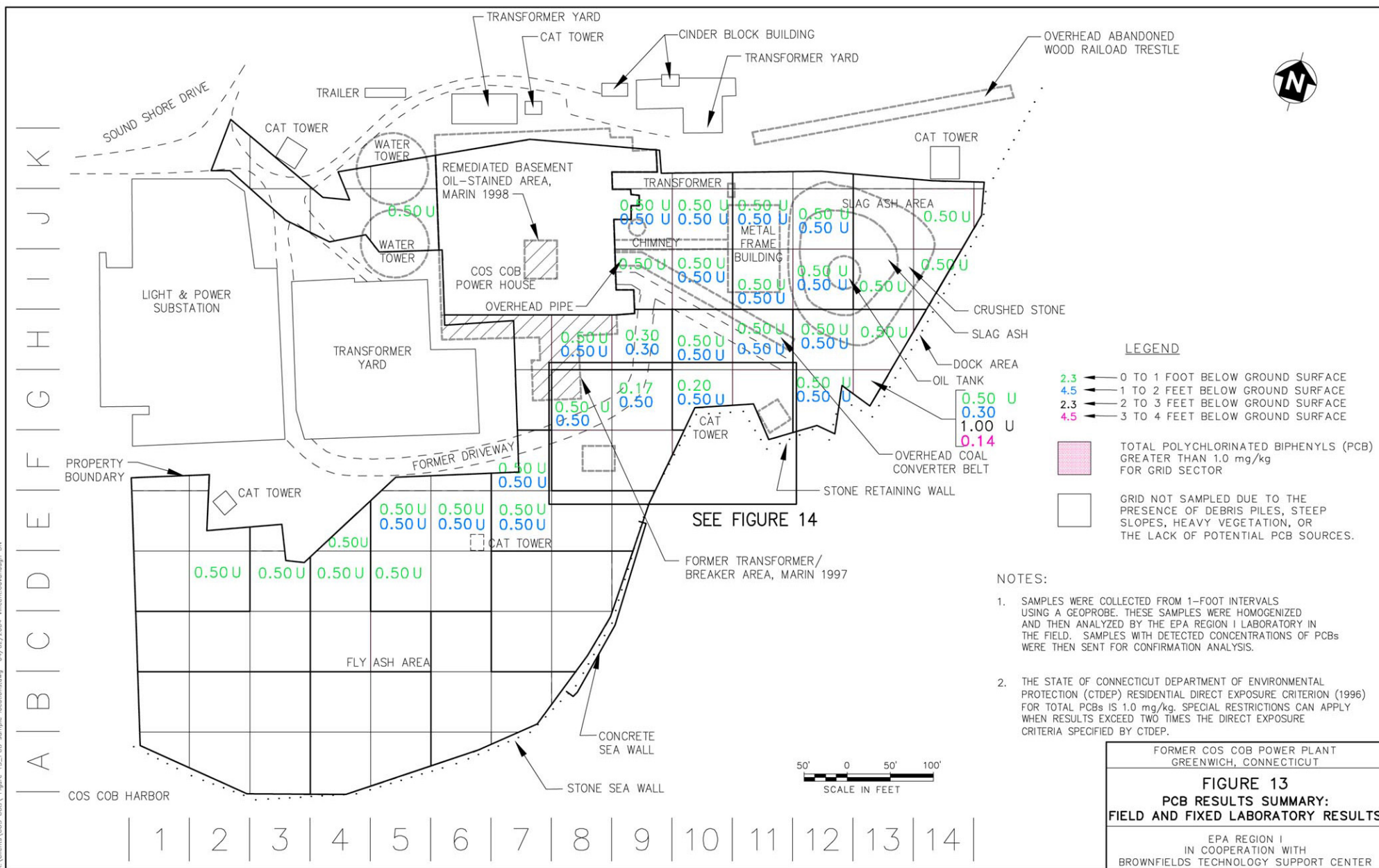


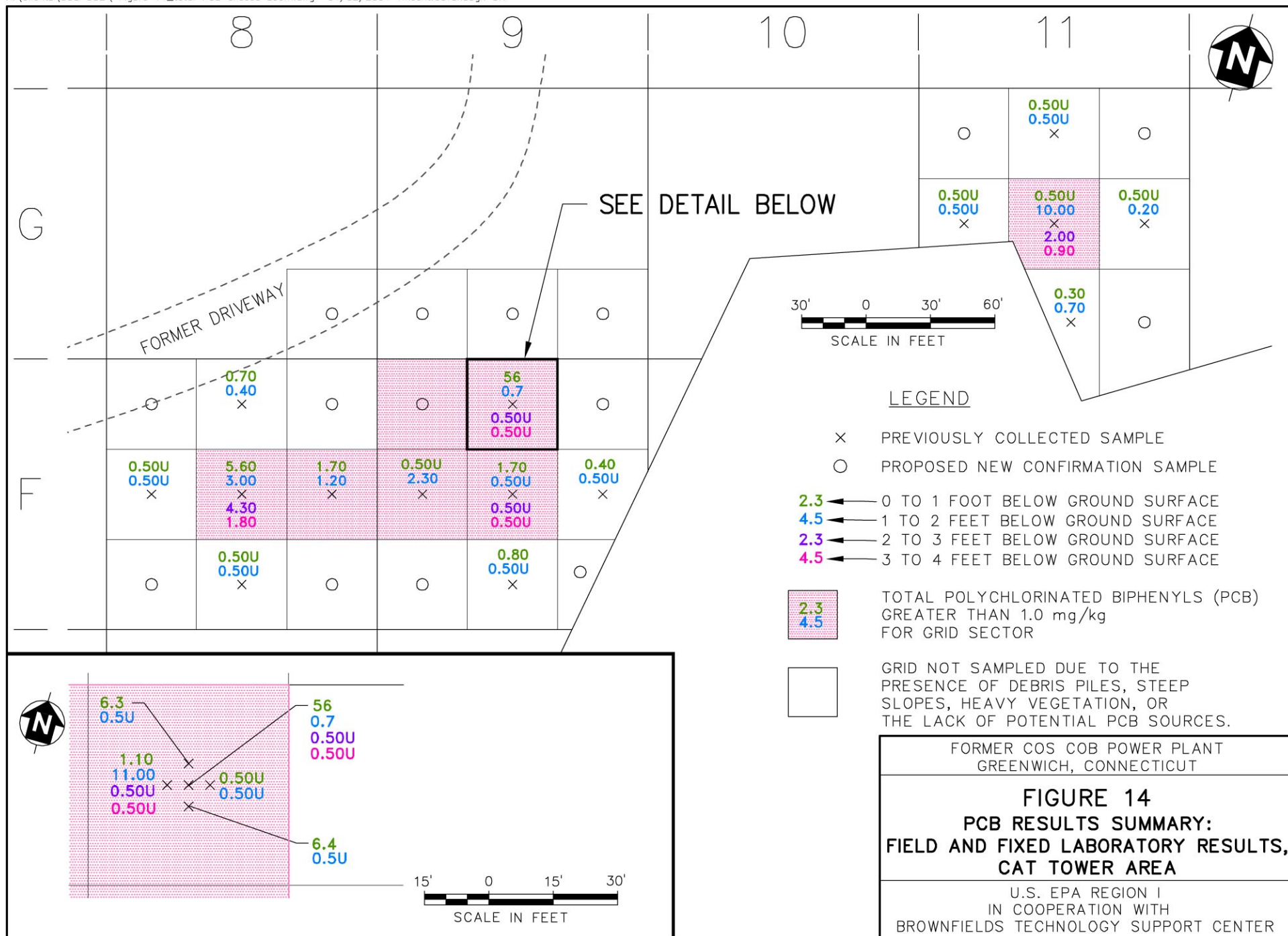
Figure 11A

Development of a Field-based Action Level for TPH When No Historical Data is Available









ENCLOSURE 1

**SOME METHOD VALIDATION ISSUES FOR THE RCRA PROGRAM:
THE FORMAL VALIDATION PROCESS FOR NEW METHODS DEVELOPMENT AND
DEMONSTRATION OF METHOD APPLICABILITY FOR A SPECIFIC PROJECT**

Reference for this published article:

Lesnik, B. "Some Method Validation Issues for the RCRA Program", *LC-GC*, pp. 1048-1056. October, 2000.

BLWP353.00

**SOME METHOD VALIDATION ISSUES FOR THE RCRA PROGRAM:
THE FORMAL VALIDATION PROCESS FOR NEW METHODS DEVELOPMENT
AND DEMONSTRATION OF METHOD APPLICABILITY
FOR A SPECIFIC PROJECT**

Introduction

I would like to thank the editors of LCGC for giving me the opportunity to discuss some important issues regarding method development and use in the U.S. EPA's hazardous waste program under the Resource Conservation and Recovery Act (RCRA), administered by the Office of Solid Waste (OSW).

The term "validation" when applied to methods or data use has a plethora of different meanings to different people. Thus, it can be a major source of confusion to laboratory analysts, quality assurance officers, and data users alike, since they tend to have very different interpretations of what it means. In this column, I will discuss two issues involving method "validation", one for new methods developers and one for methods users. I will only use the term "method validation" in the context of new methods development, and will use the term "demonstration of method applicability" when discussing issues concerning the end use of methods for generating effective environmental data, i.e., data that has been documented to be of appropriate quality to be used in making environmental decisions. I will not touch the term "data validation".

Validation of New Methods for Inclusion in SW-846

Test Methods for Evaluating Solid Waste (1), or SW-846, is the compendium of analytical and test methods published by EPA's Office of Solid Waste (OSW) for use in determining regulatory compliance under the Resource Conservation and Recovery Act (RCRA). SW-846 functions primarily as a guidance document setting forth acceptable, although not required, methods to be implemented by the user, as appropriate, in responding to RCRA-related sampling and analysis requirements. SW-846 methods have a great deal of built-in flexibility as explained in the Preface and Overview, Disclaimer and Chapter Two of the manual. However, whether SW-846 methods or alternative methods are used for a RCRA analytical application, the user must demonstrate the applicability of the methods selected for that application. Exceptions to this requirement are the "method-defined parameters", e.g., Method 1311-Toxicity Characteristic Leaching Procedure and Method 9095-Paint Filter Test, which must be performed as written, since modifying these methods changes the regulation for which the determination is

performed.

There seems to be an impression among methods developers and the regulated community that there is some esoteric or mystical process that must be followed in order to get an analytical method "approved" by regulatory agencies like the USEPA. In two guidance documents (References 2-3), OSW is attempting to dispel these misconceptions, identify some basic principles, and present a logical approach to methods development that is currently followed by OSW in developing methods for SW-846. This approach is based on sound scientific principles, and methods developed according to this process should be acceptable for use in other Agency programs as well as OSW.

In this column, I will discuss the two levels of validation for methods development that are covered in Reference 2, initial "proof of concept" and a formal validation, either single laboratory or multilaboratory. The key elements of this guidance are applicable to both new methods submitted for potential inclusion in SW-846 or for a demonstration of applicability using either existing SW-846 or alternative methods.

Levels of Validation

The RCRA Program looks at two "Levels of Validation" for new methods, proof of concept validation and a formal validation process utilizing either a single laboratory or a multiple laboratory study. Proof of concept is the preliminary stage of method development and validation where a new method or concept is tested for its potential applicability for use in the RCRA Methods Program and generally address elements 1 through 6 or 7 in Table 1. A method taken through the proof of concept stage has only utilized spiked clean matrices to determine its potential limits of performance as to scope and application, sensitivity, bias and precision, repeatability, and limited optimization and interference testing. It has not been subjected to the potential matrix effects and interferences that could be encountered in real world samples. However, if a method performs poorly at the proof of concept stage, there is little point in continuing its development, without significant modifications, if at all.

However, if a method performs well during the proof of concept stage, and the developer wishes to submit it for inclusion in SW-846, the developer must perform a formal validation addressing all of the elements in Table 1. The formal validation process includes a multilaboratory study on real world samples at multiple concentrations based on the proposed scope and application of the method. A successful multilaboratory study is important in that it demonstrates that operators other than the developer can run the method, which is a critical factor for a method to be included in a national methods manual.

Basic Principles

The RCRA method development approach utilizes three basic principles for either demonstrating "proof of concept" (See elements 1 to 6 in Table 1) or for use in a formal validation. These basic scientific principles are:

- 1) Identify the scope and application of the proposed method, (What is this method supposed to accomplish?)
- 2) Develop a procedure that will generate data that are consistent with the intended scope and application of the method, and
- 3) Establish appropriate quality control procedures which will ensure that when the proposed procedure is followed, the method will generate the appropriate data from Step 2 that will meet the criteria established in Step 1.

A developer must also meet two other specific criteria before a method will be considered for inclusion in SW-846: 1) Is there either an existing or anticipated RCRA regulatory need for this method; and 2) Is it significantly different in principle or approach from existing SW-846 methods?

Key Elements

OSW has identified eleven key elements essential to a sound method development and validation effort. These are listed in Table 1 and should be addressed in the Method Development Study Plan.

1. Identification of Scope and Application and Regulatory Need

The key factor that a developer must establish before proceeding with a method development project is a clearly defined scope and application for the proposed method. Factors to be considered should include type of method, (i.e., screening or assay), applicable target analytes, appropriate matrices, sensitivity, bias and precision, availability of equipment, and cost. All of these considerations need to be written into a flexible study plan that outlines the activities necessary for a successful method development project. When establishing the scope and application for a potential new method, it is also essential that the method developer identify that there is a regulatory need for the method, either current or anticipated by the Program Office involved. A method may be scientifically elegant, but it has very little value if there is no application for its use in the EPA Program for which it is intended.

2. Quality Control Requirements

When developing a method, the developer needs to identify the appropriate quality control procedures that must be performed to unequivocally demonstrate that the data generated by the method will meet the objectives defined in the scope and intended application(s). Examples of QC factors include appropriate calibration or tuning criteria, the need for replicate analyses, appropriate surrogates, blanks and spikes. QC criteria specific to the particular method should be well-documented and included in the QC section of the method as well as the method development project report. General and technique-specific QC requirements should also be

included in the study plan for the method development project during the planning stage and in the project report.

3. *Analytical Approach*

In developing an analytical approach, the developer should keep in mind that the ultimate goal of the project is to develop a method that will be published for general use by the analytical community. Therefore, any analytical instrumentation or equipment used in the development of the method needs to be commercially available to potential users at the time of the publication of the method. OSW encourages the use of either conventional or innovative technology, provided that it is demonstrated to be appropriate for the intended method application and provides data of sufficient quality to satisfy the criteria delineated in the scope of the method. In order for a method to be considered for inclusion in SW-846, it must be practical, i.e., has the potential for general use in the environmental analytical community, address a RCRA regulatory or monitoring need, and be significantly different from existing SW-846 methods.

4. *Method/Instrument Sensitivity (Clean Matrix or Known Standard)*

The method sensitivity for a proposed new method is influenced by several factors and should be determined in a clean matrix or with a known standard to explore the limits of sensitivity. These factors include the instrument detection limits, method quantitation limits, and the analytical requirements for the proposed applications. RCRA regulations basically require that an analyst demonstrate the ability to measure the analytes of concern in the matrices of concern at the regulatory levels. Therefore, a method must exhibit analytical sensitivity appropriate for its intended application, as delineated in the scope of the method, before it will be considered for inclusion in SW-846. Many applications in the RCRA and other EPA programs do not require the use of methods at their extreme limits of instrument or method sensitivity. Method sensitivity is an important parameter in determining method applicability and will be discussed in greater detail in that section of the column.

5. *Method Optimization and Ruggedness Testing*

After determining that the chosen analytical approach should work for its intended application with appropriate sensitivity, the method developer should begin to optimize the method and determine whether it possesses sufficient ruggedness to be considered for inclusion in SW-846. This is also accomplished using known standards.

The initial parameters should be chosen according to the analyst's best judgment. These are varied systematically (usually using Youden pairs as described in Reference 4) to obtain the greatest response, least interference, greatest repeatability, etc. Developers must determine those variables which should not be changed without adversely affecting method performance. Potential operator-sensitive steps, e.g., color development time in colorimetric methods or other timed reactions, also need to be identified at this stage.

6. *Accuracy (Bias), Precision, Repeatability (or Long-term Precision) in a Clean Matrix*

Accuracy, which in most cases is measured as method bias, is defined as nearness to the true value. Precision is defined as the dispersion of results around the mean value. Repeatability (or long-term precision) is defined as the ability to reproduce a measurement from one week to the next.

Bias is measured by determination of % recovery of target analytes spiked into the matrix of concern. An acceptable spike recovery range for most method development applications is from 80% to 120%. Precision is measured as relative % difference of target analyte concentration(s) between duplicates or duplicate spikes, and should usually be <20%. Repeatability is measured as long-term, e.g., weekly, precision, when the instrument is calibrated using comparable standards, and on a different day should not vary by more than 15%.

These are key method performance factors which determine how a method can be used in real world situations. The initial determination of bias, precision and repeatability should be made in a spiked clean matrix which is similar to a real environmental matrix, but free from interferences, e.g., reagent water, sand, soil (for inorganic methods), vermiculite or ash. These values should be obtained using multiple replicates at both high and low spike concentrations.

7. *Effect of Interferences*

The determination of method interferences, both positive and negative is a key factor in method development. It is a critical for the methods developer to determine the effects of potential analytical interferences and to develop techniques to minimize or eliminate these interferences. In chromatographic methods, interferences include coeluting peaks and/or analyte degradation due to interaction with either the injector port, transfer line or column. In spectroscopic methods, interferences can result from overlapping spectral lines causing either positive or negative signal enhancement. In immunoassay methods, interferences include cross-reacting compounds.

Method interferences should be determined in a spiked clean matrix. Developers should determine the effects of interferences in a potential new method between target analytes and other compounds reasonably expected to be present in waste matrices.

False negative rates, i.e., the percentage that a method generates a negative result when the sample contains the target analytes at or above the action level and false positive rates, i.e., the percentage that a method generates a positive result when the sample contains the target analytes below the action level, are critical factors which will determine the utility of a potential method for its intended application.

Documentation of interferences should include any coelution of target analytes, any enhancement or suppression of target analyte signals caused by interferences, any necessary or optional cleanup procedures to minimize the effect of interferences, and any matrix-specific

difficulties.

8. *Matrix Suitability*

The previous elements of the methods development process involved the use of either known standards or target analytes spiked into clean matrices, designed to indicate potential method performance in real RCRA matrices. Once the potential new method has passed all of the preliminary tests, it is now ready for the most important demonstration in the entire methods development process, i.e., how it will perform in the real world matrices for which it is intended to be used.

The method should be suitable for a variety of matrix types. Therefore, the developer should choose appropriate RCRA matrices for the demonstration of method performance. By matrix types, OSW refers to different matrices within a particular medium, e.g. water, soil and ash. Appropriate RCRA water matrices include groundwater, TCLP leachate and wastewater, while appropriate RCRA soil matrices include sand, loam and clay. Appropriate ash matrices include bottom ash, fly ash and/or combined ash. The method should perform adequately in a variety of spiked matrices and then in a variety of well-characterized natural samples or standard reference materials (SRMs) when SRMs are available. Performance data including matrix type, precision, bias, quantitation limits (see next section), and any other pertinent data should be documented in appropriate tables. A summary of the single-laboratory performance data should be included in tabular format in the method while the detailed performance data, including QC, should be included in the supporting documentation.

9. *Method Detection and Quantitation Limits*

In a new method submission, OSW is most concerned about the performance of the method in the RCRA matrices of concern. The developer should generate method quantitation limits (for assay methods) and method detection limits (for screening methods) for the analytes of concern in the matrices of concern following the guidelines established in Chapter One of SW-846 or other appropriate guidance. The practice of generating method detection limits based on reagent water is not usually a very useful parameter for most RCRA methods.

Method detection and quantitation limits are usually based on a specific sample size. The limits determined in clean matrices usually indicate the limits of the acceptable performance for the method. Matrix effects may affect the achievable quantitation limits on real world samples. However, the method quantitation limits for the target analytes in the target matrices must meet the analytical requirements for its intended application, as defined in the scope of the method, before it can be considered for inclusion in SW-846.

10. *Laboratory Reproducibility (Multiple Operators and Multiple Laboratories)*

The final stage in the method development process, prior to the submission of the method for Agency review, is the determination of laboratory reproducibility. By reproducibility, OSW

means that multiple operators and multiple laboratories should be able to obtain comparable performance data on split real world environmental samples using the method. If certified SRMs or secondary standards are available, they are the preferred samples for use in the multilaboratory validation study.

Since all of the previous elements involved single operators or single laboratories, it is necessary to demonstrate that satisfactory method performance is not limited to the individual operator or laboratory that developed the method. The minimum number of laboratories that are needed to participate in a multilaboratory method validation is three, with preferably more. Developers of new methods today need to do a limited multilaboratory evaluation and provide the individual laboratory and summary performance data in the method submission. Developers are encouraged to consult with the appropriate regulatory agency when planning a multilaboratory study.

In order to minimize the number of variables involved in method validation, the developer needs to follow a few simple guidelines to demonstrate appropriate multilaboratory method performance. When validating a sample preparation method, the participating laboratories should only perform the sample preparation procedure. The collected samples should then be sent to one laboratory for analysis. The analysis should be done by a single operator on a single instrument in a single batch to minimize analytical variability inherent to the determinative method. Conversely, if a determinative method is to be validated, the developer should have a single operator perform all of the sample preparation operations in order to minimize operator and laboratory variability inherent to the sample preparative procedures. The sample extracts should then be split and sent to the laboratories participating in the validation study for the analytical determination.

11. Document Submission and Workgroup Evaluation

When the method project is completed, the developer must assemble a package of documents describing the project, and submit it to the Agency for review and evaluation. This documentation package should include 1) draft copies, both hard and electronic, of the method in an appropriate Agency format; 2) a supporting document describing the rationale behind the methods development effort and how the key elements of the methods development project as described in this document were addressed; 3) a data package containing both the raw and summarized single laboratory and multilaboratory data; 4) any specific equipment diagrams and chromatograms, spectra, etc. pertinent to the demonstration of appropriate performance for the intended application of the method; 5) copies of any references listed in the method; and 6) any method-specific quality control criteria.

The OSW Methods Team reviews the methods submission package for completeness and quality, and then decides whether the method is ready to be sent to the appropriate SW-846 Methods Workgroup for review or back to the developer for additional work. OSW has several standing SW-846 Methods Workgroups which meet formally each year to review the methods packages submitted by developers for potential inclusion in SW-846. Workgroup members are scientists from across the Agency who are qualified experts to evaluate the procedures and

performance data submitted by the methods developers. Key evaluation criteria used by the Workgroups to determine whether a submitted methods package is appropriate for inclusion in SW-846 include: 1) Does the data package support the application and performance criteria delineated in the scope and application of the method?; 2) Can the method be performed routinely by the personnel available to an environmental laboratory?; 3) Is the equipment commercially available?; 4) Is the method cost effective?

Demonstration of Method Applicability

Having discussed method validation for new methods developers in significant detail, I will now address the primary validation issue for methods users, "demonstration of method applicability". The RCRA Program does not have "reference methods" in its methods manual, i.e., SW-846 methods are either method-defined parameters or guidance. Reference methods have been taken to mean that, if one follows a published method as written and generates the wrong data for an application, then nothing else needs to be done. For RCRA applications, the regulated party must demonstrate that the methods used, whether they are published in SW-846 or alternative methods, must be appropriate to generate effective environmental data for that application, i.e., data that has been documented to be of appropriate quality to be used in making that environmental decision. Therefore, OSW allows sufficient flexibility in method selection and modification to be able to meet this requirement using the performance-based measurement system (PBMS) approach. In a *Federal Register* Notice, EPA defines PBMS (Reference 5) as a set of processes wherein the data quality needs, mandates or limitations of a program or project are specified, and serve as criteria for selecting appropriate methods to meet those needs in a cost-effective manner.

Using the PBMS approach, the operator must use some form of systematic planning to establish the goals and data quality needs for the particular project and be able to answer the following key questions which will help determine the appropriate methods to be used:

- 1) What is the purpose of this analysis? (Why are we doing this?)
- 2) How will the data be used? (What decisions will it support?)
- 3) How good does the data have to be, or what quality of data do we need to support the decision?

Two separate factors are involved in demonstrating method applicability: 1) demonstrating that the operator can perform the method properly in a clean matrix, and 2) demonstrating that the method selected generates "effective data" in the matrix of concern. Item 1) is a laboratory or operator training or proficiency issue that I will not discuss in great detail here. Item 2) involves the same basic scientific method questions as described above for method development activities, and this section will focus on the key factors to be considered when performing this demonstration.

Operator Proficiency

Demonstration of operator proficiency in running the method(s) in question in a clean matrix is important for two primary reasons. The first is a demonstration that the operator can adequately perform the method and the second is that the method performs well in a clean matrix and therefore the analytical system is in control. Therefore, any analytical problems encountered in the real world applicability testing can be addressed in terms of matrix suitability issues, rather than operator or issues.

Determination of Method Applicability

Documentation of the determination of method applicability should be included in the project planning documents including performance data from operator proficiency and matrix suitability testing. Some of the key factors to consider, based on the data quality requirements from the project planning documents, include selection of appropriate target analytes, analytical matrix, method sensitivity, bias and precision, and reproducibility. It is usually not necessary to perform a complete formal new methods validation project for this method user validation process. However, the analyst must address many of the same key elements, but usually the demonstration of applicability may require up to the proof of concept stage, depending on the application. In some cases it may be a little more and in others a little less. Since we are dealing primarily with site-specific applications, there is little need for doing a multilaboratory validation study.

In selecting appropriate target analytes, OSW only requires the analysis of target analytes "that are reasonably expected to be present" at a site, and allows for the elimination of many analytes on a long list through process knowledge. If the application is for a site survey, a wider range of target analytes may be necessary than for a monitoring application for a well characterized site, e.g., ground water monitoring wells around a landfill. It is frequently appropriate for monitoring activities to use less expensive methods utilizing non-specific detectors, e.g., GC/PID, for a few target analytes, and treating all positives as hits, thus eliminating the need for confirmatory analyses. In some cases appropriate quantitative screening methods, e.g., immunoassays may be used for very selective monitoring at appropriate action levels for cleanup activities.

Demonstration of appropriate method sensitivity in the matrix of concern is a critical element for the applicability demonstration. The RCRA Program does not require the formal method detection limit (MDL) studies required by other EPA Offices, since many applications operate at orders of magnitude above the quantitation or detection limits of the methods used. It is necessary that the low calibration standard be selected to demonstrate that the method can unequivocally determine whether the analytes of concern are present at the action level. For analyses in the ppm range, a low standard of about 50% of the action limit is appropriate, while for analyses in the ppb range, we recommend a factor of 0.1 times the action level for the low standard. The analyst should select an appropriate calibration range to address the specific data quality needs of the project. It need not be more than one or two orders of magnitude in many

cases. The last calibration issue that I will mention is that for most RCRA applications, it is only necessary to meet calibration requirements for the analytes of concern to the project, and not for all of the analytes in the Table of Analytes list of a method. Another suggestion for demonstrating appropriate method sensitivity is to spike the target analytes of concern into an appropriate sample matrix free of target analytes at 70-80% of the action level. Run the spiked sample through the analytical sequence and if recoveries of the target analytes are sufficient for quantitation above the low standard, then method performance should be sufficiently sensitive for its intended application.

Bias and precision are also important project-specific parameters. Bias is measured using spike recovery of target analytes from the matrices of concern and precision from the analysis of either duplicate or matrix spike duplicate (if no target analytes are present) samples. Poor recoveries of target analytes generally indicate inappropriate sample preparatory conditions or method selection, interferences, or interaction with the matrix. The analyst should identify the problem and take steps to eliminate it. Poor precision at this point, since operator error has been eliminated, generally indicates sample heterogeneity and needs to be addressed as a sampling or sample handling issue. For projects involving highly contaminated sites, optimizing analyte recoveries is much less important than for projects where the objective is a site cleanup to a low action level. Sample reproducibility between operators and on repeated analyses of the same sample should be within the specific limits of the project plan.

The number of samples necessary for the demonstration of applicability will vary with sample type and proximity of the samples to the action level. Demonstrations for samples that have concentrations of target analytes that are well below action levels can be completed with relatively few samples. A demonstration for highly heterogeneous samples and samples with target analytes very close to the action level will need many more analyses to complete the demonstration and should be statistically calculated.

Summary

In this column, I have attempted to clarify the "validation" issues common to both new methods developers and methods users. A full validation of a new method for inclusion in a national methods manual involves many more steps, including a multilaboratory collaborative study, than does an on-site "demonstration of method applicability". However the key elements of scope and application, method sensitivity, bias and precision, reproducibility, and elimination of interferences are common to both activities.

Table 1: Key Elements for Regulatory Methods Development

Element 1:	Identification of Scope and Application and Regulatory Need
Element 2:	QA/QC Requirements
Element 3:	Analytical Approach
Element 4:	Method/Instrument Sensitivity (Clean Matrix)
Element 5:	Method Optimization and Ruggedness Testing
Element 6:	Accuracy, Precision and Repeatability (Clean Matrix)
Element 7:	Effect of Interferences
Element 8:	Matrix Suitability
Element 9:	Quantitation and Detection Limits
Element 10:	Laboratory Reproducibility (Multiple Operators and Multiple Laboratories)
Element 11:	Document Submission and Workgroup Evaluation

References

1. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition*, (SW-846) including Updates, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, DC, (1997).
2. OSW Guidance Document: "Guidance for Methods Development and Methods Validation for the RCRA Program", October, 1995, <http://www.epa.gov/SW-846/methdev.pdf>.
3. OSW Guidance Document: "Immunoassay Methods in SW-846: Recommended Format and Content for Documentation Supporting New Submittals, July, 1995, <http://www.epa.gov/SW-846/immunoas.pdf>.
4. W. J. Youden and E. H. Steiner (1975) *Statistical Manual of the AOAC*, Association of Official Analytical Chemists, 1111 North 19th Street, Suite 210, Arlington, VA 22209. Fifth printing in 1987.
5. 62 *FR* 52098, October 6, 1997.

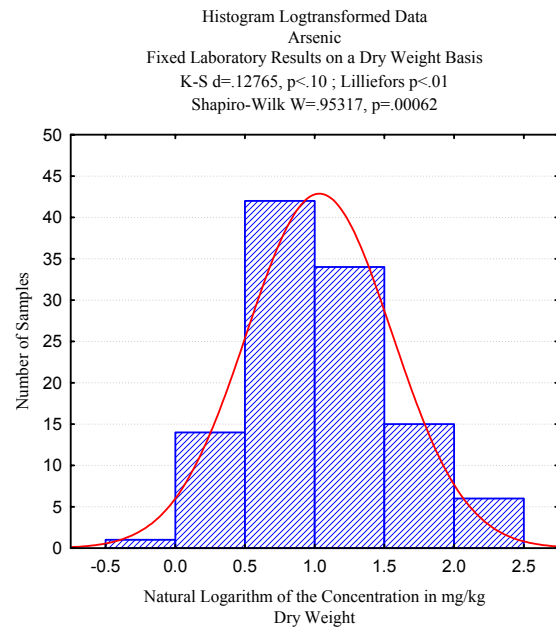
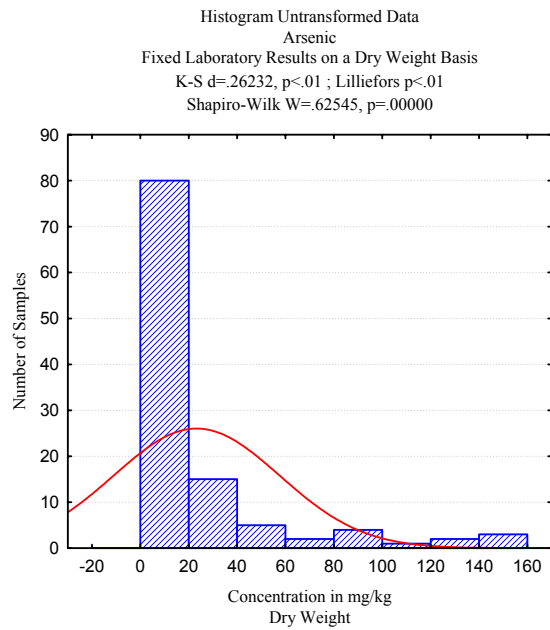
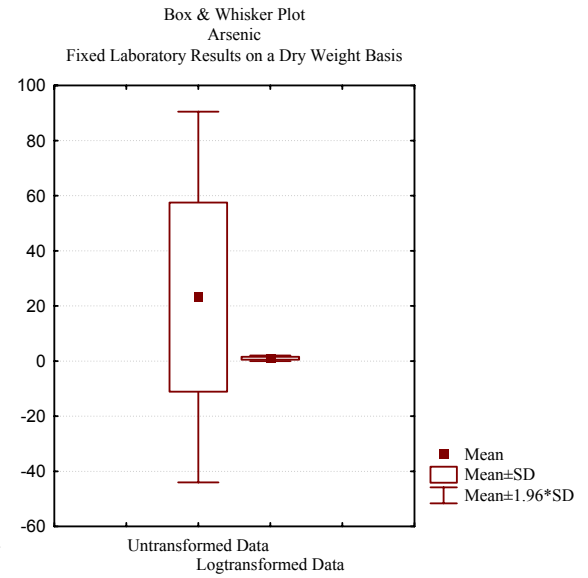
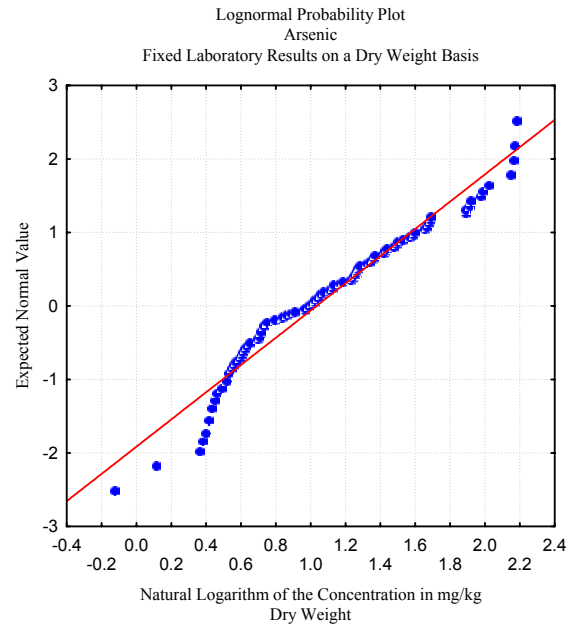
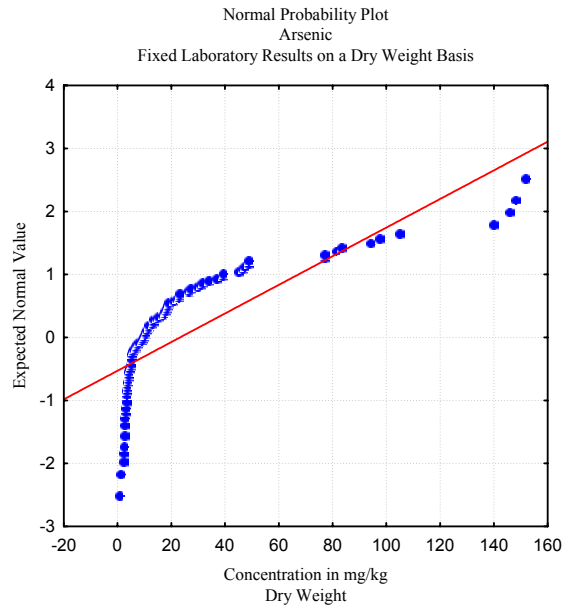
ENCLOSURE 2

**STATISTICAL PLOTS AND SUMMARY
STATISTICS FOR PROJECT TARGET ANALYTES**

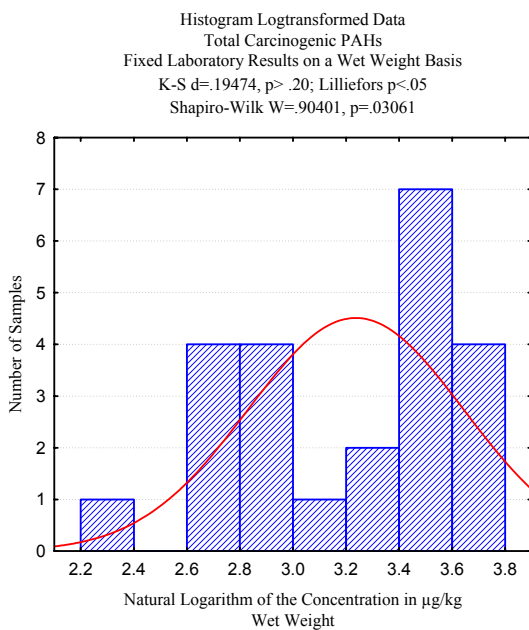
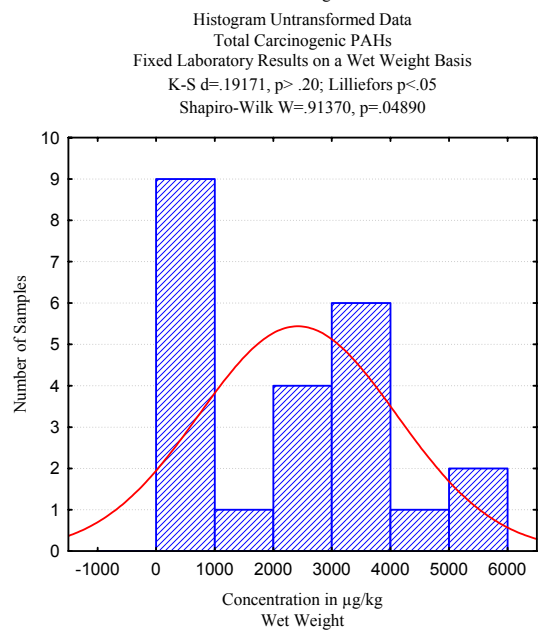
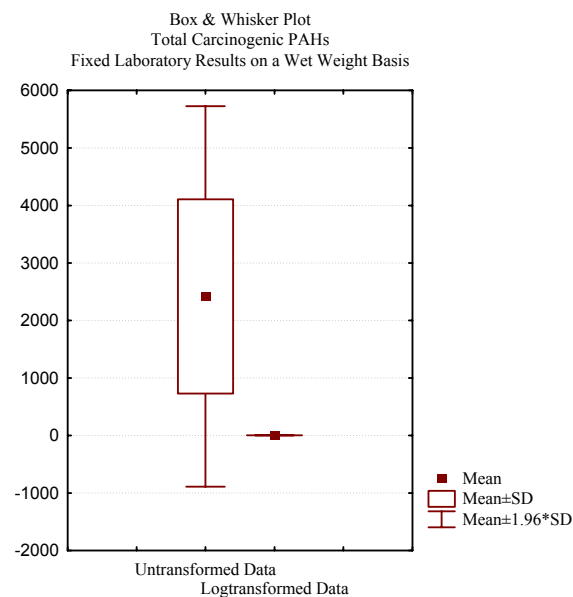
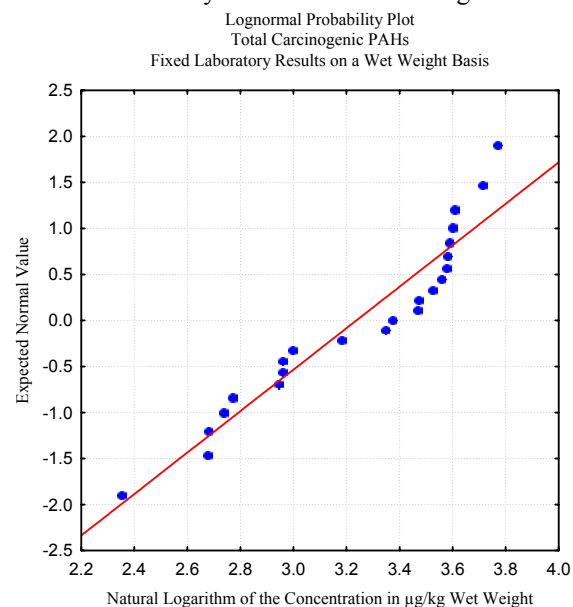
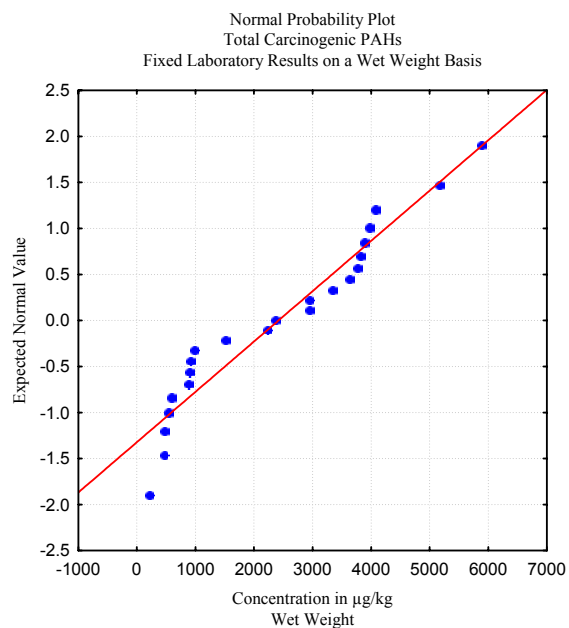
**Summary Statistics
Cos Cob Power Plant
Greenwich Connecticut**

Analysis	Method	Number of Samples	Number of Detections	% Detection	Units	Mean	Median	Geometric Mean	Minimum Detected Concentration	Maximum Detected Concentration	Standard Deviation	95% UCL
Arsenic	6010B	112	112	100	mg/Kg	23.2	9.80	10.8	0.75	152	34.3	29.7
Total Carcinogenic PAHs	8270C SIM	23	23	100	mg/Kg	2.42	2.37	1.73	0.225	5.89	1.69	3.15
Total PAHs	Field Test Kit	93	90	97	mg/Kg	180	61.8	64.5	0.1	1,860	269	235
TPH	8015	17	17	100	mg/Kg	773	411	425	13.8	3,040	802	1,190
TPH	Field Test Kit	93	92	99	mg/Kg	783	274	280	0.2	7,640	1,130	1,020
Aroclor 1260	Region 1 Mobile Lab	103	30	29	mg/Kg	1.35	0.25	0.40	0.14	56	5.72	2.47
All Aroclors	Region 1 Fixed Lab	135	13	10	mg/Kg	1.52	0.05	0.18	0.04	52	5.11	2.39

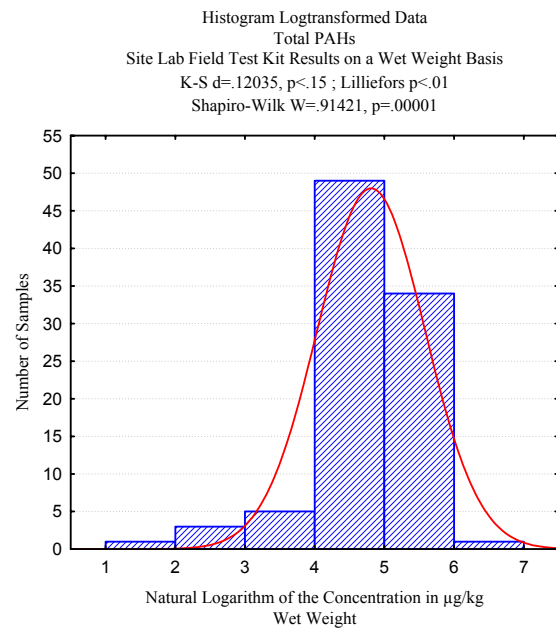
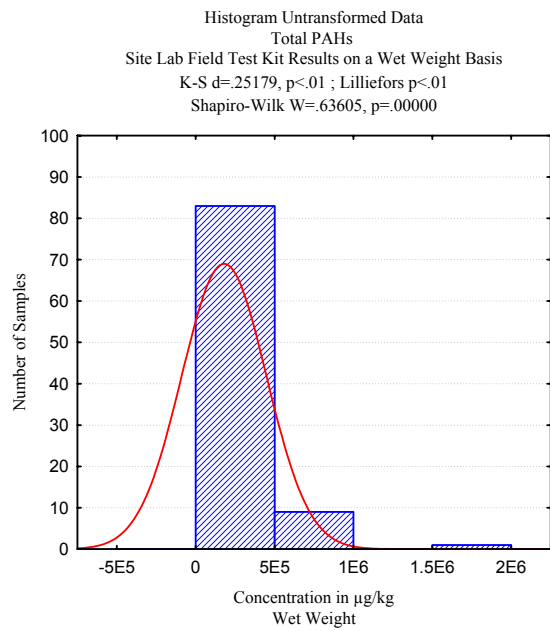
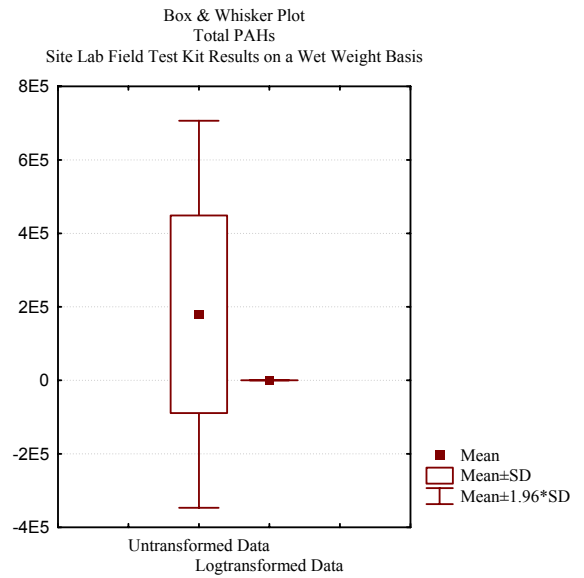
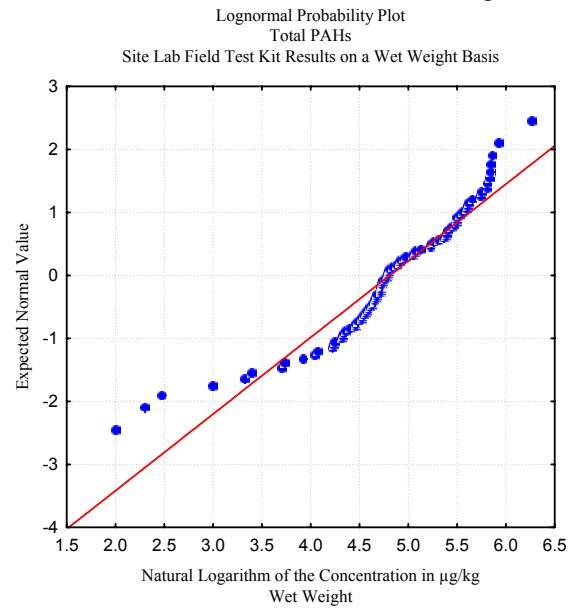
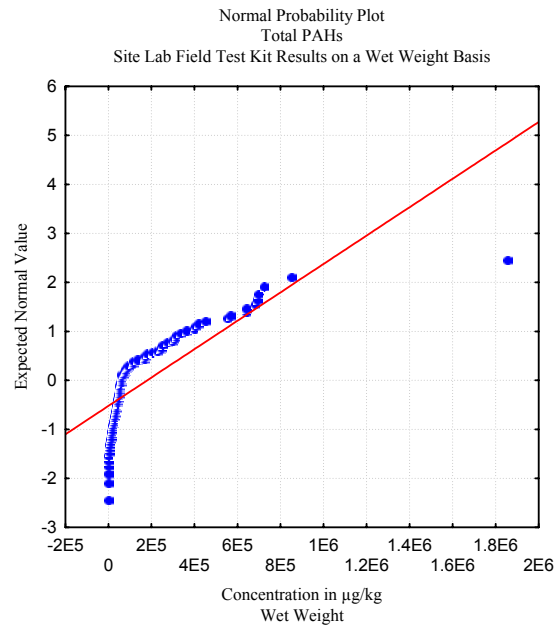
Arsenic Fixed Laboratory Results on a Dry Weight Basis



Total Carcinogenic PAHs Fixed Laboratory Results on a Wet Weight Basis

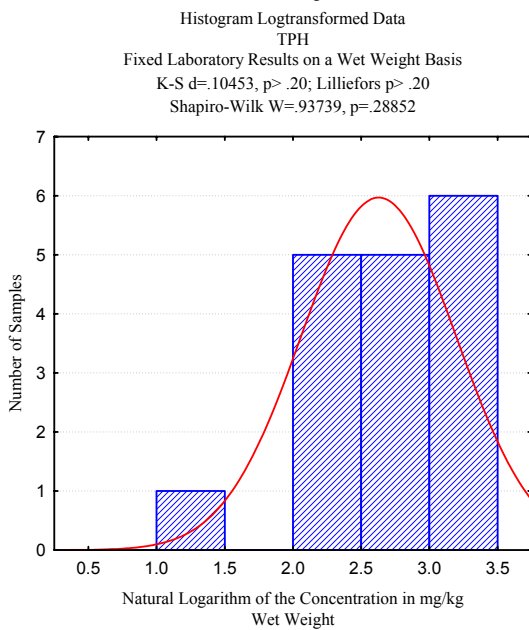
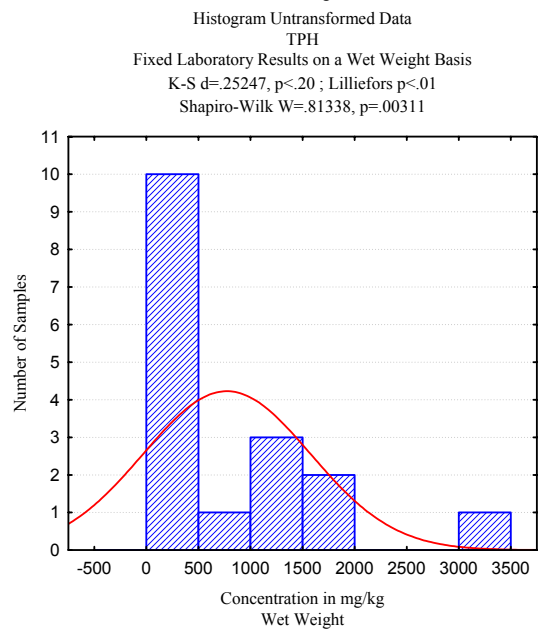
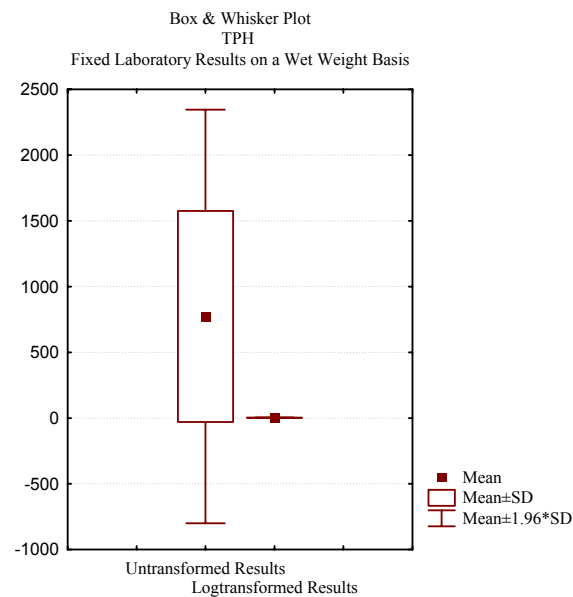
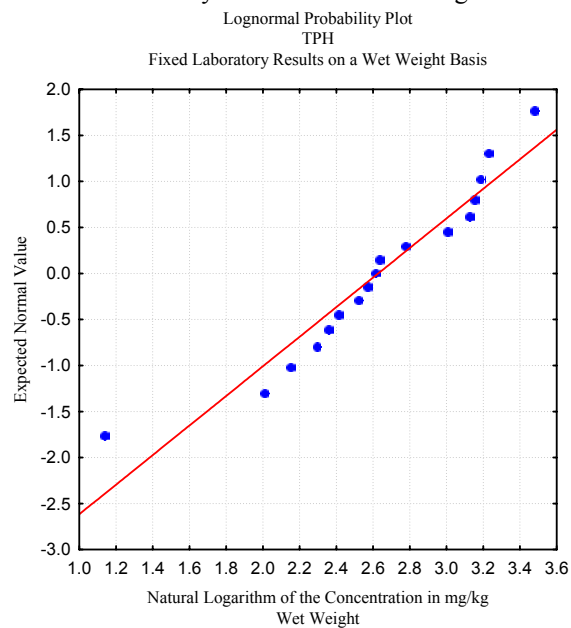
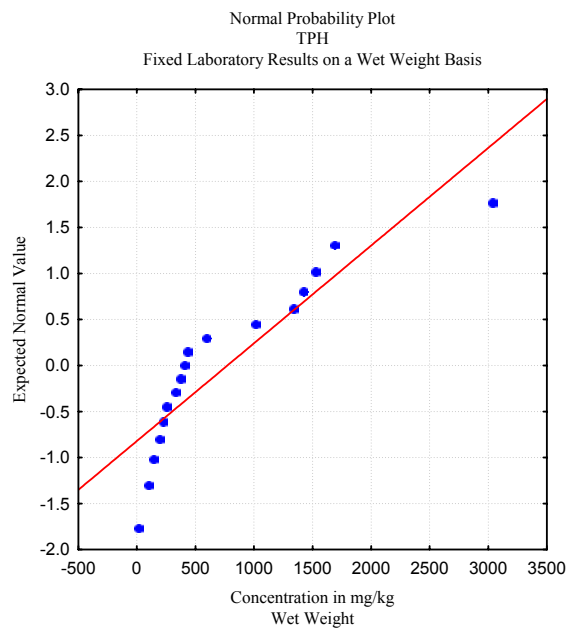


Total PAHs Site Lab Field Test Kit Results on a Wet Weight Basis



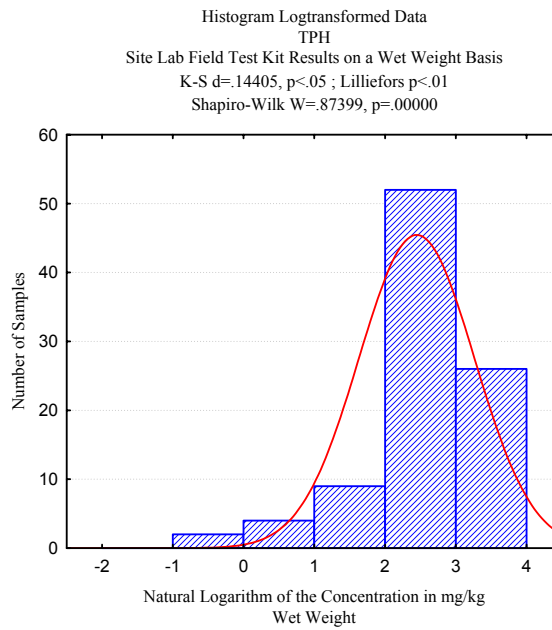
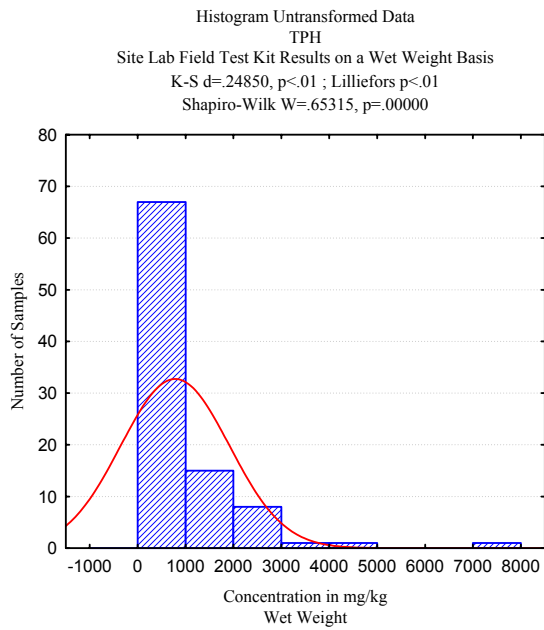
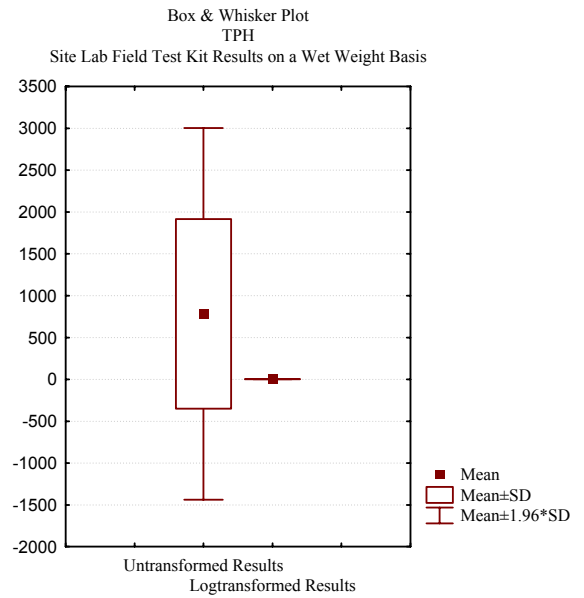
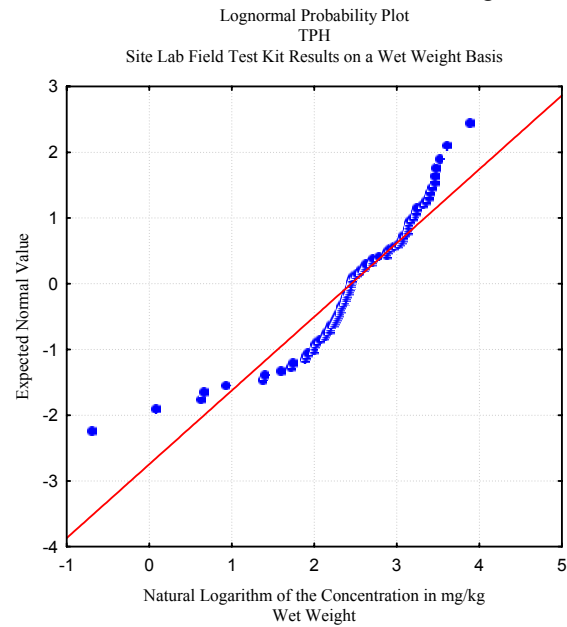
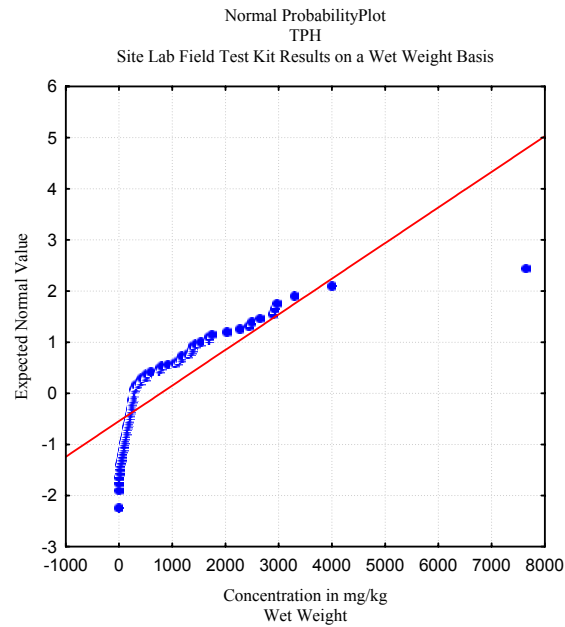
TPH

Fixed Laboratory Results on a Wet Weight Basis



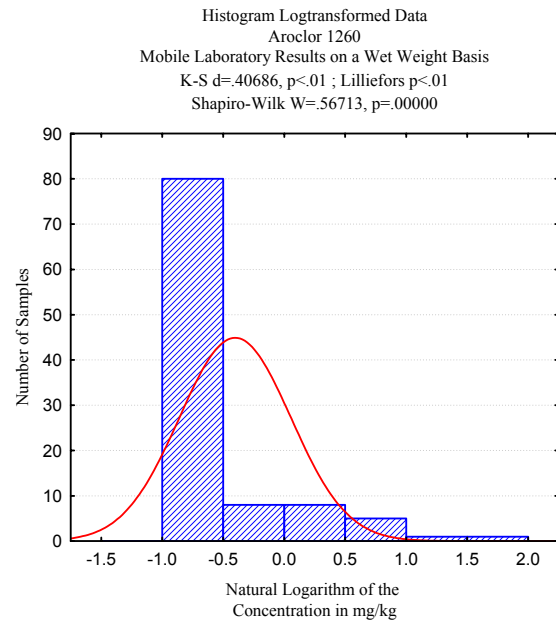
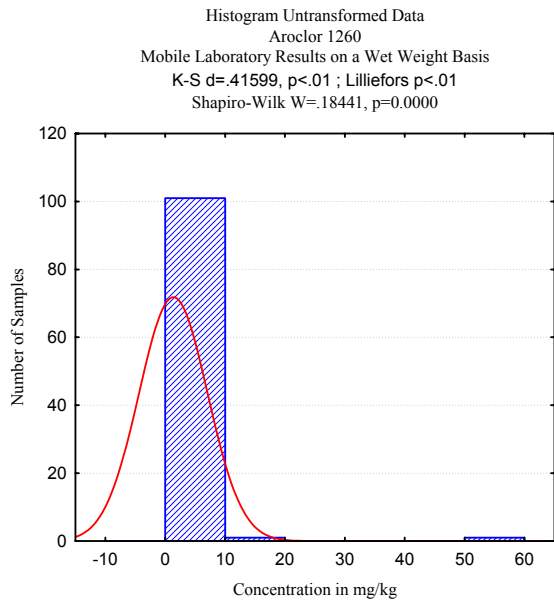
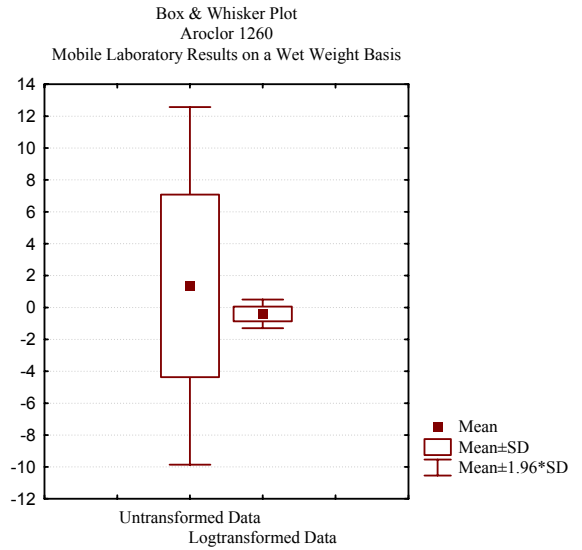
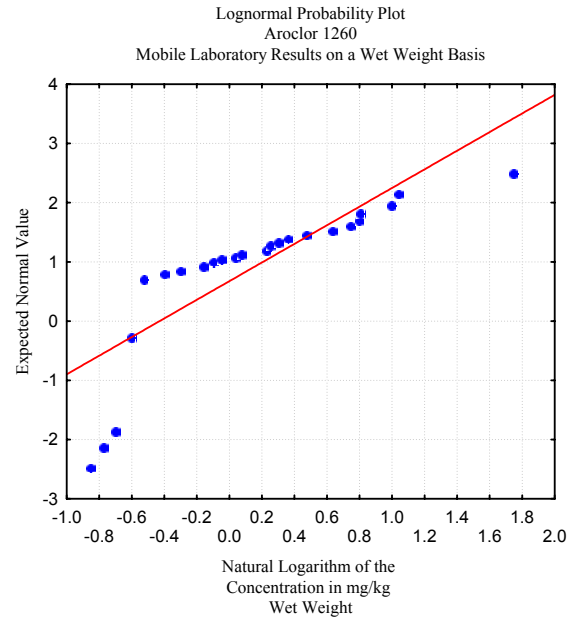
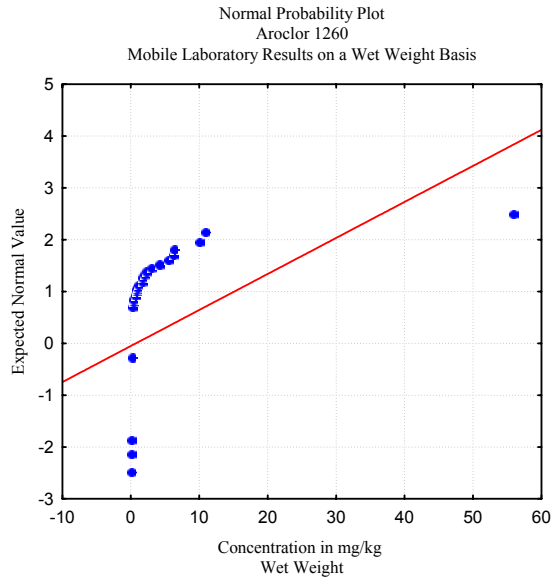
TPH

Site Lab Field Test Kit Results on a Wet Weight Basis



Aroclor 1260

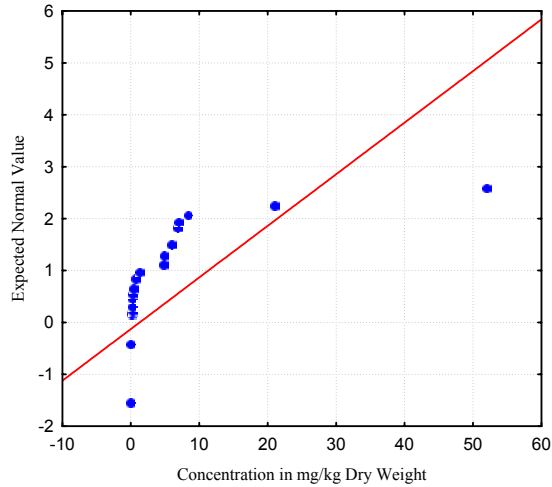
Mobile Laboratory Results on a Wet Weight Basis



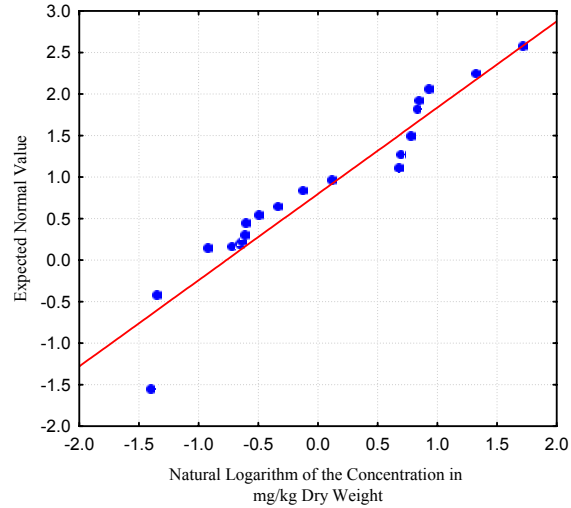
Aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, and 1268

Fixed Laboratory Results on a Dry Weight Basis

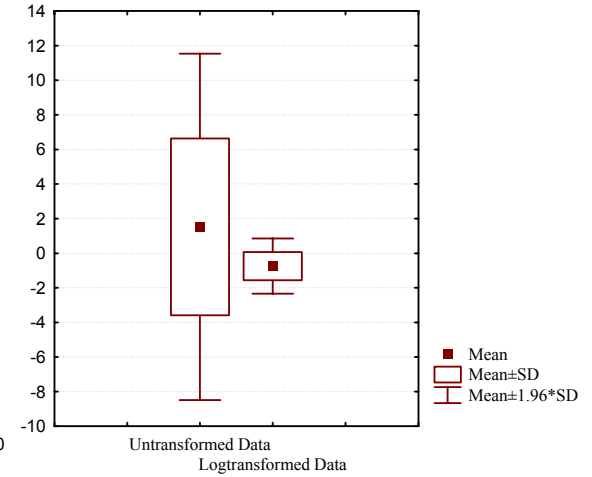
Normal Probability Plot
Aroclors 1016, 1221, 1232, 1242, 1248, 1254,
1260, 1262, and 1268
Fixed Laboratory Results on a Dry Weight Basis



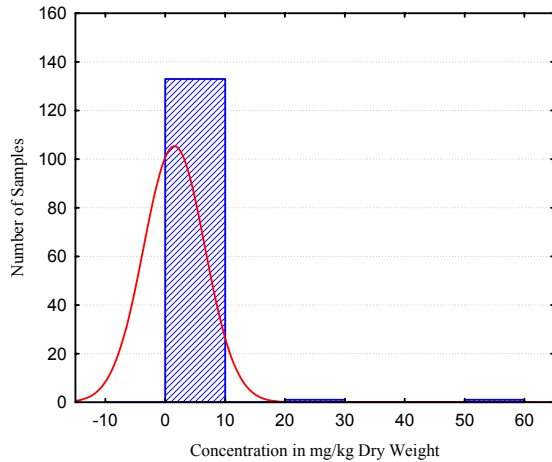
Lognormal Probability Plot
Aroclors 1016, 1221, 1232, 1242, 1248, 1254,
1260, 1262, and 1268
Fixed Laboratory Results on a Dry Weight Basis



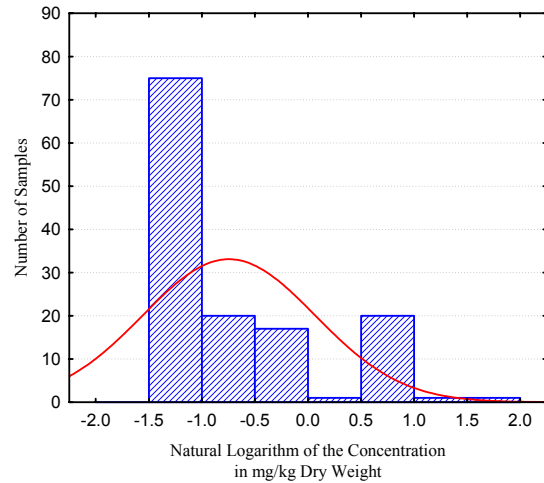
Box & Whisker Plot
Aroclors 1016, 1221, 1232, 1242, 1248, 1254,
1260, 1262, and 1268
Fixed Laboratory Results on a Dry Weight Basis



Histogram Untransformed Data
Aroclors 1016, 1221, 1232, 1242, 1248, 1254,
1260, 1262, and 1268
K-S d=.38962, p<.01 ; Lilliefors p<.01
Shapiro-Wilk W=.28667, p=.0000

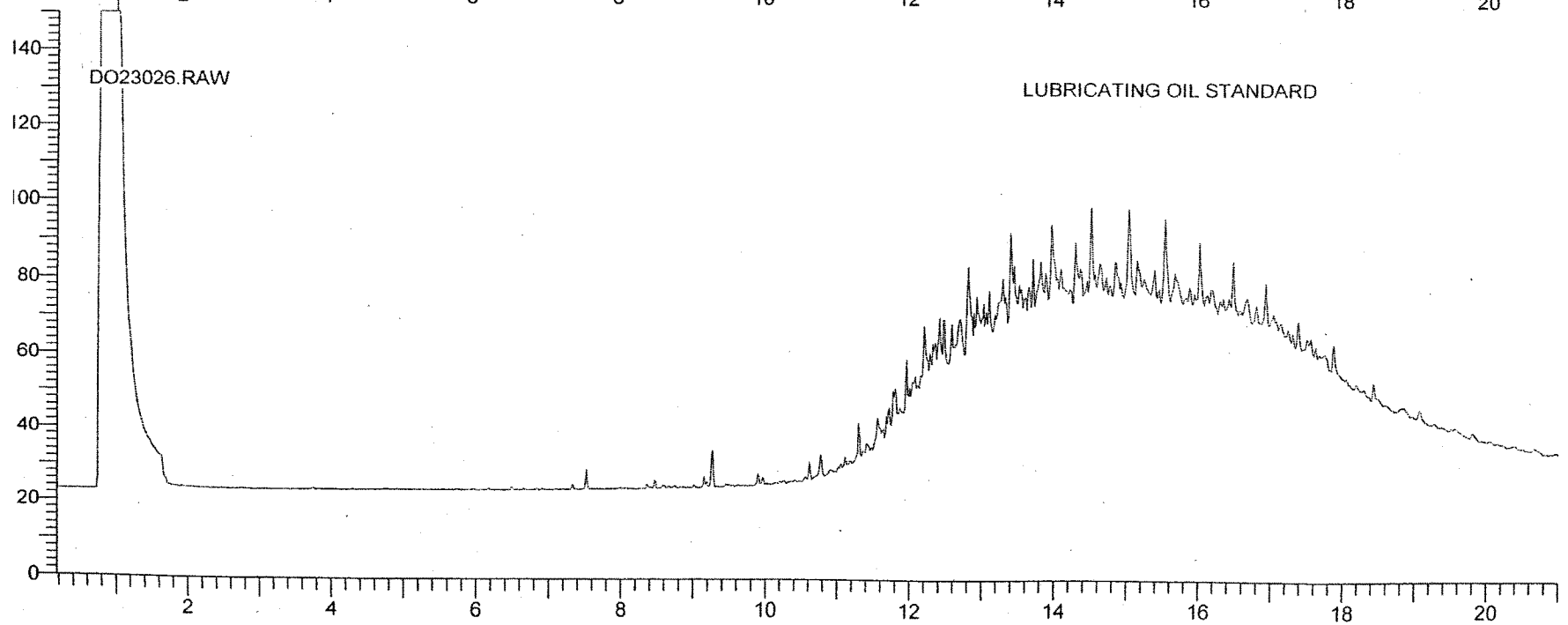
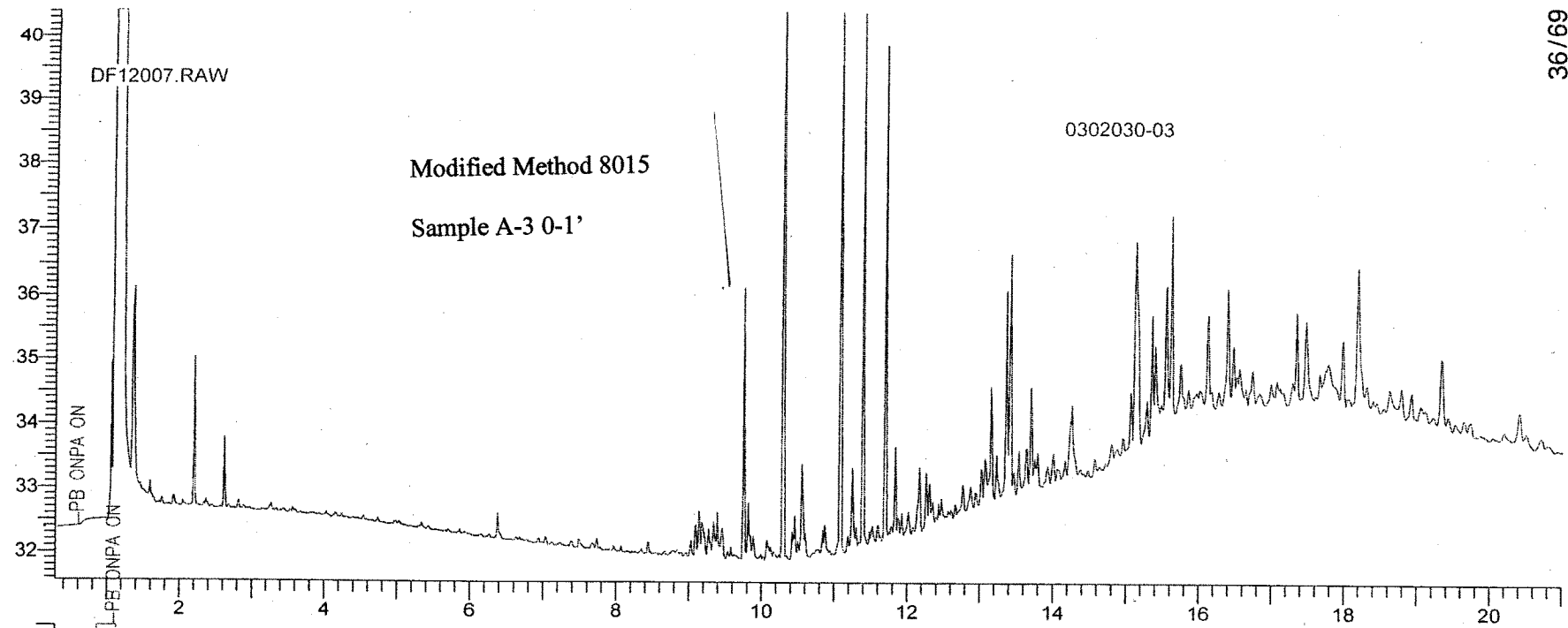


Histogram Logtransformed Data
Aroclors 1016, 1221, 1232, 1242, 1248, 1254,
1260, 1262, and 1268
K-S d=.32571, p<.01 ; Lilliefors p<.01
Shapiro-Wilk W=.76339, p=.0000



ENCLOSURE 3

**SELECTED CHROMATOGRAMS FOR SAMPLES
USED TO DEVELOP FIELD-BASED ACTION LEVELS**



04/24/2003 12:52 FAX 508 822 3288

WOODS HOLE GROUP

002

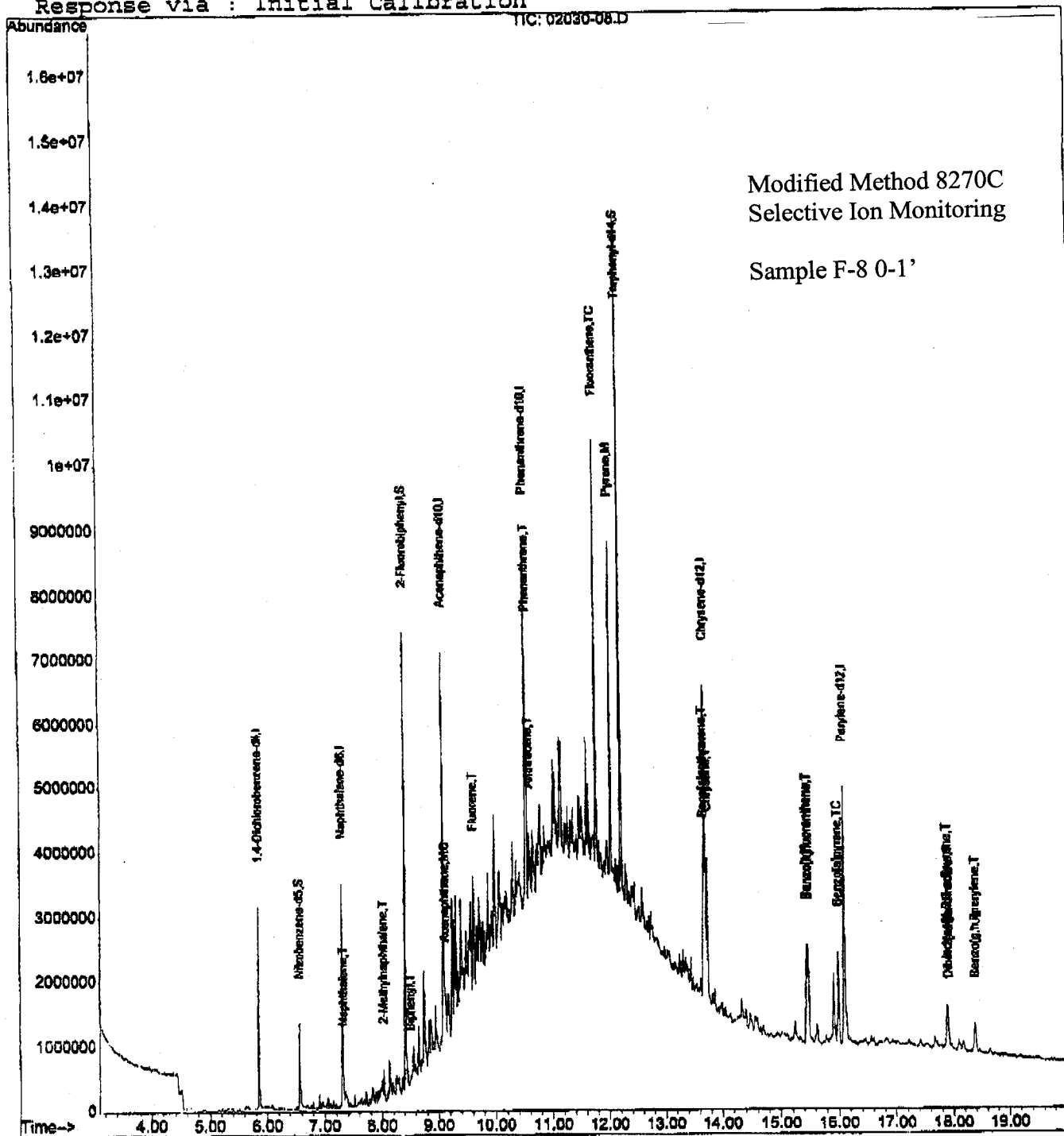
Quantitation Report

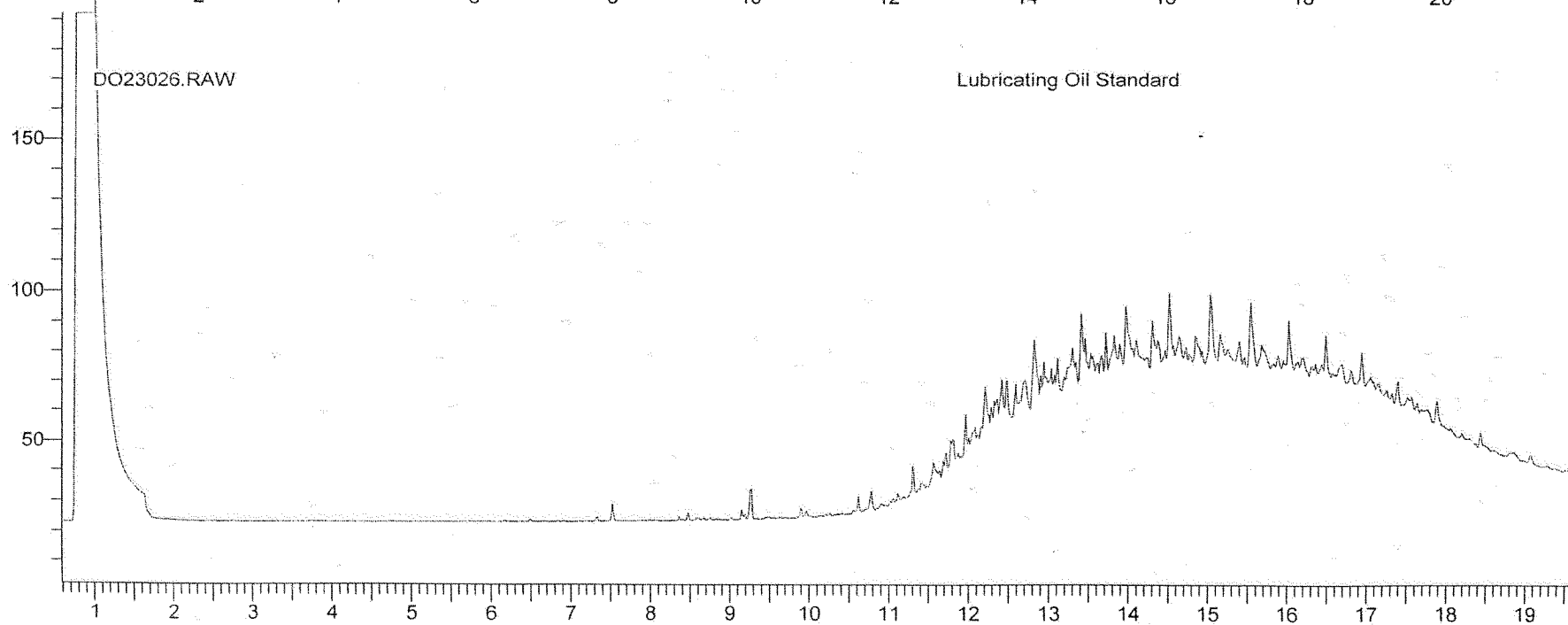
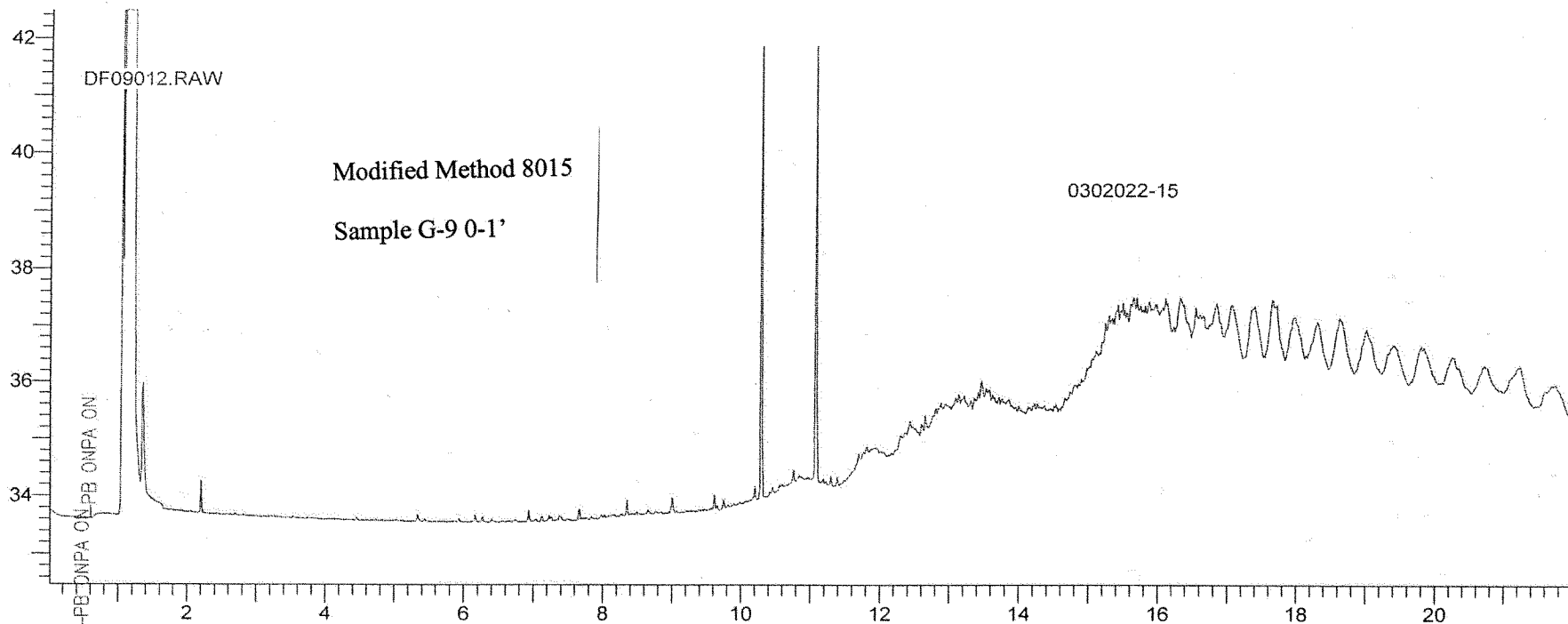
Data File : C:\HPCHEM\1\DATA\FEB14\02030-08.D
Acq On : 15 Feb 2003 12:03 am
Sample : 0302030-08
Misc : 1X
MS Integration Params: rteint.p
Quant Time: Feb 18 11:37 2003

Vial: 21
Operator: aja
Inst : HP 6890
Multiplr: 1.00

Quant Results File: PAHTIS1.RES

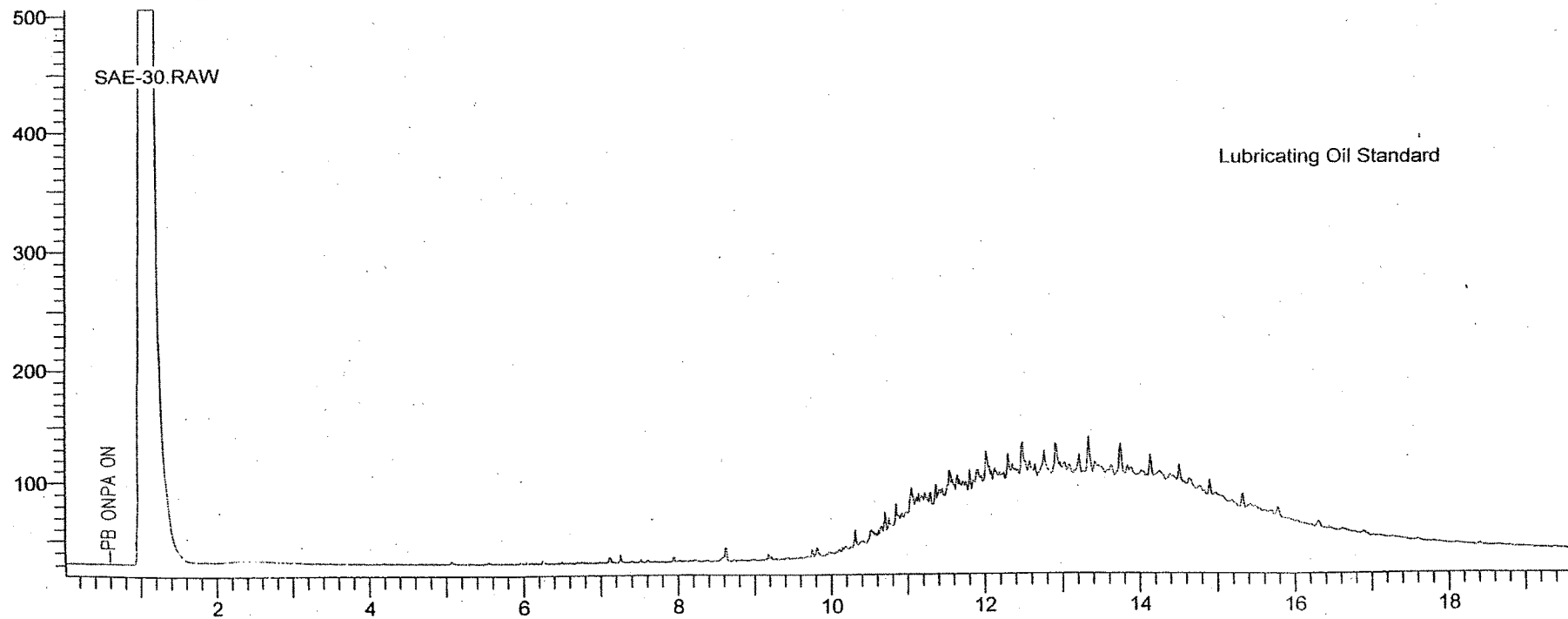
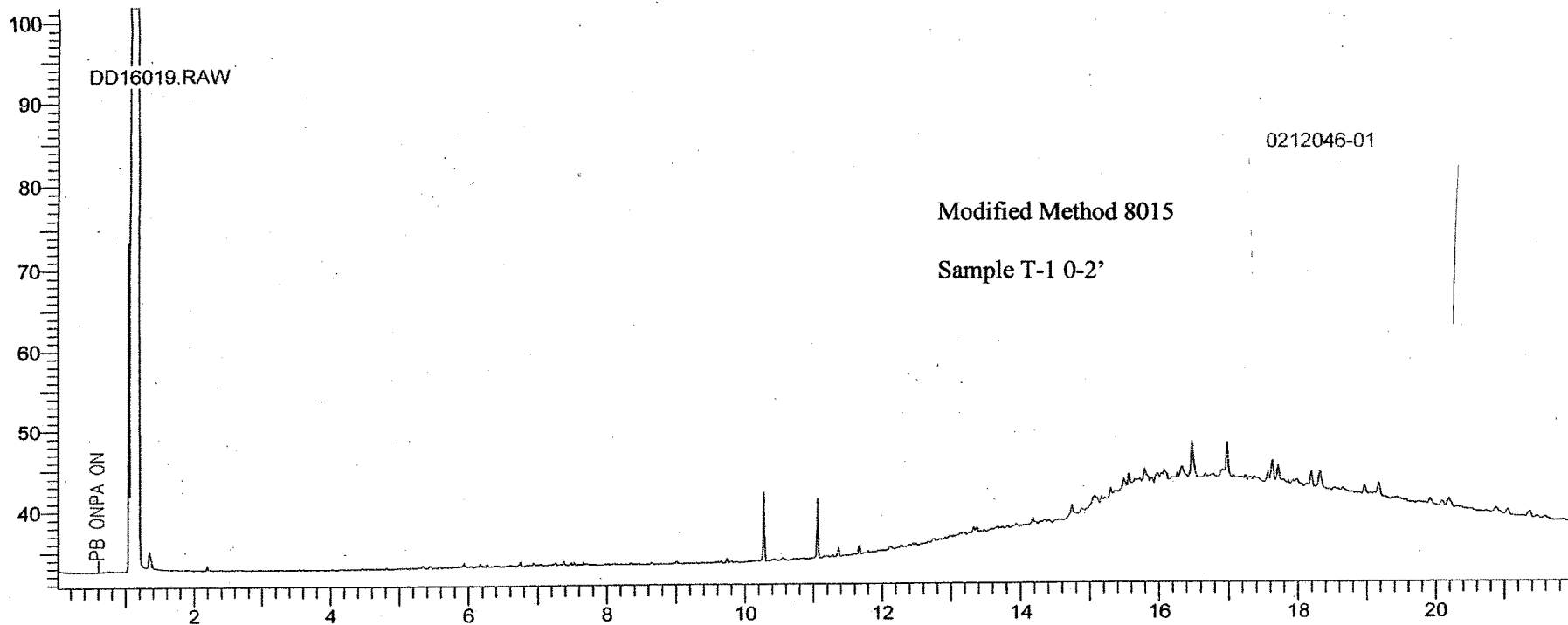
Method : O:\ORGANICS\METHODS\BNA2\2003\FRONT\PAHTIS1.M (RTE Integrato
Title : Semivolatiles by GC/MS
Last Update : Tue Feb 18 08:29:01 2003
Response via : Initial Calibration

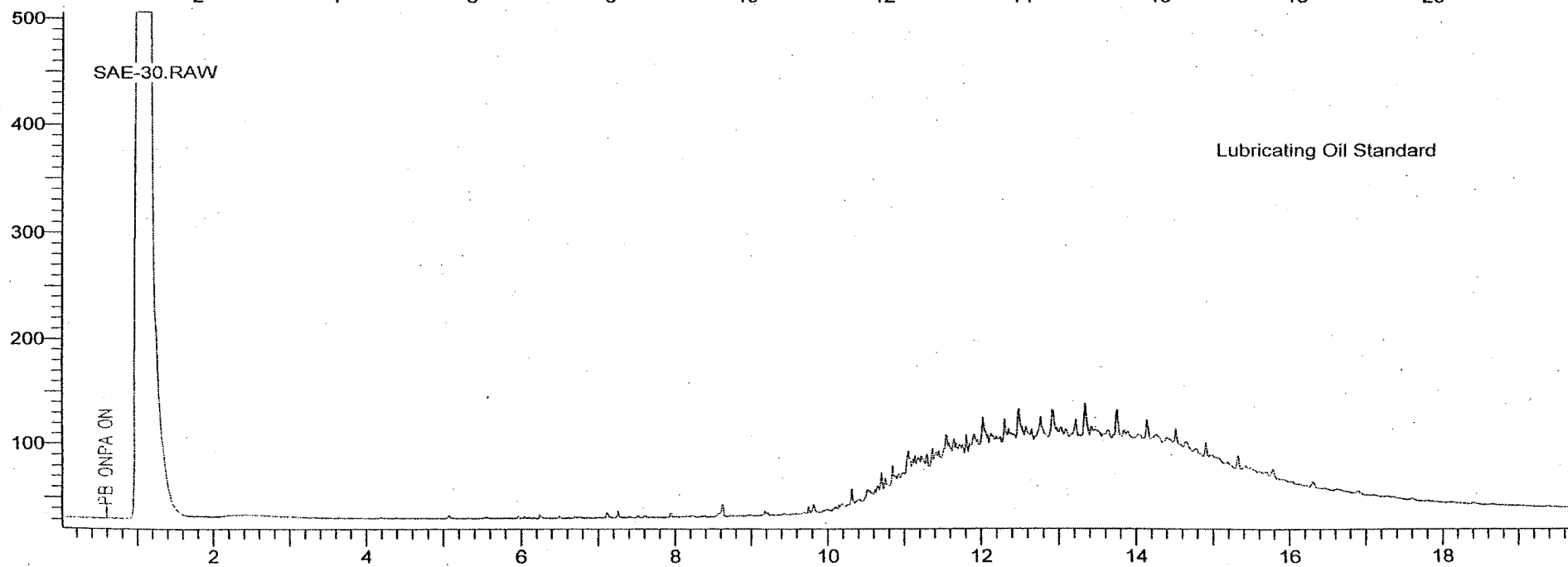
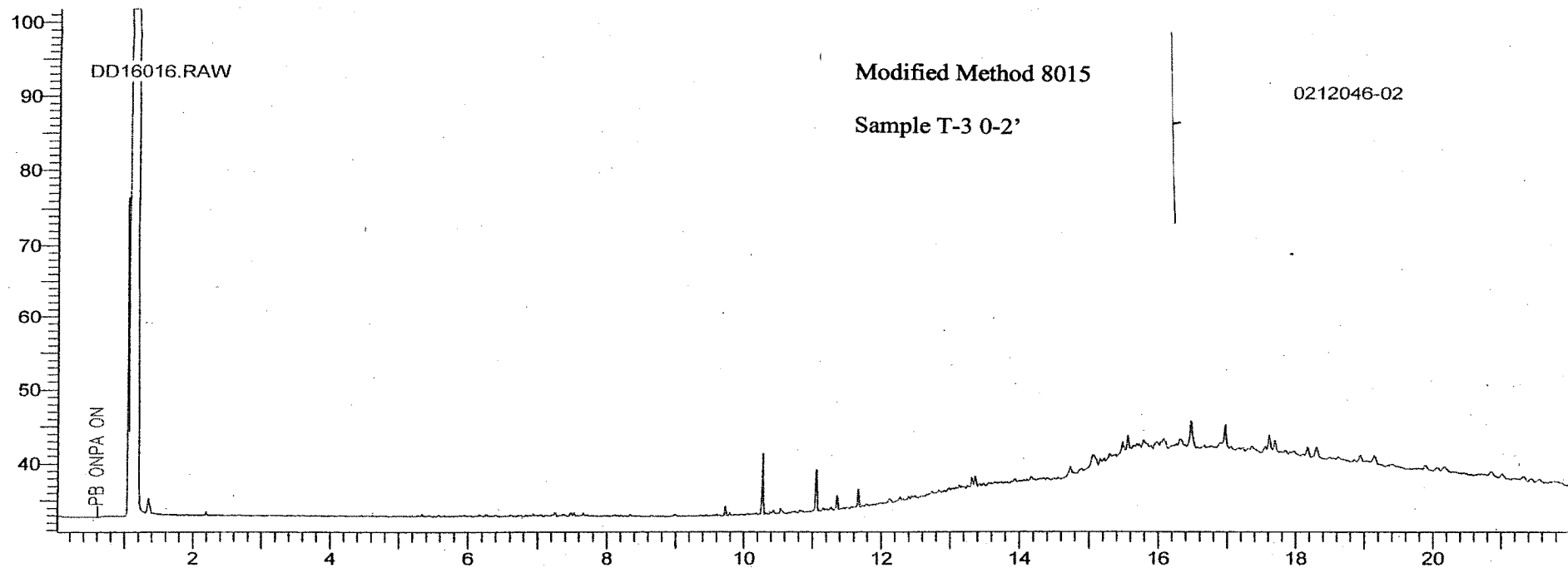


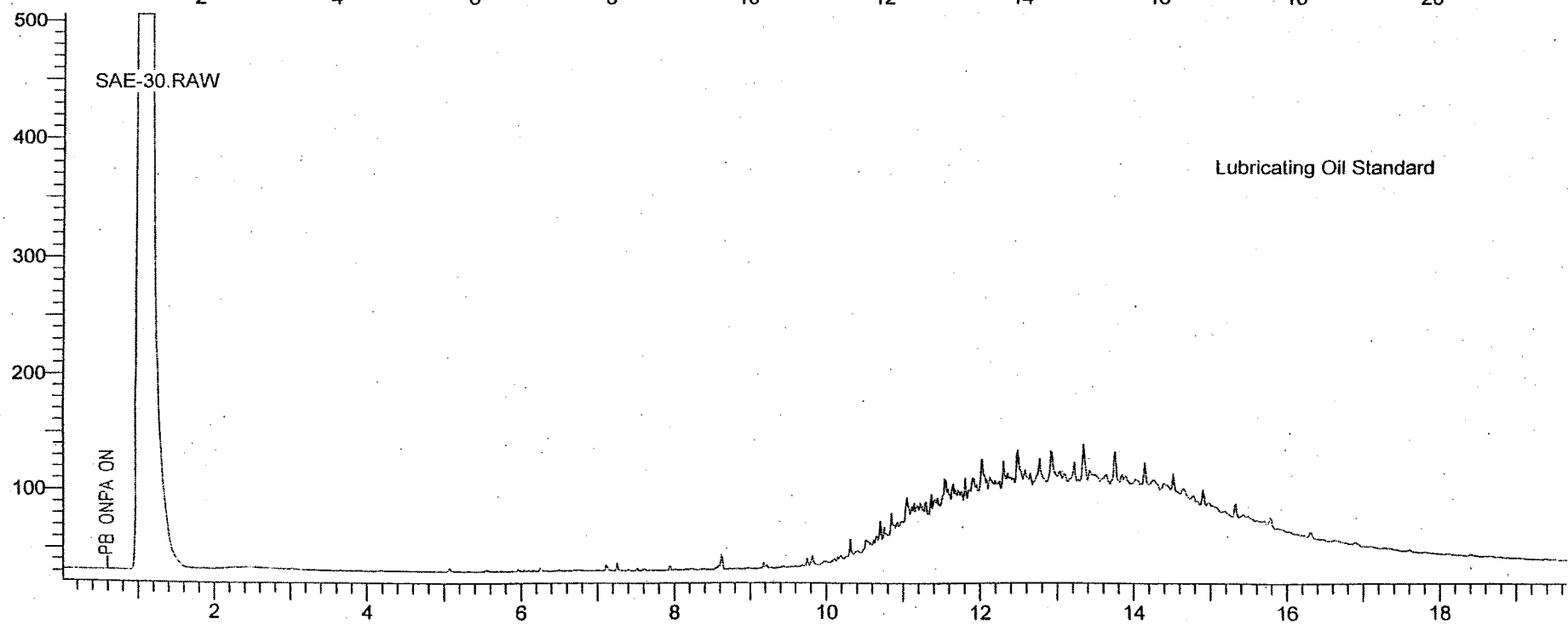
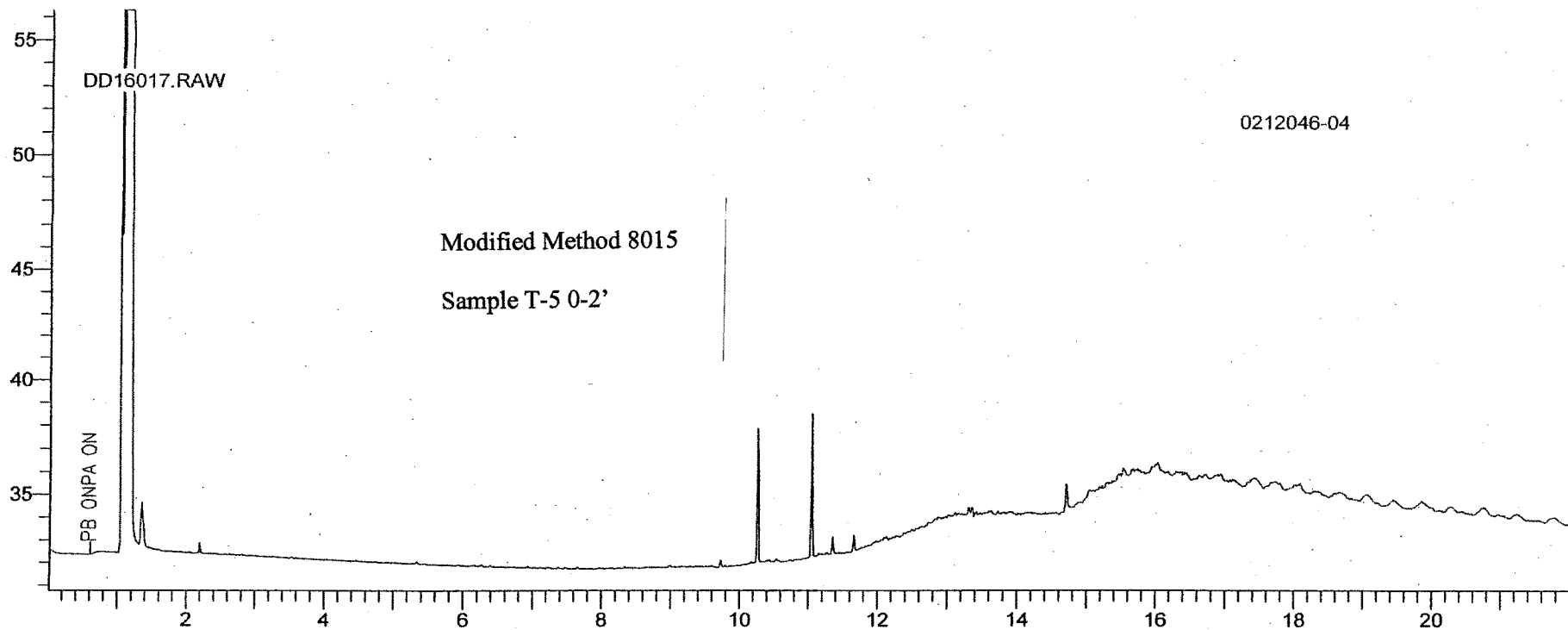


43/72

Page 2









Office of Solid Waste
and Emergency Response
(5102G)

EPA-542-R-04-008
June 2004
www.epa.gov
www.cluin.org

Official Business
Penalty for Private Use \$300