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August 1998

Environmental Technology Verification Report

Portable Gas Chromatograph/ Surface Acoustic Wave Detector

Electronic Sensor Technology 4100 Vapor Detector

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Electronic Sensor Technology 4100 Vapor Detector

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Superfund Innovative Technology
Evaluation Program

Notice

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM
VERIFICATION STATEMENT

TECHNOLOGY TYPE:	**POLYCHLORINATED BIPHENYL (PCB) FIELD ANALYTICAL TECHNIQUES**
APPLICATION:	**MEASUREMENT OF PCBs IN SOILS AND SOLVENT EXTRACTS**
TECHNOLOGY NAME:	**4100 VAPOR DETECTOR**
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The U.S. Environmental Protection Agency (EPA) has created a program to facilitate the deployment of innovative technologies through performance verification and information dissemination. The goal of the Environmental Technology Verification (ETV) Program is to further environmental protection by substantially accelerating the acceptance and use of improved and more cost effective technologies. The ETV Program is intended to assist and inform those involved in the design, distribution, permitting, and purchase of environmental technologies. This document summarizes the results of a demonstration of the Electronic Sensor Technology (EST) 4100 Vapor Detector.

PROGRAM OPERATION

The EPA, in partnership with recognized testing organizations, objectively and systematically evaluates the performance of innovative technologies. Together, with the full participation of the technology developer, they develop plans, conduct tests, collect and analyze data, and report findings. The evaluations are conducted according to a rigorous demonstration plan and established protocols for quality assurance. EPA's National Exposure Research Laboratory, which conducts demonstrations of field characterization and monitoring technologies, with the support of the U.S. Department of Energy's (DOE) Environmental Management (EM) program, selected Oak Ridge National Laboratory as the testing organization for the performance verification of polychlorinated biphenyl (PCB) field analytical techniques.

DEMONSTRATION DESCRIPTION

In July 1997, the performance of six PCB field analytical techniques was determined under field conditions. Each technology was independently evaluated by comparing field analysis results to those obtained using approved reference methods. Performance evaluation (PE) samples also were used to assess independently the accuracy and comparability of each technology.

The demonstration was designed to detect and measure PCBs in soil and solvent extracts. The demonstration was conducted at the Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee from July 22 through July 29. The study was conducted under two environmental conditions. The first site was outdoors, with naturally fluctuating temperature and relative humidity conditions. The second site was inside a controlled environmental chamber, with generally cooler temperatures and lower relative humidities. Multiple soil types, collected from sites in Ohio, Kentucky, and Tennessee, were analyzed in this study. Solutions of PCBs were also analyzed to simulate extracted surface wipe samples. The results of the soil and extract analyses conducted under field conditions by the technology were compared with results from analyses of

homogeneous replicate samples conducted by conventional EPA SW-846 methodology in an approved reference laboratory. Details of the demonstration, including a data summary and discussion of results, may be found in the report entitled *Environmental Technology Verification Report: Portable Gas Chromatograph/Surface Acoustic Wave Detector, Electronic Sensor Technology 4100 Vapor Detector*, EPA/600/R-98/114.

TECHNOLOGY DESCRIPTION

A handheld, portable (35 lbs.) chromatography system equipped with a non-specific Surface Acoustic Wave (SAW) detector is used to speciate and quantify PCBs. The SAW detector is an integrating mass detector (micro-balance) with the ability to quantify chromatographic peaks, with peak widths measured in milliseconds. Measurement speed makes the instrument well suited to rapid screening of soil samples. Early separation of those soil samples below the regulatory level from those which require laboratory validation by GC/MS reduces the cost associated with site characterization and monitoring.

A sampling pump and loop trap are used to sample and inject analyte into a GC capillary column. Speciation is based upon retention time measurements using a temperature programmed DB-5 column. Quantification is based upon the frequency shift produced by the PCB congeners as they exit the GC column. By focusing the effluent onto a specific area on the surface of a temperature controlled piezoelectric crystal, high sensitivity is achieved with a 10 second analysis time. The 4100 Vapor Detector is able to screen selectively and quantify PCB levels of Aroclors in soil and flyash.

VERIFICATION OF PERFORMANCE

The following performance characteristics of the 4100 Vapor Detector were observed:

Detection limits: EPA defines the method detection limit (MDL) as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. Because there was a significant "site effect" inherent to the PE samples, separate MDLs were calculated for both the outdoor and chamber conditions. The MDL was calculated to be 26 ppm under outdoor conditions and 62 ppm under chamber conditions.

Throughput: Throughput was 5 to 6 samples/hour under outdoor conditions and 10 samples/hour under chamber conditions. This rate included sample preparation and analysis.

Ease of Use: Two operators were used for the demonstration due to the number of samples and working conditions, but the technology can be run by a single operator. Operators generally require several hours of training and should have a basic knowledge of gas chromatographic techniques. These methods should be used by, or under the supervision of, analysts experienced in the use of sampling techniques and gas chromatography.

Completeness: The 4100 generated results for all 232 PCB samples for a completeness of 100%.

Blank results: EST did not specify a method detection limit prior to the demonstration, therefore, any PCB concentration that was detected was considered real. PCBs were detected in all of the soil blanks, resulting in 100% false positive results. PCBs were also detected in 3 of 8 of the extract blanks or 38% false positive results. The 4100 reported 5% false negative results for soils and no false negative results for extracts.

Precision: The overall precision, based on average relative standard deviations (RSDs), was 87% for soil samples and 65% for extract samples. The 4100 was imprecise compared to the reference laboratory's precision (21% for soils and 14% for extracts).

Accuracy: Accuracy was assessed using PE soil and extract samples. The study was conducted under two experimental conditions to detect and control for "site effects." The data showed that the 4100 exhibited a significant site effect, and the results were generally biased high. The overall accuracy, based on average percent recoveries, was 177% (outdoor

site) and 631% (chamber) for PE soil samples. For the extract samples, the results indicated a high bias (267% recovery) on the lower concentration samples and a low bias on the higher concentration samples (54% recovery).

Comparability: The demonstration showed that the 4100 generated data that exhibited low correlation to the reference laboratory data. The coefficient of determination (R^2) which is a measure of the degree of correlation between the reference laboratory and the 4100 data was 0.177 when all soil samples (0 to 700 ppm) were considered. For the concentration range from 0 to 125 ppm, the R^2 value was 0.115. Most of the percent difference values were greater than 100%, when the 4100 results were compared directly with the reference laboratory results. The comparability of the extract samples also exhibited low correlation.

Regulatory Decision-making: One objective of this demonstration was to assess the technology's ability to perform at regulatory decision-making levels for PCBs, specifically 50 ppm for soils and 100 µg/100cm^2 for surface wipes. For PE and environmental soil samples in the range of 40 to 60 ppm, the precision was low (72% RSD) and the accuracy was variably biased with both high and low recoveries (an average recovery of 132%). For extract samples representing surface wipe sample concentrations of 100 µg/100cm^2 and 1000 µg/100cm^2 (assuming a 100 cm^2 wipe sample), measurements were also imprecise (65% RSD) and indicated a high bias (161% recovery).

Data quality levels: The overall performance of the EST 4100 Vapor Detector was characterized as biased and imprecise. EST is working to improve the performance of the methodology.

The results of the demonstration show that certain cautions should be considered when using this technology for PCB analysis due to its bias and imprecision. This technology should be employed in well-defined applications for PCB analysis, and only in conjunction with a stringent quality assurance plan. As with any technology selection, the user must determine if the technology is appropriate for the application and the project data quality objectives. For more information on this and other verified technologies, visit the ETV web site at *http://www.epa.gov/etv*.

Gary J. Foley, Ph.D.
Director
National Exposure Research Laboratory
Office of Research and Development

NOTICE: EPA verifications are based on an evaluation of technology performance under specific, predetermined criteria and the appropriate quality assurance procedures. EPA makes no expressed or implied warranties as to the performance of the technology and does not certify that a technology will always, under circumstances other than those tested, operate at the levels verified. The end user is solely responsible for complying with any and all applicable Federal, State, and Local requirements.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's natural resources. The National Exposure Research Laboratory (NERL) is EPA's center for the investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. NERL's research goals are to (1) develop and evaluate technologies for the characterization and monitoring of air, soil, and water; (2) support regulatory and policy decisions; and (3) provide the science support needed to ensure effective implementation of environmental regulations and strategies.

EPA created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative technologies through performance verification and information dissemination. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. The ETV Program is intended to assist and inform those involved in the design, distribution, permitting, and purchase of environmental technologies. This program is administered by NERL's Environmental Sciences Division in Las Vegas, Nevada.

The U.S. Department of Energy's (DOE) Environmental Management (EM) program has entered into active partnership with EPA, providing cooperative technical management and funding support. DOE EM realizes that its goals for rapid and cost effective cleanup hinges on the deployment of innovative environmental characterization and monitoring technologies. To this end, DOE EM shares the goals and objectives of the ETV.

Candidate technologies for these programs originate from the private sector and must be commercially ready. Through the ETV Program, developers are given the opportunity to conduct rigorous demonstrations of their technologies under realistic field conditions. By completing the evaluation and distributing the results, EPA establishes a baseline for acceptance and use of these technologies.

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Abstract

In July 1997, the U.S. Environmental Protection Agency (EPA) conducted a demonstration of polychlorinated biphenyl (PCB) field analytical techniques. The purpose of this demonstration was to evaluate field analytical technologies capable of detecting and quantifying PCBs in soils and solvent extracts. The fundamental objectives of this demonstration were (1) to obtain technology performance information using environmental and quality control samples, (2) to determine how comparable the developer field analytical results were with conventional reference laboratory results, and (3) to report on the logistical operation of the technology. The demonstration design was subjected to extensive review and comment by EPA's National Exposure Research Laboratory (NERL) Environmental Sciences Division in Las Vegas, Nevada; Oak Ridge National Laboratory (ORNL); EPA Regional Offices; the U.S. Department of Energy (DOE); and the technology developers.

The demonstration study was conducted at ORNL under two sets of environmental conditions. The first site was outdoors, with naturally variable temperature and relative humidity conditions typical of eastern Tennessee in the summer. A second site was located inside a controlled environmental chamber having lower, and relatively stable, temperature and relative humidity conditions. The test samples analyzed during this demonstration were performance evaluation soil, environmental soil, and extract samples. Actual environmental soil samples, collected from sites in Ohio, Kentucky, and Tennessee, were analyzed, and ranged in concentration from 0.1 to 700 parts per million (ppm). Extract samples were used to simulate surface wipe samples, and were evaluated at concentrations ranging from 0 to 100 µg/mL. The reference laboratory method used to evaluate the comparability of data was EPA SW-846 Method 8081.

The field analytical technologies tested in this demonstration were the L2000 PCB/Chloride Analyzer (Dexsil Corporation), the PCB Immunoassay Kit (Hach Company), the 4100 Vapor Detector (Electronic Sensor Technology), and three immunoassay kits: D TECH, EnviroGard, and RaPID Assay System (Strategic Diagnostics Inc.). The purpose of an Environmental Technology Verification Report (ETVR) is to document the demonstration activities, present demonstration data, and verify the performance of the technology. This ETVR presents information regarding the performance of Electronic Sensor Technology's 4100 Vapor Detector. Separate ETVRs have been published for the other technologies demonstrated.

The 4100 Vapor Detector is a handheld, portable (35-lb) chromatography system equipped with a nonspecific surface acoustic wave (SAW) detector designed to speciate and quantify PCBs. The SAW detector is an integrating mass detector (microbalance) with the ability to quantify chromatographic peaks, with peak widths measured in milliseconds. A sampling pump and loop trap are used to sample and inject analyte into the gas chromatography capillary column. Speciation is based upon retention time measurements using a temperature-programmed DB-5 column. Quantification is based upon the frequency shift produced by the PCB congeners as they exit the column. By focusing the effluent onto a specific area

on the surface of a temperature-controlled piezoelectric crystal, high sensitivity is achieved with a 10-s analysis time. Because of the short analysis time, Aroclor speciation is limited to low, medium, and high classifications, based on the percentage of chlorine within each Aroclor.

The 4100's quantitative results were based on initial calibrations. The method detection limit (MDL) is often defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The field-based MDLs were site-specific and were calculated to be 26 ppm under outdoor conditions and 62 ppm under chamber conditions. Electronic Sensor Technology did not specify an MDL prior to the demonstration. The study was conducted under two experimental conditions to detect and control "site effects" (i.e., differences in performance due to environmental conditions). In general, the 4100's results for soils were biased high and exhibited a significant site effect (177% recovery outdoors and 631% recovery in the chamber). For the extract samples, the results indicated a high bias (267% recovery) on the lower-concentration samples and a low bias on the higher-concentration samples (54% recovery). The overall precision, based on relative standard deviation (RSD), for soil samples was 87% compared with the reference laboratory's 21%. The precision for the extract samples was also low at 65% RSD. Comparability, based on coefficients of determination (R^2), was 0.177 for all soil samples (0 to 700 ppm), where an R^2 of 1.0 denotes perfect correlation. Most of the percent difference values were greater than 100% when the 4100 results were compared directly with the reference laboratory results. The 4100 also exhibited low correlation for the extract samples.

During the demonstration the 4100 was found to be light, easily transportable, and rugged. The system is shock mounted into a field-portable fiberglass shipping case that can be checked as airplane baggage. The 4100 was simple to operate in the field, requiring less than 1 h for two operators to set up initially and prepare for sample analysis. Operators generally require several hours of training and should have a basic knowledge of gas chromatographic techniques. These methods should be used by, or under the supervision of, analysts experienced in the use of sampling techniques and gas chromatography. Once operational, the 4100 had a throughput of 5 to 10 samples per hour during the demonstration. Measurement speed makes the instrument well suited to rapid screening of soil samples. Early separation of those soil samples below the regulatory level from those that require laboratory validation by gas chromatography/mass spectroscopy reduces the cost associated with site characterization and monitoring. The overall performance of the Electronic Sensor Technology 4100 Vapor Detector was characterized as biased, imprecise, and having significant "site effects." EST is working to improve the performance of the methodology for PCB analysis.

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List of Abbreviations and Acronyms

AL	action level
ANOVA	analysis of variance
ASTM	American Society for Testing and Materials
BHC	benzenehexachloride
C	concentration at which the false positive error rate is specified
CASD	Chemical and Analytical Sciences Division
CCV	continuing calibration verification standard
CSCT	Consortium for Site Characterization Technology
DCB	decachlorobiphenyl
DOE	U. S. Department of Energy
DQO	data quality objective
EM	Environmental Management
EPA	U. S. Environmental Protection Agency
ERA	Environmental Resource Associates
EST	Electronic Sensor Technology
ETTP	East Tennessee Technology Park
ETV	Environmental Technology Verification Program
ETVR	Environmental Technology Verification Report
EvTEC	Environmental Technology Evaluation Center
fn	false negative result
FN	false negative decision error rate
fp	false positive result
FP	false positive decision error rate
GC	gas chromatography
HEPA	high-efficiency particulate air
ID	identifier
INEL	Idaho National Engineering Laboratory
LCS	laboratory control sample

LMER	Lockheed Martin Energy Research
LMES	Lockheed Martin Energy Systems
LV	Las Vegas
MDL	method detection limit
MS	matrix spike
MSD	matrix spike duplicate
n	number of samples
NERL	National Exposure Research Laboratory
NRC	Nuclear Regulatory Commission
OPDDT	open path direct desorption tube
ORD	EPA's Office of Research and Development
ORNL	Oak Ridge National Laboratory
ORO	Oak Ridge Operations
OTD	open tubular desorption
PARCC	precision, accuracy, representativeness, completeness, comparability
PCB	polychlorinated biphenyl
PE	performance evaluation
ppb	parts per billion
ppm	parts per million; equivalent units: mg/kg for soils and µg/mL for extracts
Pr	probability
QA	quality assurance
QC	quality control
R^2	coefficient of determination
RDL	reporting detection limit
RH	relative humidity
RFD	request for disposal
RPD	relative percent difference
RSD	percent relative standard deviation
RT	regulatory threshold
S^2	variance for the measurement
SARA	Superfund Amendments and Reauthorization Act of 1986
SAW	surface acoustic wave
SD	standard deviation

SDI	Strategic Diagnostics Inc.
SITE	Superfund Innovative Technology Evaluation
SMO	sample management office
SOP	standard operating procedure
SSM	synthetic soil matrix
TCMX	tetrachloro-m-xylene
TSCA	Toxic Substance Control Act
Z_{1-p}	the $(1 - p)^{th}$ percentile for the standard normal distribution
% D	percent difference

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Section 1
Introduction

The performance evaluation of innovative and alternative environmental technologies is an integral part of the U.S. Environmental Protection Agency's (EPA's) mission. Early efforts focused on evaluating technologies that supported the implementation of the Clean Air and Clean Water Acts. In 1987, the Agency began to evaluate the cost and performance of remediation and monitoring technologies under the Superfund Innovative Technology Evaluation (SITE) program. This was in response to the mandate in the Superfund Amendments and Reauthorization Act (SARA) of 1986. In 1990, the U.S. Technology Policy was announced. This policy placed a renewed emphasis on "making the best use of technology in achieving the national goals of improved quality of life for all Americans, continued economic growth, and national security." In the spirit of the Technology Policy, the Agency began to direct a portion of its resources toward the promotion, recognition, acceptance, and use of U.S.-developed innovative environmental technologies both domestically and abroad.

The Environmental Technology Verification (ETV) Program was created by the Agency to facilitate the deployment of innovative technologies through performance verification and information dissemination. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. The ETV Program is intended to assist and inform those involved in the design, distribution, permitting, and purchase of environmental technologies. The ETV Program capitalizes upon and applies the lessons that were learned in the implementation of the SITE Program to the verification of twelve categories of environmental technology: Drinking Water Systems, Pollution Prevention/Waste Treatment, Pollution Prevention/ Innovative Coatings and Coatings Equipment, Indoor Air Products, Air Pollution Control, Advanced Monitoring Systems, EvTEC (an independent, private-sector approach), Wet Weather Flow Technologies, Pollution Prevention/Metal Finishing, Source Water Protection Technologies, Site Characterization and Monitoring Technology [also referred to as the Consortium for Site Characterization Technology (CSCT)], and Climate Change Technologies. The performance verification contained in this report was based on the data collected during a demonstration of polychlorinated biphenyl (PCB) field analytical technologies. The demonstration was administered by CSCT.

For each pilot, EPA utilizes the expertise of partner "verification organizations" to design efficient procedures for conducting performance tests of environmental technologies. To date, EPA has partnered with federal laboratories and state, university, and private sector entities. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from all major stakeholder/customer groups associated with the technology area.

In July 1997, CSCT, in cooperation with the U.S. Department of Energy's (DOE's) Environmental Management (EM) Program, conducted a demonstration to verify the performance of six field analytical

technologies for PCBs: the L2000 PCB/Chloride Analyzer (Dexsil Corporation), the PCB Immunoassay Kit (Hach Company), the 4100 Vapor Detector [Electronic Sensor Technology (EST)], and three immunoassay kits from Strategic Diagnostics Inc.: D TECH, EnviroGard, and RaPID Assay System. This environmental technology verification report (ETVR) presents the results of the demonstration study for one PCB field analytical technology, EST's 4100 Vapor Detector. Separate ETVRs have been published for the other five technologies.

Technology Verification Process

The technology verification process is intended to serve as a template for conducting technology demonstrations that will generate high-quality data that EPA can use to verify technology performance. Four key steps are inherent in the process:

- Needs identification and technology selection
- Demonstration planning and implementation
- Report preparation
- Information distribution

Needs Identification and Technology Selection

The first aspect of the technology verification process is to determine technology needs of EPA and the regulated community. EPA, DOE, the U.S. Department of Defense, industry, and state agencies are asked to identify technology needs and interest in a technology. Once a technology need is established, a search is conducted to identify suitable technologies that will address this need. The technology search and identification process consists of reviewing responses to *Commerce Business Daily* announcements, searches of industry and trade publications, attendance at related conferences, and leads from technology developers. Characterization and monitoring technologies are evaluated against the following criteria:

- meets user needs;
- may be used in the field or in a mobile laboratory;
- is applicable to a variety of environmentally impacted sites;
- has high potential for resolving problems for which current methods are unsatisfactory;
- is cost competitive with current methods;
- performs better than current methods in areas such as data quality, sample preparation, or analytical turnaround time;

- uses techniques that are easier and safer than current methods; and
- is a commercially available, field-ready technology.

Demonstration Planning and Implementation

After a technology has been selected, EPA, the verification organization, and the developer agree to the responsibilities for conducting the demonstration and evaluating the technology. The following tasks are undertaken at this time:

- identifying demonstration sites that will provide the appropriate physical or chemical environment, including contaminated media;
- identifying and defining the roles of demonstration participants, observers, and reviewers;
- determining logistical and support requirements (for example, field equipment, power and water sources, mobile laboratory, communications network);
- arranging analytical and sampling support; and
- preparing and implementing a demonstration plan that addresses the experimental design, sampling design, quality assurance/quality control (QA/QC), health and safety considerations, scheduling of field and laboratory operations, data analysis procedures, and reporting requirements.

Report Preparation

Innovative technologies are evaluated independently and, when possible, against conventional technologies. The field technologies are operated by the developers in the presence of independent technology observers. The technology observers are provided by EPA or a third-party group. Demonstration data are used to evaluate the capabilities, limitations, and field applications of each technology. Following the demonstration, all raw and reduced data used to evaluate each technology are compiled into a technology evaluation report, which is mandated by EPA as a record of the demonstration. A data summary and detailed evaluation of each technology are published in an ETVR.

Information Distribution

The goal of the information distribution strategy is to ensure that ETVRs are readily available to interested parties through traditional data distribution pathways, such as printed documents. Documents are also available on the World Wide Web through the ETV Web site (*http://www.epa.gov/etv*) and through a Web site supported by the EPA Office of Solid Waste and Emergency Response's Technology Innovation Office *(http://CLU-in.com)*.

Demonstration Purpose

The purpose of this demonstration was to obtain performance information for PCB field analytical technologies, to compare the results with conventional fixed-laboratory results, and to provide supplemental information (e.g., cost, sample throughput, and training requirements) regarding the operation of the technology. The demonstration was conducted under two climatic conditions. One set of activities was conducted outdoors, with naturally fluctuating temperatures and relative humidity conditions. A second set was conducted in a controlled environmental facility, with lower, relatively stable temperatures and relative humidities. Multiple soil types, collected from sites in Ohio, Kentucky, and Tennessee, were used in this study. PCB soil concentrations ranged from approximately 0.1 to 700 parts per million (ppm). Developers also analyzed 24 solutions of known PCB concentration that were used to simulate extracted wipe samples. The extract samples ranged in concentration from 0 to 100 µg/mL.

Section 2
Technology Description

Objective
The objective of this section is to describe the technology being demonstrated, including the operating principles underlying the technology and the overall approach to its use. The information provided here is excerpted from that provided by the developer. Performance characteristics described in this section are specified by the developer, which may or may not be substantiated by the data presented in Section 5.

System Overview
The EST 4100 Vapor Detector is a handheld, portable (35-lb) gas chromatography (GC) system equipped with a nonspecific surface acoustic wave (SAW) detector. The unit can be used to speciate and quantify PCBs. A sampling pump and loop trap are used to sample and inject analyte into a short gas chromatography (GC) capillary column. The analyte mixture travels through the temperature-programmed column and is separated into its components according to conventional chromatographic principles. The effluent is focused onto a specific area on the surface of a temperature-controlled piezoelectric crystal that acts as the SAW detector. Speciation of the analytes is based upon retention-time measurements using a temperature-programmed J&W Durabond DB-5® capillary column (22.5 in. long, 0.25-mm internal diameter, 0.25-μm phase thickness). Quantification is based upon the frequency shift due to mass loading of the SAW detector produced by the analytes as they exit the GC column. The system has the ability to quantify chromatographic peaks at the picogram level, with peak widths measured in milliseconds. Measurement speed and accuracy make the instrument well suited for rapid screening of soil samples. Early segregation through rapid field screening of those soil samples below the regulatory level from those that require laboratory analysis reduces the cost associated with site characterization and monitoring.

Because the GC column is short (22.5 in.), other environmental components may co-elute with the PCB target analytes and be sensed by the nonspecific SAW detector. Any such compounds detected may be misidentified and quantified as a PCB. If the quantification level is above a given criterion threshold, the developer recommends that the soil sample be laboratory tested and the SAW/GC screening measurement validated. Impurities from contaminants within the instrument or inlet train desorption tubing may interfere with the analysis. Contamination by carryover can also occur whenever high-concentration and low-concentration samples are analyzed sequentially. To minimize these types of interferences, use of the system as a screening tool mandates that acceptably low instrument blank values be obtained before and after all positive measurements.

Sample Preparation and Analysis Procedures

Two procedures for extracting PCBs from soil matrices can be used with the 4100 Vapor Detector. Both procedures have been tested on the following Aroclors: 1016, 1221, 1232, 1242, 1248, 1254, 1260, and 1262. The first procedure uses a direct thermal desorption of the PCBs in the soil matrix packed in a heated tube (referred to as the open-path direct desorption tube [OPDDT]). This method is best suited for relatively clean soil samples with PCB levels below 250 ppb. The second procedure involves the liquid extraction of soil using a mixture of hexane, water, and methanol. A small amount of the hexane layer is subsequently injected into the 4100 Vapor Detector inlet. The second procedure is best suited to testing soil with contamination levels of 250 ppb or higher because of the sample dilution inherent in the method.

Direct Thermal Extraction/Analysis

The 4100 Vapor Detector inlet sample port is glass-lined stainless steel for sampling vapors directly into the instrument. Total extraction from soil is performed using an open heated glass tube fitted with a glass-to-Luer adapter attached directly to the inlet of the instrument. After loading tube with approximately 250 mg of soil, the Luer adapter is attached to one end of the sample tube. The sample tube is attached to the Luer inlet fitting of the 4100. The heater jacket, preheated to 200°C, is slid over the sample tube, and thermal desorption of the soil is immediately initiated, with desorption duration set to 30 s. The desorbed PCB vapors are swept onto the head of the GC column, separated, and quantified by the SAW detector. The thermal desorption/analysis is repeated for 30-s periods at 1-min intervals until analyte concentration readings are less then 10% of initial sample values. The concentration mass, in nanograms, for each sample measurement, N_i, as well as the total of all sample measurements, N_T, are recorded. The sample tube packed with soil is weighed. The weight of the empty tube is subtracted, and the result is designated as WSOIL in grams. If the soil contents of the tube are not to be measured immediately, the ends of the glass tube are sealed with slip-on septa covers.

Calibration is performed using a syringe to inject calibration standard solutions directly into the OPDDT. Note that QA measurements require GC validation using only standards certified by an independent laboratory. All spiking solutions, prior to their use in soil recovery analyses or calibration by direct injection, must first be validated by GC measurement.

Blank samples must be run before and after each analytical run to monitor for background levels or carryover. The analysis of blank samples is continued until the PCB levels are below preset minimums. Each sample tube is weighed and prescreened (desorbed and analyzed) before being loaded with soil. The instrument should be used with the SAW/GC method and instrument settings for which the calibration was performed. Use of any other method requires the generation of a new calibration curve. The operator must save all chromatograms, including blanks and calibration checks performed with liquid standards.

Liquid Extraction and Injection/Analysis

This method is well suited to the analysis of soils with high concentrations of PCBs. First the PCBs are extracted from the soil using a mixture of hexane (1.0 mL), methanol (1.5 mL), and water (0.4 mL). A weighed amount of soil (0.3–0.5 g) is shaken until the soil is well dispersed. The slurry is then allowed to stand until the hexane layer is clearly separated and floats on top of methanol-water layer with soil sediment resting on the bottom of the vial. Approximately 0.25 mL of the hexane is removed. The extract is

filtered through a disposable pipette packed with glass wool and is transferred into a clean vial, which is then capped with a septum.

Desorption of the PCBs from the extract solution is performed using an open-path thermal desorption tube packed with glass wool. The tube is fitted with a glass-to-Luer adapter that attaches directly to the inlet of the instrument.

With the heater jacket removed and the extraction tube at room temperature, an aliquot of the hexane extract (0.2 to 10 µL) is placed into the tube. Analysis cycles with the 4100 are initiated to remove the volatile components from the hexane solvent. This is continued until liquid can no longer be seen in the glass tube. Then, the heater jacket, preheated to 200°C, is slid over the sample tube, and thermal desorption of the PCB-containing residue is immediately initiated, with desorption duration set to 30 s. The desorbed PCB vapors are swept onto the head of the GC column, separated, and quantified by the SAW detector. The thermal desorption/analysis is repeated for 30-s periods at 1-min intervals until analyte concentration readings are less then 10% of initial sample values. The PCB mass, in nanograms, for each sample measurement, N_i, and the total of all sample measurements, N_T, are recorded. Calibration standards are injected directly into the open-path desorption tube. It should be noted that for all of the samples analyzed for the verification study, the liquid extraction method was used.

Instrument Analysis Checklist

The following items must be checked prior sample analysis:

- If the instrument has been previously calibrated in the laboratory, perform a single mid-level calibration check for each analyte. If the value of the check is within 30% of the laboratory value, then the response factor is confirmed. If the value is greater than 30%, then the instrument must be recalibrated.

- Check instrument status. Measure the instrument sample flow using the mass flow meter. Record the sample flow and enter the value in the Peak File software dialog screen under sample flow in cc/min units.

- Run an instrument blank. Verify that the background is below 10 ppb for any compound in the peak file. The blank should be a solvent injected into an empty desorption tube.

- Create a calibration standard solution. Fill a 4-mL vial with an appropriate amount of standard solution and an appropriate amount of solute so that a concentration (measured in nanograms per microliter) is achieved that is mid-level to the desired measurement range. Seal the vial with a new septum lid.

- To determine the instrument response factor, SF (measured in hertz per picogram), inject a liquid with a known standard into the desorption tube. The instrument reading, Fm, in measurement units of frequency (hertz) and the total amount of analyte injected, M_a (measured in picograms) defines the response factor:

$$SF = \frac{F_m}{M_a} \tag{2-1}$$

- Confirm the retention-time windows for each component to be analyzed. Make three injections of the component and calculate the standard deviation of the retention time of each component. For each analyte, the average retention time and response factor are calculated and saved in the peak recognition file.

Aroclor Pattern Recognition/Quantification

PCB Aroclor mixtures typically contain 40 or more congeners. The system software provides the operator with the capability to use either the sum of peaks over a retention time range or the sum of selected peaks as the basis for calibration. A single average response factor for the sum of the peaks within the mixture is used to calculate the concentration of the Aroclor mixture.

Commercial Aroclor mixtures of PCB isomers are commonly found at environmental sites; their composition and vapor signature can readily be recognized by a trained operator. Once the peak identification files for the Aroclor mixtures have been created, an unknown sample can be identified as containing PCBs and the PCBs can be quantified. Data logging to Excel spreadsheets using different peak-recognition file patterns for the raw data provides documentation and archival of all 4100 Vapor Detector measurements.

Calculations

Windows 95, SAW/GC system software (Version 4.0), and Excel and are required to operate the system, log data, and provide measurement documentation. Three calibration options are provided with the system software. The operator may select individual compound peaks and calibrate based upon the measured signal in hertz and the standard input in nanograms. Alternatively, the operator may use either the total area of all peaks over a specified range of retention times or the sum of a set of “tagged” peaks specified in a calibration file to determine a response factor in terms of a standard input. Soil contamination is expressed in either ppm (mg/kg), ppb (µg/kg), or ppt (ng/kg). To calculate soil contamination, the following calculation is performed:

$$Conc_{SOIL} = \frac{\sum N_i}{W_{SOIL}} = \frac{N_T}{W_{SOIL}} \tag{2-2}$$

For liquid extractions the result from Eq. 2-2 must be multiplied by the dilution ratio (the total amount of hexane solution divided by the amount of solution extract injected).

Section 3
Site Description and Demonstration Design

Objective
This section describes the demonstration site, the experimental design for the verification test, and the sampling plan (sample types analyzed and the collection and preparation strategies). Included in this section are the results from the predemonstration study and a description of the deviations made from the original demonstration design.

Demonstration Site Description
Site Name and Location
The demonstration of PCB field analytical technologies was conducted at Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee. PCB-contaminated soils from three DOE sites (Oak Ridge; Paducah, Kentucky; and Piketon, Ohio) were used in this demonstration. The soil samples used in this study were brought to the demonstration testing location for evaluation of the field analytical technologies.

Site History
Oak Ridge is located in the Tennessee River Valley, 25 miles northwest of Knoxville. Three DOE facilities are located in Oak Ridge: ORNL, the Oak Ridge Y-12 Plant, and East Tennessee Technology Park (ETTP). Chemical processing and warhead component production have occurred at the Y-12 Plant, and ETTP is a former gaseous diffusion uranium enrichment plant. At both facilities, industrial processing associated with nuclear weapons production has resulted in the production of millions of kilograms of PCB-contaminated soils. Two other DOE facilities—the Paducah plant in Paducah, Kentucky, and the Portsmouth plant in Piketon, Ohio—are also gaseous diffusion facilities with a history of PCB contamination. During the remediation of the PCB-contaminated areas at the three DOE sites, soils were excavated from the ground where the PCB contamination occurred, packaged in containers ranging in size from 55-gal to 110-gal drums, and stored as PCB waste. Samples from these repositories—referred to as "Oak Ridge," "Portsmouth," and "Paducah" samples in this report—were used in this demonstration.

In Oak Ridge, excavation activities occurred between 1991 and 1995. The Oak Ridge samples were comprised of PCB-contaminated soils from both Y-12 and ETTP. Five different sources of PCB contamination resulted in soil excavations from various dikes, drainage ditches, and catch basins. Some of the soils are EPA-listed hazardous waste due to the presence of other contaminants (e.g., diesel fuels).

A population of over 5000 drums containing PCB-contaminated soils was generated from 1986 to 1987 during the remediation of the East Drainage Ditch at the Portsmouth Gaseous Diffusion Plant. The ditch was reported to have three primary sources of potential contamination: (1) treated effluent from a radioactive liquid treatment facility, (2) runoff from a biodegradation plot where waste oil and sludge were disposed of, and (3) storm sewer discharges. In addition, waste oil was reportedly used for weed control in

the ditch. Aside from PCB contamination, no other major hazardous contaminants were detected in these soils. Therefore, no EPA hazardous waste codes are assigned to this waste.

Twenty-nine drums of PCB-contaminated soils from the Paducah plant were generated as part of a spill cleanup activity at an organic waste storage area (C-746-R). The waste is considered a listed hazardous waste for spent solvents (EPA hazardous waste code F001) because it is known to contain trichloroethylene. Other volatile organic compounds, such as xylene, dichlorobenzene, and cresol, were also detected in the preliminary analyses of some of the Paducah samples.

Site Characteristics

PCB-contaminated environmental soil samples from Oak Ridge, Portsmouth, and Paducah were collected from waste containers at storage repositories at ETTP and Paducah. Many of the soils contained interfering compounds such as oils, fuels, and other chlorinated compounds (e.g., trichloroethylene). Specific sample descriptions of the environmental soils used in this demonstration are given in Appendix A. In addition, each sample was characterized in terms of its soil composition, pH, and total organic carbon content. Those results are summarized in Appendix B.

Field demonstration activities occurred at two sites at ORNL: a natural outdoor environment (the outdoor site) and inside a controlled environmental atmosphere chamber (the chamber site). Figure 3-1 shows a schematic map of a section of ORNL indicating the demonstration area where the outdoor field activities occurred. Generally, the average summer temperature in eastern Tennessee is 75.6°F, with July and August temperatures averaging 79.1°F and 76.8°F, respectively. Average temperatures during the testing periods ranged from 79 to 85°F, as shown in Appendix C. Studies were also conducted inside a controlled environmental atmosphere chamber, hereafter referred to as the “chamber,” located in Building 5507 at ORNL. Demonstration studies inside the chamber were used to evaluate performance under environmental conditions that were markedly different from the ambient outdoor conditions at the time of the test. Average temperatures in the chamber during the testing periods ranged from 55 to 70°F. The controlled experimental atmosphere facility consists of a room-size walk-in chamber 10 ft wide and 12 ft long with air processing equipment to control temperature and humidity. The chamber is equipped with an environmental control system, including reverse osmosis water purification that supplies the chamber humidity control system. High efficiency particulate air (HEPA) and activated charcoal filters are installed for recirculation and building exhaust filtration.

Experimental Design

The analytical challenge with PCB analysis is to quantify a complex mixture that may or may not resemble the original commercial product (i.e., Aroclor) due to environmental aging, and to report the result as a single number [1]. The primary objective of the verification test was to compare the performance of the field technology to laboratory-based measurements. Often, verification tests involve a direct one-to-one comparison of results from field-acquired samples. However, because sample heterogeneity can preclude replicate field or laboratory comparison, accuracy and precision data must often be derived from the analysis of QC and performance evaluation (PE) samples. In this study, replicates of all three sample types (QC, PE, and environmental soil) were analyzed. The ability to use environmental soils in the verification

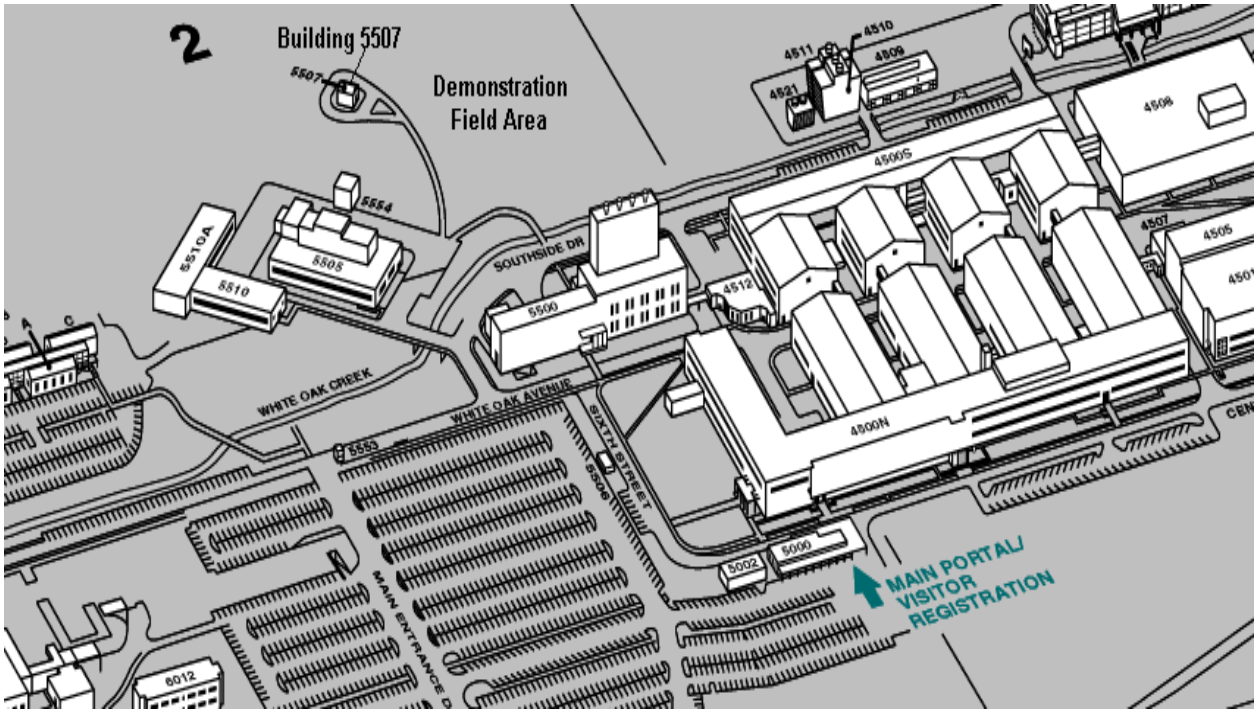

Figure 3-1. Schematic map of ORNL, indicating the demonstration area.

test was made possible because the samples, collected from drums containing PCB-contaminated soils, could be thoroughly homogenized and characterized prior to the demonstration. This facet of the design, allowing additional precision data to be obtained on actual field-acquired samples, provided an added performance factor in the verification test.

Another objective of this demonstration was to evaluate the field technology's capability to support regulatory compliance decisions. For field methods to be used in these decisions, the technology must be capable of informing the user, with known precision and accuracy, that soil concentrations are greater than or less than 50 ppm, and that wipe samples are greater than or less than 100 µg/100 cm^2 [2]. The samples selected for analysis in the demonstration study were chosen with this objective in mind.

The experimental design is summarized in Table 3-1. This design was approved by all participants prior to the start of the demonstration study. In total, the developers analyzed 208 soil samples, 104 each at both locations (outdoors and chamber). The 104 soil samples comprised 68 environmental samples (17 unique environmental samples prepared in quadruplicate) ranging in PCB concentration from 0.1 to 700 ppm and 36 PE soils (9 unique PE samples in quadruplicate) ranging in PCB concentration from 0 to 50 ppm. To determine the impact of different environmental conditions on the technology's performance, each batch of 104 samples contained five sets of quadruplicate soil samples from DOE's Paducah site. These were analyzed under both sets of environmental conditions (i.e., outdoor and chamber conditions). For the developers participating in the extract sample portion (i.e., simulated wipe samples) of the demonstration, 12 extracts, ranging in concentration from 0 to 100 µg/mL, were analyzed in each

location (chamber and outdoors). All samples were analyzed without prior knowledge of sample type or concentration and were analyzed in a randomized order that was unique for each developer.

Table 3-1. Summary of experimental design by sample type

Concentration Range	Sample ID [a]		Total # Samples Analyzed
	Outdoor Site	Chamber Site	
PE Materials			
0	126	226	8
2.0 ppm	118	218	8
2.0 ppm	124	224	8
5.0 ppm	120	220	8
10.9 ppm	122	222	8
20.0 ppm	119	219	8
49.8 ppm	125	225	8
50.0 ppm	121	221	8
50.0 ppm	123	223	8
Environmental Soils			
0.1–2.0 ppm	101, 107, 108, 109, 113, 114	201, 202, 206	36
2.1–20.0 ppm	102, 103, 104, 115	203, 207, 212, 213	32
20.1–50.0 ppm	111, 116	204, 208, 209, 214, 215	28
50.1–700.0 ppm	105, 106, 110, 112, 117	205, 210, 211, 216, 217	40
Extracts			
0	129 [b]/132 [c]	229/232	8
10 µg/mL	127/130	227/230	8
100 µg/mL	128/131	228/231	8
Grand Total	**116**	**116**	**232** [d]

[a] Each sample ID was analyzed in quadruplicate.
[b] Extract prepared in iso-octane for Dexsil and the reference laboratory.
[c] Extract prepared in methanol for Electronic Sensor Technology, Strategic Diagnostics Inc., and the reference laboratory.
[d] All samples were analyzed in random order.

Environmental Conditions during Demonstration
As mentioned above, field activities were conducted both outdoors under natural environmental conditions and indoors in a controlled environmental atmosphere chamber to evaluate the effect of environmental conditions on technology performance. The weather outside was relatively uncomfortable during the July demonstration, with highs approaching 100°F and 90% relative humidity (RH). Daily average temperatures were around 85°F with 70% RH. While outside, the developers set up canopies to provide shade and protection from frequent late afternoon thundershowers.

In the indoor chamber tests, conditions were initially set to 55°F and 25% RH. An independent check of the conditions inside the chamber revealed that the temperature was closer to 68°F with a 38% RH on the first day of testing. A maintenance crew was called in to address the inconsistencies between the set and actual conditions. By the middle of the third day of testing, the chamber was operating properly at 55°F and 50% RH.

Appendix C contains a summary of the environmental conditions (temperature and relative humidity) during the demonstration. The EST team worked outdoors July 22, 23, and 24, 1997, and in the chamber on July 24 and 25, 1997.

Sample Descriptions
PCBs ($C_{12}H_{10-x}Cl_x$) are a class of compounds that are chlorine-substituted linked benzene rings. There are 209 possible PCB compounds (also known as congeners). PCBs were commercially produced as complex mixtures beginning in 1929 for use in transformers, capacitors, paints, pesticides, and inks [1]. Monsanto Corporation marketed products that were mixtures of 20 to 60 PCB congeners under the trade name Aroclor. Aroclor mixtures are identified by a number (e.g., Aroclor 1260) that represents the mixture's chlorine composition as a percentage (e.g., 60%).

Performance Evaluation Materials
Samples of Tennessee reference soil [3] served as the blanks. Preprepared certified PE samples were obtained from Environmental Resource Associates (ERA) of Arvada, Colorado, and the Analytical Operations and Data Quality Center of EPA's Office of Solid Waste and Emergency Response. The soils purchased from ERA had been prepared using ERA's semivolatile blank soil matrix. This matrix was a topsoil that had been dried, sieved, and homogenized. Particle size was approximately 60 mesh. The soil was approximately 40% clay. The samples acquired from EPA's Analytical Operations and Data Quality Center had been prepared using contaminated soils from various sites around the country in the following manner: The original soils had been homogenized and diluted with a synthetic soil matrix (SSM). The SSM had a known matrix of 6% gravel, 31% sand, and 43% silt/clay; the remaining 20% was topsoil. The dilution of the original soils was performed by mixing known amounts of contaminated soil with the SSM in a blender for no less than 12 h. The samples were also spiked with target pesticides (α, β, Δ, and δ-BHC, methoxychlor, and endrin ketone) to introduce some compounds that were likely to be present in an actual environmental soil. The hydrocarbon background from the original sample and the spiked pesticides produced a challenging matrix. The PE soils required no additional preparation by ORNL and were split for the developer and reference laboratory analyses as received.

Environmental Soil Samples
As noted in the site description above, PCB-contaminated environmental soil samples from Oak Ridge, Portsmouth, and Paducah were used in this demonstration. The soils were contaminated with PCBs as the result of spills and industrial processing activities at the various DOE facilities. Originally, the contaminated soils were excavated from dikes, drainage ditches, catch basins, and organic waste storage areas. The excavated soils were then packaged into waste containers and stored at the repositories in ETTP and Paducah in anticipation of disposal by incineration. The environmental soil samples used in this study were collected from these waste containers. Many of the soils contained interfering compounds such as oils, fuels, and other chlorinated compounds, while some contained multiple Aroclors. For more information on sampling locations and sample characteristics (soil composition, pH, and total organic carbon content), refer to Appendices A and B, respectively.

Extract Samples
Traditionally, the amount of PCBs on a contaminated surface is determined by wiping the surface with a cotton pad saturated with hexane. The pad is then taken to the laboratory, extracted with additional hexane, and analyzed by gas chromatography. Unlike soil samples, which can be more readily homogenized and divided, equivalent wipe samples (i.e., contaminated surfaces or post- wipe pads) were not easily obtainable. Therefore, interference-free solutions of PCBs were analyzed to simulate an extracted surface wipe pad. Extract sample analyses provided evaluation data that relied primarily on the technology's performance rather than on elements critical to the entire method (i.e., sample collection and preparation). Because different developers required the extract samples prepared in different solvents (e.g., methanol and iso-octane), the reference laboratory analyzed sets of extracts in both solvents. EST analyzed extracts prepared in methanol. A total of 12 extracts were analyzed per site; these consisted of four replicates each of a blank and two concentration levels (10 and 100 µg/mL).

Sampling Plan
Sample Collection
Environmental soil samples were collected from April 17 through May 7, 1997. Portsmouth and Oak Ridge Reservation soils were collected from either storage boxes or 55-gal drums stored at ETTP. Briefly, the following procedure was used to collect the soil samples. Approximately 30 lb of soil were collected from the top of the drum or B-25 box using a scoop and placed in a plastic bag. The soil was sifted to remove rocks and other large debris, then poured into a plastic-lined 5-gal container. All samples were subjected to radiological screening and were determined to be nonradioactive. Similarly, soil samples were collected from 55-gal drums stored at Paducah and shipped to ORNL in lined 5-gal containers.

Sample Preparation, Labeling, and Distribution
Aliquots of several of the environmental soils were analyzed and determined to be heterogeneous in PCB concentration. Because this is unsatisfactory for accurately comparing the performance of the field technology with the laboratory-based method, the environmental soils had to be homogenized prior to sample distribution. Each Portsmouth and Oak Ridge environmental soil sample was homogenized by first placing approximately 1500 g of soil in a glass Pyrex dish. The dish was then placed in a large oven set at 35°C, with the exhaust and blower fans turned on to circulate the air. After drying overnight, the soil was

pulverized using a conventional blender and sieved using a 9-mesh screen (2 mm particle size). Last, the soil was thoroughly mixed using a spatula. A comparison of dried and undried soils showed that a minimal amount of PCBs (< 20%) was lost due to sample drying, making this procedure suitable for use in the preparation of the soil samples. The Paducah samples, because of their sandy characteristics, only required the sieving and mixing preparation steps. Extract sample preparation involved making solutions of PCBs in methanol and iso-octane at two concentration levels (10 and 100 µg/mL). Multiple aliquots of each sample were analyzed using the analytical procedure described below to confirm the homogeneity of the samples with respect to PCB concentration.

To provide the developers with soils contaminated at higher concentrations of PCBs, some of the environmental soils (those labeled with an "S" in Appendix B) were spiked with additional PCBs. Spiked soils samples were prepared after the soil was first dried in a 35°C oven overnight. The dry soil was ground using a conventional blender and sieved through a 9-mesh screen (2 mm particle size). Approximately 1500 g of the sieved soil were spiked with a diethyl ether solution of PCBs at the desired concentration. The fortified soil was agitated using a mechanical shaker and then allowed to air-dry in a laboratory hood overnight. A minimum of four aliquots were analyzed using the analytical procedure described below to confirm the homogeneity of the soil with regard to the PCB concentration.

The environmental soils were characterized at ORNL prior to the demonstration study. The procedure used to confirm the homogeneity of the soil samples entailed the extraction of 3 to 5 g of soil in a mixture of solvents (1 mL water, 4 mL methanol, and 5 mL hexane). After the soil/solvent mixture was agitated by a mechanical shaker, the hexane layer was removed and an aliquot was diluted for analysis. The hexane extract was analyzed on a Hewlett Packard 6890 gas chromatograph equipped with an electron capture detector and autosampler. The method used was a slightly modified version of EPA's SW-846 dual-column Method 8081 [4].

After analysis confirming homogeneity, the samples were split into jars for distribution. Each 4-oz sample jar contained approximately 20 g of soil. Four replicate splits of each soil sample were prepared for each developer. The samples were randomized in two fashions. First, the order in which the filled jars were distributed was randomized, such that the same developer did not always receive the first jar filled for a given sample set. Second, the order of analysis was randomized so that each developer analyzed the same set of samples, but in a different order. The extract samples were split into 10-mL aliquots and placed into 2-oz jars. The extracts were stored in the refrigerator (at ≤4°C) until released to the developers. Each sample jar had three labels: (1) developer order number; (2) sample identifier number; and (3) a PCB warning label. The developer order number corresponded to the order in which the developer was required to analyze the samples (e.g., EST 1001 through EST 1116). The sample identifier number was in the format of "xxxyzz," where "xxx" was the three-digit sample ID (e.g., 101) listed in Table 3-1, "y" was the replicate (e.g., 1 to 4), and "zz" was the aliquot order of each replicate (e.g., 01 to 11). For example, sample identifier 101101 corresponded to sample ID "101" (an Oak Ridge soil from RFD 40022, drum 02), "1" corresponded to the first replicate from that sample, and "01" corresponded to the first jar filled in that series.

Once the samples were prepared, they were stored at a central sample distribution center. During the demonstration study, developers were sent to the distribution center to pick up their samples. Samples were

distributed sequentially in batches of 12 to ensure that samples were analyzed in the order specified. Completion of chain-of-custody forms and scanning of bar code labels documented sample transfer activities. Some of the developers received information regarding the samples prior to analysis. This was provided to simulate the type of information that would be available during actual field testing. EST did not request any sample information. The developers returned the unused portions of the samples with the analytical results to the distribution center when testing was completed. The sample bar codes were scanned upon return to document sample throughput time.

Three complete sets of extra samples, called archive samples, were available for distribution in case the integrity of a sample was compromised. Very few (<5) archive samples were utilized over the course of the demonstration.

Predemonstration Study

Ideally, environmental soil samples are sent to the developers prior to the demonstration study to allow them the opportunity to analyze representative samples in advance of the verification test. This gives developers the opportunity to refine and calibrate their technologies and revise their operating procedures on the basis of the predemonstration study results. The predemonstration study results can also be used as an indication that the selected technologies are of the appropriate level of maturity to participate in the demonstration study.

According to ORNL regulations, however, one of two conditions must exist in order to ship environmental soils that were once classified as mixed hazardous waste. First, the recipient—in this case, the developer's facilities—must have proper Nuclear Regulatory Commission (NRC) licensing to receive and analyze radiological materials. Second, the soils must be certified as entirely free of radioactivity, beyond the no-rad certification issued from radiological screening tests based on ORNL standards. Because none of the developers had proper NRC licensing and proving that the soils were entirely free of radioactivity was prohibitive, spiked samples of Tennessee reference soil were used for the predemonstration study. The developers had an opportunity to evaluate the Tennessee reference soils spiked with PCBs at concentrations similar to what would be used in the demonstration study. The developers also analyzed two performance evaluation samples and one solvent extract. The reference laboratory analyzed the same set of samples, which included two extracts samples, prepared in the two solvents (methanol and iso-octane) requested by the developers.

Predemonstration Sample Preparation

Two soil samples were prepared by ORNL using Tennessee reference soil [3]. The soil was a Captina silt loam from Roane County, Tennessee, that was slightly acidic (pH ~5) and low in organic carbons (~1.5%). The soil composition was 7.7% sand, 29.8% clay, and 62.5% silt. To prepare a spiked sample, the soil was first ground either using a mortar and pestle or a conventional blender. The soil was then sieved through a 16-mesh screen (1 mm particle size). Approximately 500 g of the sieved soil was spiked with a diethyl ether solution of PCBs at the desired concentration. The soil was agitated using a mechanical shaker, then allowed to air-dry overnight in a laboratory hood. A minimum of five aliquots were analyzed by gas chromatography using electron capture detection. The PCB concentration of the spiked samples was determined to be homogeneous. The remaining two soil samples used in the predemonstration study were performance evaluation materials acquired from ERA and EPA (see the section "Performance Evaluation

Materials" above). In addition, a solvent extract was prepared by ORNL to simulate an extracted surface wipe sample. The extracts were prepared in two different solvents (iso-octane and methanol) to accommodate developer requests.

Predemonstration Results

The predemonstration samples were sent to the developers and the reference laboratory on June 2, 1997. Predemonstration results were received by June 26, 1997. Table 3-2 summarizes the 4100's results for the predemonstration samples. Acceptable results for three of the five performance evaluation samples indicated that the 4100 was ready for field evaluation.

Table 3-2. Summary of the 4100's predemonstration results

Sample Description	4100 result (ppm)	Certified Concentration (ppm)	Acceptance Limits [a] (ppm)
30 ppm of Aroclor 1242	21.7	30.2	12 - 45
20 ppm of Aroclor 1260	16.2	21.9	12 - 27
11 ppm of Aroclor 1260	1.3	11	4 - 12
50 ppm of Aroclor 1254	7.4	50	20 - 63
blank	0	0	0

[a] Acceptance limits provided by supplier of performance evaluation materials.

Deviations from the Demonstration Plan

A few deviations from the demonstration plan occurred. In Appendix B of the technology demonstration plan [5], the reference laboratory's procedure states that no more than 10 samples will be analyzed with each analytical batch (excluding blanks, standards, QC samples, and dilutions). The analytical batch is also stated as 10 samples in the Quality Assurance Project Plan of the demonstration plan. The reference laboratory actually analyzed 20 samples per analytical batch. Because a 20-sample batch is recommended in SW-846 Method 8081, this deviation was deemed acceptable.

Table 5 of the demonstration plan [5] delineates the environmental soils according to concentration. The classification was based on a preliminary analysis of the soils at ORNL. Table 3-1 of this report arranges the concentrations as characterized by the reference laboratory. The reference laboratory determined that five sample sets (sample IDs 102, 105, 110, 111, and 210) were in the next highest concentration range, differing from what was originally outlined in the demonstration plan. Also, the highest concentration determined by the reference laboratory was 700 ppm, while the preliminary analysis at ORNL found the highest concentration to be 500 ppm.

During the demonstration study, the EST team made several modifications to the procedure described in the technology demonstration plan [5].

- Reduced the sample size from ~1.5 g to ~0.5g.
- If the extract appeared oily or dirty, the extract was diluted by a factor of 4 prior to analysis.
- A centrifuge step was added to the liquid extraction procedure.
- The slide heater jacket temperature was reduced from 200°C to 180°C.
- The time to heat the slide heater jacket was reduced from 30 s to 10 s.

These changes were applied to compensate for what the EST referred to as “ high oil concentrations” encountered in the samples.

Section 4
Reference Laboratory Analytical Results and Evaluation

Objective and Approach

The purpose of this section is to present the evaluation of the PCB data generated by the reference laboratory. Evaluation of the results from the analysis of PE, environmental soil, and extract samples was based on precision, accuracy, representativeness, completeness, comparability (PARCC) parameters [6]. This section describes how the analytical data generated by the reference laboratory were used to establish a baseline performance for PCB analysis.

Reference Laboratory Selection

The Oak Ridge Sample Management Office (SMO) has been tasked by DOE Oak Ridge Operations (DOE-ORO) with maintaining a list of qualified laboratories to provide analytical services. The technology demonstration plan [5] contains the SMO's standard operating procedures (SOPs) for identifying, qualifying, and selecting analytical laboratories. Laboratories are qualified as acceptable analytical service providers for the SMO by meeting specific requirements. These requirements include providing pertinent documentation (such as QA and chemical hygiene plans), acceptance of the documents by the SMO, and satisfactory performance on an on-site prequalification audit of laboratory operations. All laboratory qualifications are approved by a laboratory selection board, composed of the SMO operations manager and appointees from all prime contractors that conduct business with the SMO.

All of the qualified laboratories were invited to bid on the demonstration study sample analysis. The lowest-cost bidder was LAS Laboratories, in Las Vegas, Nevada. A readiness review conducted by ORNL and the SMO confirmed the selection of LAS as the reference laboratory. Acceptance of the reference laboratory was finalized by satisfactory performance in the predemonstration study (see Table 3-2). The SMO contracted LAS to provide full data packages for the demonstration study sample analyses within 30 days of sample shipment.

The SMO conducts on-site audits of LAS annually as part of the laboratory qualification program. At the time of selection, the most recent audit of LAS had occurred in February 1997. Results from this audit indicated that LAS was proficient in several areas, including program management, quality management, and training programs. No findings regarding PCB analytical procedure implementation were noted. A second on-site audit of LAS occurred August 11–12, 1997, during the analysis of the demonstration study samples. This surveillance focused specifically on the procedures that were currently in use for the analysis of the demonstration samples. The audit, jointly conducted by the SMO, DOE-ORO, and EPA-Las Vegas (LV), verified that LAS was procedurally compliant. The audit team noted that LAS had excellent adherence to the analytical protocols and that the staff were knowledgeable of the requirements of the method. No findings impacting data quality were noted in the audit report.

Reference Laboratory Method

The reference laboratory's analytical method, also presented in the technology demonstration plan [5], followed the guidelines established in EPA SW-846 Method 8081 [4]. According to LAS's SOP, PCBs were extracted from 30-g samples of soil by sonication in hexane. Each extract was then concentrated to a final volume that was further subjected to a sulfuric acid cleanup to remove potential interferences. The analytes were identified and quantified using a gas chromatograph equipped with dual electron-capture detectors. Each extract was analyzed on two different chromatographic columns with slightly different separation characteristics (primary column: RTX-1701, 30 m × 0.53 mm ID × 0.5 µm; confirmatory column: RTX-5, 30 m × 0.53 mm ID × 0.5 µm). PCBs were identified when peak patterns from a sample extract matched the patterns of standards for both columns. PCBs were quantified based on the initial calibration of the primary column.

Calibration

Method 8081 states that, because Aroclors 1016 and 1260 include many of the peaks represented in the other five Aroclor mixtures, it is only necessary to analyze two multilevel standards for these Aroclors to demonstrate the linearity of the detector response for PCBs. However, per LAS SOPs, five-point (0.1 to 4 ppm) initial calibration curves were generated for Aroclors 1016, 1248, 1254, and 1260 and the surrogate compounds [decachlorobiphenyl (DCB) and tetrachloro-m-xylene (TCMX)]. Single mid-level standards were analyzed for the other Aroclors (1221, 1232, and 1242) to aid in pattern recognition. All of the multi-point calibration data, fitted to quadratic models, met the QC requirement of having a coefficient of determination (R^2) of 0.99 or better over the calibration range specified. The detection limits for soil samples were 0.033 ppm (µg/g) for all Aroclors except Aroclor 1221, which was 0.067 ppm. For extract samples, the detection limits were 0.010 ppm (µg/mL) for all Aroclors except Aroclor 1221, which was 0.020 ppm. Reporting detection limits were calculated based on the above detection limits, the actual sample weight, and the dilution factor.

Sample Quantification

For sample quantification, Aroclors were identified by comparing the samples' peak patterns and retention times with those of the respective standards. Peak height ratios, peak shapes, sample weathering, and general similarity in detector response were also considered in the identification. Aroclor quantifications were performed by selecting three to five representative peaks, confirming that the peaks were within the established retention time windows, integrating the selected peaks, quantifying the peaks based on the calibrations, and averaging the results to obtain a single concentration value for the multicomponent Aroclor. If mixtures of Aroclors were suspected to be present, the sample was typically quantified in terms of the most representative Aroclor pattern. If the identification of multiple Aroclors was definitive, total PCBs in the sample were calculated by summing the concentrations of both Aroclors. Aroclor concentrations were quantified within the concentration range of the calibration curve. If PCBs were detected and the concentrations were outside of the calibration range, the sample was diluted and reanalyzed until the concentration was within the calibration range. If no PCBs were detected, the result was reported as a non-detect (i.e., "≤ reporting detection limit").

Sample Receipt, Handling, and Holding Times
The reference laboratory was scheduled to analyze a total of 256 PCB samples (208 soil samples, 24 iso-octane extract samples, and 24 methanol extract samples). Of these same samples, the developer was scheduled to analyze a total of 232 PCB samples (208 soil samples and 24 extract samples in solvent of choice). The samples were shipped to LAS at the start of the technology demonstration activities (July 22). Shipment was coordinated through the SMO. Completion of chain-of-custody forms documented sample transfer. The samples were shipped on ice in coolers to maintain <6°C temperatures during shipment. Samples were shipped with custody seals to ensure sample integrity and to prevent tampering during transport.

Upon receipt of the samples, the reference laboratory checked the receipt temperature and conditions of the sample containers, assigned each sample a unique number, and logged each into its laboratory tracking system. All samples were received at the proper temperature and in good condition. Demonstration samples were divided into 11 analytical batches (with no more than 20 samples per batch). The samples were analyzed in an order specified by ORNL to ensure that the analysis of sample types was randomized. Analyses of QC samples, supplied by the reference laboratory to indicate method performance, were performed with each analytical batch of soils.

Prior to analysis, samples were stored in refrigerators kept at 4 to 6° C to maintain analyte integrity. The reference laboratory was required to analyze the extract samples and to extract the soil samples within 14 days of shipment from ORNL. Once the soils were extracted, the reference laboratory had an additional 40 days to analyze the soil extracts. Maximum holding times were not exceeded for any of the demonstration samples. The final reference laboratory data package for all samples was received at ORNL in 72 days, on October 1, 1997. The contractual obligation was 30 days.

The remainder of this section is devoted to summarizing the data generated by the reference laboratory and to assessing the analytical performance.

Quality Control Results
Objective
The purpose of this section is to provide an assessment of the data generated by the reference laboratory's QC procedures. The QC samples included continuing calibration verification standards (CCVs), instrument blanks, method blanks, surrogate spikes, [laboratory control samples (LCSs)], and MS/MSD samples. Each control type is described in more detail in the following text and in the technology demonstration plan [5]. Because extraction of these liquid samples was not required, calibration check standards and instrument blanks were the only control samples implemented for the extract samples. The reference laboratory's implementation of QC procedures was consistent with SW-846 guidance.

Continuing Calibration Verification Standard Results
A CCV is a single calibration standard of known concentration, usually at the midpoint of the calibration range. This standard is evaluated as an unknown and is quantified against the initial calibration. The calculated concentration is then compared with the nominal concentration of the standard to determine whether the initial calibration is still valid. CCVs were analyzed with every 10 samples or at least every 12. The requirement for acceptance was a percentage difference of less than 15% for the CCV relative to the

initial calibration. This QC requirement was met for all Aroclors and surrogates, except for one standard that had a 16% difference for DCB. These results indicated that the reference laboratory maintained instrument calibrations during the course of sample analysis.

Instrument and Method Blank Results

Instrument blanks (hexane) were analyzed prior to each CCV. The QC requirement was that instrument blanks must contain less than the reporting detection limit for any analyte. All instrument blanks were acceptable.

A method blank is an analyte-free soil matrix sample that is taken through the extraction process to verify that there are no laboratory sources of contamination. One method blank was analyzed for each analytical batch. The QC requirement was that method blanks must contain less than the reporting detection limit for any Aroclor. No PCBs were detected in any of the eleven method blanks that were analyzed. These results demonstrated that the reference laboratory was capable of maintaining sample integrity, and that it did not introduce PCB contamination to the samples during preparation.

Surrogate Spike Results

A surrogate is a compound that is chemically similar to the analyte group but is not expected to be present in the environmental sample. A surrogate is added to test the extraction and analysis methods to verify the ability to isolate, identify, and quantify a compound similar to the analyte(s) of interest without interfering with the determination. Two different surrogate compounds, DCB and TCMX, were used to bracket the retention time window anticipated in the Aroclor chromatograms. All soil samples, including QC samples, were spiked with surrogates at 0.030 ppm prior to extraction. Surrogate recoveries were deemed to be within QC requirements if the measured concentration fell within the QC acceptance limits that were established by past method performance. (For LAS this was 39 to 117% for DCB, and 66 to 128% for TCMX). The results were calculated using the following equation:

$$percent\ \ recovery = \frac{measured\ \ amount}{actual\ \ amount} \times 100\% \qquad (4\text{-}1)$$

In all undiluted samples, both of the surrogates had percentage recoveries that were inside the acceptance limits. Surrogate recoveries in diluted samples were uninformative because the spike concentration (0.030 ppm, as specified by the method) was diluted below the instrument detection limits. The surrogate recovery results for undiluted samples indicated that there were no unusual matrix interferences or batch-processing errors for these samples.

Laboratory Control Sample Results

A LCS is an aliquot of a clean soil that is spiked with known quantities of target analytes. The LCS is spiked with the same analytes and at the same concentrations as the matrix spike (MS). (MSs are described in the next section.) If the results of the MS analyses are questionable (i.e., indicating a potential matrix effect), the LCS results are used to verify that the laboratory can perform the analysis in a clean, representative matrix.

Aroclors 1016 and 1260 were spiked into the clean soil matrix at approximately 0.300 ppm, according to the reference laboratory's SOP. The QC requirements (defined as percent recovery) for the LCS analyses were performance-based acceptance limits that ranged from 50 to 158%. In all but one of the eleven LCSs analyzed, both Aroclor percent recoveries fell within the acceptance limits. Satisfactory recoveries for LCS verified that the reference laboratory performed the analyses properly in a clean matrix.

Matrix Spike Results

In contrast to a laboratory control sample (LCS), a MS sample is an actual environmental soil sample into which target analytes are spiked at known concentrations. MS samples are used to assess the efficiency of the extraction and analytical methods for real samples. This is accomplished by determining the amount of spiked analyte that is quantitatively recovered from the environmental soil. A duplicate matrix spike (MSD) sample is spiked and analyzed to provide a measure of method precision. Ideally, to evaluate the MS/MSD results, the environmental soil is analyzed unspiked so that the background concentrations of the analyte in the sample are considered in the recovery calculation.

For the demonstration study samples, one MS and MSD pair was analyzed with each analytical batch. The MS samples were spiked under the same conditions and QC requirements as the LCS (50 to 158% acceptance limits), so that MS/MSD and LCS results could be readily compared. The QC requirement for MS and MSD samples was a relative percent difference (RPD) of less than 30% between the MS/MSD pair. RPD is defined as:

$$RPD = \frac{\left| MS\ recovery - MSD\ recovery \right|}{average\ recovery} \times 100\% \qquad (4\text{-}2)$$

A total of eleven MS/MSD pairs were analyzed. Because the MS/MSD spiking technique was not always properly applied (e.g., a sample which contained 100 ppm of Aroclor 1254 was spiked ineffectively with 0.300 ppm of Aroclor 1260), many of the MS/MSD results were uninformative. For the samples that were spiked appropriately, all MS/MSD QC criteria were met.

Conclusions of the Quality Control Results

The reference laboratory results met performance acceptance requirements for all of the samples where proper QC procedures were implemented. Acceptable performance on QC samples indicated that the reference laboratory was capable of performing analyses properly.

Data Review and Validation

Objective

The purpose of validating the reference laboratory data was to ensure usability for the purposes of comparison with the demonstration technologies. The data generated by the reference laboratory were used as a baseline to assess the performance of the technologies for PCB analysis. The reference laboratory data were independently validated by ORNL and SMO personnel, who conducted a thorough quality check and reviewed all sample data for technical completeness and correctness.

Corrected Results
Approximately 8% of the results provided by the reference laboratory (20 of 256) were found to have correctable errors. So as not to bias the assessment of the technology's performance, errors in the reference laboratory data were corrected. These changes were made conservatively, based on the guidelines provided in the SW-846 Method 8081 for interpreting and calculating Aroclor results. The errors (see Appendix D, Table D-3) were categorized as transcription errors, calculation errors, and interpretation errors. The corrections listed in Table D-3 were made in the final data set that was used for comparison with the demonstration technologies.

Suspect Results
Normally, one would not know if a single sample result was "suspect" unless (1) the sample was a performance evaluation sample, where the concentration is known or (2) a result was reported and flagged as suspect for some obvious reason (e.g., no quantitative result was determined). The experimental design implemented in this demonstration study provided an additional indication of the abnormality of data through the inspection of the replicate results from a homogenous soil sample set (i.e., four replicates were analyzed for each sample ID).

Data sets were considered suspect if the standard deviation (SD) of the four replicates was greater than 30 ppm and the percent relative standard deviation (RSD) was greater than 50%. Five data sets (sample IDs 106, 205, 216, 217, 225) contained measurements that were considered suspect using this criteria, and the suspect data are summarized in Table 4-1. A number of procedural errors may have caused the suspect measurements (e.g., spiking heterogeneity, extraction efficiencies, dilution, etc.). In the following subsections for precision and accuracy, the data were evaluated with and without these suspect values to represent the best and worst case scenarios.

Table 4-1. Suspect measurements within the reference laboratory data

Criteria	Sample ID	PCB Concentration (ppm)		Data Usability
		Replicate Results (ppm)	Suspect Result(s) (ppm)	
SD > 30 ppm and RSD > 50%	106	255.9, 269.9, 317.6	649.6	Performed data analysis with and without this value
	205	457.0, 483.3, 538.7	3,305.0	
	216	47.0, 54.3, 64.0	151.6	
	217	542.8, 549.8, 886.7	1,913.3	
	225	32.1, 36.5, 56.4	146.0	
Qualitative Result	110	≤ reporting detection limits	≤ 66, ≤ 98, ≤ 99, ≤ 490	Used as special case for comparison with developer results
	112		≤ 66, ≤ 130, ≤ 200,≤ 200	

Samples that did not fall into the above criteria, but were also considered suspect, were non-blank samples that could not be quantified and were reported as "≤ the reporting detection limit." This was the case for

environmental soil sample IDs 110 and 112. It is believed that the reference laboratory had trouble quantifying these soil samples because of the abundance of chemical interferences. These samples were diluted by orders of magnitude to reduce interferences, thereby diluting the PCB concentrations to levels that were lower than the instrument detection limits. With each dilution, the reporting detection limits values were adjusted for sample weight and dilution, which accounts for the higher reporting detection limits (up to 490 ppm). It is believed that these samples should have been subjected to additional pre-analytical cleanup to remove these interferences before quantification was attempted. Sample IDs 110 and 112 were collected from the same cleanup site (see Appendix B), so it is not surprising that similar difficulties were encountered with both sample sets. Because the results for sample IDs 110 and 112 were not quantitative, these data were compared with the technology data only on a special case basis.

Data Assessment

Objective

The purpose of this section is to provide an evaluation of the performance of the reference laboratory results through statistical analysis of the data. The reference laboratory analyzed 72 PE, 136 environmental soil, and 48 extract samples. All reference laboratory analyses were performed under the same environmental conditions. Therefore, site differentiation was not a factor in data assessment for the reference laboratory. For comparison with the technology data, however, the reference laboratory data are delineated into “outdoor site” and “chamber site” in the following subsections. For consistency with the technology review, results from both sites were also combined to determine the reference laboratory’s overall performance for precision and accuracy. This performance assessment was based on the raw data compiled in Appendix D. All statistical tests were performed at a 5% significance level.

Precision

The term “precision” describes the reproducibility of measurements under a given set of conditions. The SD of four replicate PCB measurements was used to quantify the precision for each sample ID. SD is an absolute measurement of precision, regardless of the PCB concentration. To express the reproducibility relative to the average PCB concentration, RSD is used to quantify precision, according to the following equation:

$$RSD = \frac{Standard\ Deviation}{Average\ Concentration} \times 100\% \qquad (4\text{-}3)$$

Performance Evaluation Samples

The PE samples were homogenous soils containing certified concentrations of PCBs. Results for these samples represent the best estimate of precision for soil samples analyzed in the demonstration study. Table 4-2 summarizes the precision of the reference laboratory for the analysis of PE samples. One suspect measurement (sample ID 225, 146.0 ppm) was reported for the PE soil samples. The RSDs for the combined data ranged from 9 to 33% when the suspect measurement was excluded, and from 9 to 79%, including the suspect measurement. The overall precision, determined by the mean RSD for all PE samples, was 21% for the worst case (including the suspect result) and 18% for the best case (excluding the suspect result).

Table 4-2. Precision of the reference laboratory for PE soil samples

Outdoor Site				Chamber Site				Combined Sites		
Sample ID	Average Concentration (ppm)	SD (ppm)	RSD (%)	Sample ID	Average Concentration (ppm)	SD (ppm)	RSD (%)	Average Concentration (ppm)	SD (ppm)	RSD (%)
126 [a]	0	n/a	n/a	226	0	n/a	n/a	0	n/a	n/a
118	1.6	0.6	39	218	2.6	0.2	6	2.1	0.7	33
124	1.7	0.2	13	224	1.7	0.5	29	1.7	0.4	21
120	5.0	1.0	20	220	5.8	1.8	31	5.4	1.4	26
122	11.1	0.9	8	222	12.8	0.3	3	11.9	1.1	9
119	20.1	3.4	17	219	23.3	6.1	26	21.7	4.9	23
125	37.9	6.9	18	225	41.7 [b]	12.9 [b]	31 [b]	39.5 [c]	9.2 [c]	23 [c]
121	54.6	3.4	6	221	44.9	11.3	25	49.8	9.3	19
123	60.1	4.6	8	223	55.8	7.7	14	58.0	6.3	11

[a] All PCB concentrations were reported as non-detects.
[b] Results excluding the suspect value (results including the suspect value: mean = 67.8 ppm, SD = 53.2 ppm, and RSD =79%).
[c] Results excluding the suspect value (results including the suspect value: mean = 52.8 ppm, SD = 38.6 ppm, and RSD = 73%).

Environmental Soil Samples

The precision of the reference laboratory for the analysis of environmental soil samples is reported in Table 4-3. In this table, results including suspect measurements are presented in parentheses. Average concentrations were reported by the reference laboratory as ranging from 0.5 to 1,196 ppm with RSDs that ranged from 7 to 118% when the suspect results were included. Excluding the suspect results, the highest average concentration decreased to 660 ppm, and the largest RSD decreased to 71%. Because the majority of the samples fell below 125 ppm, precision was also assessed by partitioning the results into two ranges: low concentrations (< 125 ppm) and high concentrations (> 125 ppm). For the low concentrations, the average RSD was 23% excluding the suspect value and 26% including the suspect value. These average RSDs were only slightly larger than the RSDs for the PE soils samples of comparable concentration (18% for best case and 21% for worst case). Five soil sample sets (sample IDs: 106, 117, 205, 211 and 217) were in the high-concentration category. The average precision for high concentrations was 56% for the worst case and 19% for the best case. The precision estimates for the low and high concentration ranges were comparable when the suspect values were excluded. This indicated that the reference laboratory's precision for the environmental soils was consistent (approximately 21% RSD), and comparable to the PE soil samples when the suspect values were excluded.

The Paducah soils (indicated as bold sample IDs in Table 4-3) were analyzed by the technologies under both outdoor and chamber conditions to provide a measure of the effect that two different environmental

Table 4-3. Precision of the reference laboratory for environmental soil samples

Outdoor Site				Chamber Site			
Sample ID	**Average Concentration (ppm)**	**Standard Deviation (ppm)**	**RSD (%)**	**Sample ID**	**Average Concentration (ppm)**	**Standard Deviation (ppm)**	**RSD (%)**
101	0.5	0.1	16	206	1.9	0.9	49
102	2.0	0.3	16	207	18.8	3.5	19
103	2.3	0.6	27	208	30.5	7.9	26
104	9.4	4.0	43	209	40.2	28.5	71
105	59.4	16.5	28	210	88.6	25.6	29
106	281.0 (373.2) [a]	32.4 (186.2)	12 (50)	211	404.5	121.8	30
107	1.3	0.3	20	212	3.2	1.6	50
108	1.8	0.1	8	213	8.1	1.6	20
109	2.0	0.4	20	214	25.2	3.7	15
110	n/a [b]	n/a	n/a	215	26.7	3.2	12
111	38.7	4.3	11	216	55.1 (79.2)	8.5 (48.7)	15 (62)
112	n/a	n/a	n/a	217	659.8 (973.2)	196.6 (647.0)	30 (66)
113 [c]	1.1	0.6	55	**201**	0.9	0.2	24
114	1.3	0.3	20	**202**	1.4	0.2	12
115	14.8	1.8	12	**203**	13.9	1.7	12
116	41.3	5.9	14	**204**	44.3	2.9	7
117	383.9	55.2	14	**205**	493.0 (1196.0)	41.7 (1406.4)	8 (118)

[a] Data in parentheses include suspect values.
[b] n/a indicates that qualitative results only were reported for this sample.
[c] Bold sample IDs were matching Paducah sample pairs (i.e., 113/201, 114/202, 115/203, 116/204, 117/205).

conditions had on the technology's performance. Although this was not an issue for the reference laboratory (because all the samples were analyzed under laboratory conditions), the reference laboratory's results were delineated into the different site categories for comparison with the technologies. Sample IDs 113 and 201, 114 and 202, 115 and 203, 116 and 204, and 117 and 205 each represent a set of eight replicate samples of the same Paducah soil. The RSDs for four of the five Paducah pairs (excluding the suspect value for sample ID 205) ranged from 11 to 17%. The result from one pair (sample IDs 113 and 201) had an RSD of 42%, but the reported average concentration was near the reporting limits.

Extract Samples

The extract samples, which were used to simulate surface wipe samples, were the simplest of all the

demonstration samples to analyze because they required no extraction and were interference-free. Three types of extract samples were analyzed: solvent blanks, spikes of Aroclor 1242 at 10 µg/mL, and spikes of Aroclor 1254 at 100 µg/mL. Identical extract samples were prepared in two solvents (iso-octane and methanol) to accommodate the developer's request. The reference laboratory analyzed both solvent sets. A Student's t-test [7, 8] was used to compare the reference laboratory's average PCB concentrations for the two different solvents and showed that no significant differences were observed at either concentration. Therefore, the reference laboratory results for the two extract solvents were combined. Additionally, all blank samples were quantified as non-detects by the reference laboratory.

Table 4-4 summarizes the reference laboratory results for the extract samples by site. RSDs for the four replicates for each sample ID ranged from 3 to 24%. For the combined data set (16 replicate measurements), the average RSD at the 10-µg/mL level was 19%, while the average RSD at the 100-µg/mL level was 8%. For the entire extract data set, an estimate of overall precision was 14%. The overall precision for the extract samples was comparable to the best-case precision for environmental soil samples (21%) and PE soil samples (18%).

Table 4-4. Precision of the reference laboratory for extract samples

Outdoor Site				Chamber Site				Combined Sites		
Sample ID	Average Conc (µg/mL)	SD (µg/mL)	RSD (%)	Sample ID	Average Conc (µg/mL)	SD (µg/mL)	RSD (%)	Average Conc (µg/mL)	SD (µg/mL)	RSD (%)
129 [a]	0	n/a	n/a	229	0	n/a	n/a	0	n/a	n/a
132 [a]	0	n/a	n/a	232	0	n/a	n/a			
127	10.9	0.4	4	227	9.6	0.8	8	10.4	1.9	19
130	12.1	2.9	24	230	8.9	1.4	16			
128	67.4	2.3	3	228	65.2	5.1	8	63.5	5.2	8
131	63.8	5.0	8	231	57.7	3.1	5			

[a] All PCB concentrations reported as non-detects by the laboratory.

Accuracy

Accuracy represents the closeness of the reference laboratory's measured PCB concentrations to the accepted values. Accuracy was examined by comparing the measured PCB concentrations (for PE soil and extract samples) with the certified PE values and known spiked extract concentrations. Percent recovery was used to quantify the accuracy of the results. The optimum percent recovery value is 100%. Percent recovery values greater than 100% indicate results that are biased high, and values less than 100% indicate results that are biased low.

Performance Evaluation Soil Samples

The reference laboratory's performance for the PE samples is summarized in Table 4-5. Included in this table are the performance acceptance ranges and the certified PCB concentration values. The acceptance ranges, based on the analytical verification data, are guidelines established by the provider of the PE materials to gauge acceptable analytical results. As shown in Table 4-5, all of the average concentrations

were within the acceptance ranges, with the exception of sample ID 218. The average result of sample ID 225 was outside of the acceptance range only when the suspect result was included. All of the replicate measurements in sample ID 225 were biased slightly high. Average percent recoveries for the PE samples (excluding suspect values) ranged from 76 to 130%. Overall accuracy was estimated as the average recovery for all PE samples. The overall percent recovery was 105% as a worst case when the suspect value was included. Excluding the suspect value as a best case slightly lowered the overall percent recovery to 101%. A regression analysis [9] indicated that the reference laboratory's results overall were unbiased estimates of the PE sample concentrations.

Table 4-5. Accuracy of the reference laboratory for PE soil samples

Certified Concentration (ppm) (Acceptance Range, ppm)	Outdoor Site			Chamber Site			Combined Sites	
	Sample ID	Average Conc (ppm)	Recovery (%)	Sample ID	Average Conc (ppm)	Recovery (%)	Average Conc (ppm)	Recovery (%)
0 [a] (n/a)	126	0	n/a	226	0	n/a	0	n/a
2.0 (0.7-2.2)	118	1.6	79	218	2.6	130	2.1	105
2.0 (0.9-2.5)	124	1.7	85	224	1.7	85	1.7	85
5.0 (2.1-6.2)	120	5.0	99	220	5.8	117	5.4	108
10.9 (4.0-12.8)	122	11.1	102	222	12.8	117	11.9	109
20.0 (11.4-32.4)	119	20.1	100	219	23.3	116	21.7	109
49.8 (23.0-60.8)	125	37.9	76	225	41.7 [b]	84 [b]	39.5 [c]	79 [c]
50.0 (19.7-63.0)	121	54.6	109	221	44.9	90	49.8	100
50.0 (11.9-75.9)	123	60.1	120	223	55.8	112	58.0	116

[a] All PCB concentrations reported as non-detects by the laboratory.
[b] Results excluding the suspect value (results including the suspect value: average = 67.8 ppm and recovery = 136%).
[c] Results excluding the suspect value (results including the suspect value: average = 52.8 ppm and Recovery = 106%).

Extract Samples

Percent recovery results for extract samples are summarized in Table 4-6 for the reference laboratory. The average percent recoveries for extract samples ranged from 58 to 121%. In terms of concentration levels, the average recovery at the 10-µg/mL level (for both solvents) was 104%, compared with 64% at the 100-µg/mL level. The reference laboratory classified all 16 samples spiked at 10 µg/mL as Aroclor 1016;

however, these samples were actually spiked with Aroclor 1242. Despite this misclassification, the results did not appear to be biased. In contrast, the samples spiked at 100 µg/mL were correctly classified as Aroclor 1254 but were all biased low. Although these results suggested that Aroclor classification had little effect on the quantification of the extract samples, there was an obvious, consistent error introduced into the analysis of the 100-µg/mL samples to cause the low bias. For the entire extract data set, the overall percent recovery was 84%.

Table 4-6. Accuracy of the reference laboratory for extract samples

Spike Concentration (µg/mL)	Outdoor Site			Chamber Site			Combined Sites	
	Sample ID	Avg Conc (µg/mL)	Recovery (%)	Sample ID	Avg Conc (µg/mL)	Recovery (%)	Avg Conc (µg/mL)	Recovery (%)
0 [a]	129	0	n/a	229	0	n/a	0	n/a
0 [a]	132	0	n/a	232	0	n/a		
10	127	10.9	109	227	9.6	96	10.4	104
10	130	12.1	121	230	8.9	89		
100	128	67.4	67	228	65.2	65	63.5	64
100	131	63.8	64	231	57.7	58		

[a] All PCB concentrations reported as non-detects by the laboratory.

Representativeness

Representativeness expresses the degree to which sample data accurately and precisely represent the capability of the method. Representativeness of the method was assessed based on the data generated for clean-QC samples (i.e., method blanks and laboratory control samples) and PE samples. Based on the data assessment (discussed in detail in various parts of this section), it was determined that the representativeness of the reference laboratory data was acceptable. In addition, acceptable performance on laboratory audits substantiated that the data set was representative of the capabilities of the method. In all cases, the performance of the reference laboratory met all requirements for both audits and QC analyses.

Completeness

Completeness is defined as the percentage of measurements that are judged to be usable (i.e., the result was not rejected). Usable results were obtained for 248 of the 256 samples submitted for analysis by the reference laboratory. Eight results (for sample IDs 110 and 112) were deemed incomplete and therefore not valid because the measurements were not quantitative. To calculate completeness, the total number of complete results were divided by the total number of samples submitted for analysis, and then multiplied by 100 to express as a percentage. The completeness of the reference laboratory was 97%, where a completeness of 95% or better is typically considered acceptable.

Comparability

Comparability refers to the confidence with which one data set can be compared with another. The demonstration study was designed to have a one-to-one, sample-by-sample comparison of the PCB results obtained by the reference laboratory and the PCB results obtained by the technology being evaluated. Based on thorough examination of the data and acceptable results on the PE samples, it was concluded that the reference laboratory's SOPs for extraction and analysis, and the data generated using these procedures, were of acceptable quality for comparison with the field technology results. Additional information on comparability was available because the experimental design incorporated randomized analysis of blind, replicate samples. Evaluation of the replicate data implicated some of the individual data points as suspect (see Table D-2). The reference laboratory's suspect data were compared with the technology data on a special-case basis, and exceptions were noted.

Summary of Observations

Table 4-7 provides a summary of the performance of the reference laboratory for the analysis of all sample types used in the technology demonstration study. As shown in Table 4-7, the precision of the PE soils was comparable to the environmental soils. A weighted average, based on the number of samples, gave a best-case precision of 21% and a worst-case precision of 28% for all the soil data (PE and

Table 4-7. Summary of the reference laboratory performance

Sample Matrix	Sample Type	Number of Samples	Precision (Average % RSD)	Accuracy (Average %Recovery)
Blank	Soil Extract	8 16	n/a [a]	All samples were reported as non-detects.
Environmental soil with interferences	Sample ID 110 Sample ID 112	4 4	n/a [a]	All samples were reported as non-detects.
Soil Best Case (excluding suspect data)	PE Environmental < 125 ppm > 125 ppm overall	63 107 17 187	18 23 19 21	101 n/a [b] n/a [b] 101
Soil Worst Case (including suspect data)	PE Environmental < 125 ppm > 125 ppm overall	64 108 20 192	21 26 56 28	105 n/a [b] n/a [b] 105
Extract	10 ppm 100 ppm overall	16 16 32	19 8 14	104 64 84

[a] Because the results were reported as non-detects, precision assessment is not applicable.
[b] Accuracy assessment calculated for samples of known concentration only.

environmental). The extract samples had a smaller overall RSD of 14%. Evaluation of overall accuracy was based on samples with certified or known spiked concentrations (i.e., PE and extract samples). The overall accuracy, based on percent recovery, for the PE samples was 105% for the worst case (which included the suspect value) and 101% for the best case (which excluded the suspect value). These results indicated that the reference laboratory measured values were unbiased estimates of the certified PE concentrations (for samples that contained $\leq$50 ppm of PCBs). Accuracy for the extract samples at 10 ppm was also unbiased, with an average percent recovery of 104%. However, the accuracy for the extract samples at 100 ppm was biased low, with an average recovery of 64%. Overall, the average percent recovery for all extract samples was 84%. The reference laboratory correctly reported all blank samples as non-detects, but had difficulty with two soil sample IDs (110 and 112) that contained chemical interferences. In general, the reference laboratory's completeness would be reduced, at the expense of an improvement in precision and accuracy, if the suspect measurements were excluded from the data analysis. Based on this analysis, it was concluded that the reference laboratory results were acceptable for comparison with the developer's technology.

Section 5
Technology Performance and Evaluation

Objective and Approach

The purpose of this section is to present the evaluation of data generated by EST's 4100 Vapor Detector. The technology's precision and accuracy performance are presented for the data generated in the demonstration study. In addition, an evaluation of comparability, through a one-to-one comparison with the reference laboratory data, is presented. An evaluation of other aspects of the technology (such as detection limits, cost, sample throughput, hazardous waste generation, and logistical operation) is also presented in this section.

Data Assessment

The purpose of the data assessment section is to present the evaluation of the performance of EST's 4100 Vapor Detector through a statistical analysis of the data. PARCC parameters were used to evaluate the technology's ability to measure PCBs in PE, environmental soil, and extract samples. The developer analyzed splits of replicate samples that were also analyzed by the reference laboratory (72 PE soil samples, 136 environmental soil samples, and 24 extract samples). See Section 4 for a more detailed analysis of the reference laboratory's results. Replicate samples were analyzed by the developer at two different sites (under outdoor conditions and inside an environmentally controlled chamber) to evaluate the effect of environmental conditions on performance; see Section 3 for further details on the different sites. Evaluation of the data sets indicated that there were no significant differences in the precision of the measurements made at each site. There were significant differences, however, in the accuracy of the measured concentrations determined at each site. In cases where the environmental conditions did not affect results significantly, data from both sites were combined for each parameter (precision and accuracy) to determine overall performance. All statistical tests were performed at the 5% significance level. Appendix D contains the raw data that were used to assess the performance of the 4100 Vapor Detector.

Precision

Precision, as defined in Section 4, is the reproducibility of measurements under a given set of conditions. The SD and RSD of four replicate measurements were used to quantify the technology's precision. The average PCB concentration for a replicate set was used to calculate the RSD for each sample ID (see Eq. 4-3). For more information regarding the reference laboratory's precision, refer to the data presented in Section 4 under the heading of "Precision."

Performance Evaluation Samples

Table 5-1 summarizes the precision of the 4100 Vapor Detector for the analysis of PE samples. Operating under the outdoor conditions, the RSDs ranged from 51 to 162%. RSDs ranged from 37 to 116%, while operating inside the chamber. In Table 5-1, the data generated under both environmental conditions were also combined to provide an overall assessment of precision. The performance for the combined site data indicated RSDs ranging from 62 to 165%.

Table 5-1. Precision of the 4100 Vapor Detector for PE soil samples

Outdoor Site				Chamber Site				Combined Sites		
Sample ID	Average Concentration (ppm)	SD (ppm)	RSD (%)	Sample ID	Average Concentration (ppm)	SD (ppm)	RSD (%)	Average Concentration (ppm)	SD (ppm)	RSD (%)
126 [a]	33.5	42.5	127	226 [a]	77.8	78.9	101	55.6	63.3	114
118	9.2	10.5	115	218	39.8	25.2	63	24.5	24.2	99
124	8.3	4.5	54	224	32.1	11.9	37	20.2	15.2	75
120	8.2	11.0	133	220	27.0	14.1	52	17.6	15.4	88
122	20.9	33.7	161	222	8.1	9.4	116	14.5	23.9	165
119	2.3	3.7	162	219	45.6	29.9	65	24.0	30.4	127
125	30.9	19.9	64	225	120.1	73.1	61	75.5	68.8	91
121	39.1	20.0	51	221	142.9	68.9	48	91.0	72.7	80
123	18.4	12.5	68	223	44.3	16.5	37	31.1	19.4	62

[a] The 4100 detected PCBs in the blanks. The blank data were not included in the calculation of the overall average RSD.

Environmental Soil Samples

The precision of the 4100 Vapor Detector for the analysis of environmental soil samples is reported in Table 5-2. Operating under the outdoor conditions, the RSDs ranged from 33 to 187%. RSDs ranged from 25 to 151%, while operating inside the chamber. Because most of the measurements fell below 125 ppm, precision was also assessed by partitioning the results into two ranges: low concentrations (reference laboratory values < 125 ppm) and high concentrations (reference laboratory values > 125 ppm). See Section 4 for delineation of sample IDs in each concentration range. For the low-concentration range, the average RSD was 93%, in contrast to that of the high-concentration range, which was 50%.

The Paducah soils (indicated by bold sample IDs in Table 5-2) were analyzed at both sites to provide an assessment of the 4100's performance under different environmental conditions. For these samples, the data generated under both environmental conditions were also combined to provide an overall assessment of precision. Sample IDs 113 and 201, 114 and 202, 115 and 203, 116 and 204, and 117 and 205 represented replicate Paducah soil sample sets, where the "100" series were samples analyzed under the outdoor conditions and the "200" series were samples analyzed inside the chamber. An analysis of variance (ANOVA) test was used to compare the effect of the two environmental conditions on the average measurements. Results from the ANOVA analysis showed that there were no significant differences in the RSDs generated at each site, however, the average measured concentrations were different, indicating that environmental conditions had an effect on the 4100's ability to measure PCB concentrations, but that the precision of the measurements was similar at each site, as illustrated in Table 5-2. When the 4100 Vapor Detector was used under the outdoor conditions, the RSDs for the Paducah samples ranged from 33 to

116%, and from 48 to 116% operating inside the chamber. RSDs for the combined site data (8 replicates per paired Paducah sample ID) ranged from 65 to 160%.

Table 5-2. Precision of the 4100 Vapor Detector for environmental soil samples

Outdoor Site				Chamber Site				Combined Site
Sample ID	**Average Concentration (ppm)**	**SD (ppm)**	**RSD (%)**	**Sample ID**	**Average Concentration (ppm)**	**SD (ppm)**	**RSD (%)**	**RSD (%)**
107	3.7	2.3	62	206	53.5	80.5	151	n/a [b]
104	5.6	5.3	95	212	58.9	19.9	34	n/a
108	7.3	10.9	150	213	135.9	96.0	71	n/a
101	14.5	14.3	99	215	205.3	145.6	71	n/a
105	27.8	18.8	68	214	253.5	239.4	94	n/a
109	35.2	36.4	103	207	258.5	158.5	61	n/a
103	41.8	49.3	118	210	396.9	145.3	37	n/a
110	53.5	100.0	187	209	406.4	259.9	64	n/a
102	55.2	101.1	183	216	430.3	108.8	25	n/a
111	73.3	93.1	127	208	470.4	271.4	58	n/a
106	151.3	105.6	70	217	537.8	375.7	70	n/a
112	693.3	891.9	129	211	717.9	204.1	28	n/a
113 [a]	5.9	4.5	77	**201**	11.2	13.0	116	111
114	16.0	17.2	108	**202**	23.0	26.1	113	107
115	8.2	9.5	116	**203**	14.2	14.5	103	106
116	4.4	4.4	101	**204**	104.1	104.5	100	160
117	119.5	39.1	33	**205**	295.1	142.1	48	65

[a] Bold sample IDs were matching Paducah sample pairs (i.e., 113/201, 114/202, 115/203, 116/204, 117/205).
[b] Combined site results were not applicable because these environmental samples were not replicate pairs.

Extract Samples

Table 5-3 summarizes the 4100 Vapor Detector results for the extract samples used to simulate surface wipe samples. Refer to Section 3 under the heading of “Extract Samples” for further clarification of this sample type. When the 4100 Vapor Detector was used under the outdoor conditions, the RSDs ranged from 9 to 60%. RSDs ranged from 47 to 63% when it was used inside the chamber. For the combined site data, the average RSD at the 10-µg/mL level was 71%; the average RSD at the 100-µg/mL level was 59%.

Table 5-3. Precision of the 4100 Vapor Detector for extract samples

Outdoor Site				Chamber Site				Combined Sites		
Sample ID	Average Concentration (µg/mL)	SD (µg/mL)	RSD (%)	Sample ID	Average Concentration (µg/mL)	SD (µg/mL)	RSD (%)	Average Concentration (µg/mL)	SD (µg/mL)	RSD (%)
132 [a]	0.2	0.4	200	232 [a]	33.3	66.2	199	16.7	46.8	280
130	14.1	8.5	60	230	39.3	18.6	47	26.7	19.0	71
131	40.5	3.7	9	231	68.3	43.3	63	54.4	32.1	59

[a] The 4100 detected PCBs in the blanks. The blank data were not included in the calculation of the overall average RSD.

Precision Summary

The overall precision was characterized by three summary values for the RSD: mean (i.e., average), median (i.e., 50th percentile value at which 50% of all individual RSD values are below and 50% are above), and 95th percentile (i.e., the value at which 95% of all individual RSD values are below and 5% are above). These values are summarized in Table 5-4 for each of the sample types. The 4100 Vapor Detector's overall precision for the PE samples was a mean RSD of 81%, a median RSD of 64%, and the 95th percentile of all individual RSDs was 161%. The environmental soil sample RSD results were a mean of 90%, a median of 95%, and a 95th percentile of 162%. The overall precision for all extract samples was a mean RSD of 65%; the 95th percentile and median data were not presented because the number of data points was limited .

Table 5-4. Overall precision of the 4100 Vapor Detector for all sample types

Statistic	PE Samples			Environmental Soil Samples			Extract Samples		
	%RSD			%RSD			%RSD		
	Outdoor	Chamber	Combined	Outdoor	Chamber	Combined [a]	Outdoor	Chamber	Combined
Mean	101	60	81	107	73	90	34	55	65
Median	91	57	64	103	70	95	n/a [b]	n/a	n/a
95th percentile	162	98	161	184	123	162	n/a	n/a	n/a

[a] Combined data were only generated for the Paducah soil samples.
[b] Median and 95th percentile statistics were not applicable to extract samples.

Accuracy

Accuracy, as defined in Section 4, represents the closeness of the technology's measured PCB concentrations to the accepted values. Accuracy was examined in terms of percent recovery (see Eq. 4-1), and average percent recoveries were calculated by averaging the four replicates within a sample ID. For comparative information on the performance of the reference laboratory, refer to Section 4 under the heading of "Accuracy."

Performance Evaluation Soil Samples

The 4100 Vapor Detector's performance for the PE samples is summarized in Table 5-5. Included in this table are the performance acceptance ranges and the certified PCB concentration values. Most of the average concentrations determined by the 4100 were outside of the acceptance ranges and most were biased high. This was also reflected in the average percent recoveries, which ranged as high as 1,990%. Average percent recoveries ranged from 12 to 460% while operating under the outdoor conditions. Under chamber conditions, average percent recoveries ranged from 74 to 1,990%.

A regression analysis [9] indicated that there were significant differences between outdoor and chamber results. These differences could be caused by changes in the analytical procedure, which are noted in Section 3 under the heading of "Deviations from the Demonstration Plan." Because there appeared to be significant differences in the data generated at the two sites, the data were not combined. Additionally, there was low correlation of the 4100's measured PCB concentrations with the certified PE values. This is illustrated in Figure 5-1.

Extract Samples

Percent recovery results for the extract samples are summarized in Table 5-6 for the 4100 Vapor Detector. The average percent recoveries for extract samples ranged from 41 to 141% when the 4100 was operated under the outdoor conditions and ranged from 68 to 393% inside the chamber. In terms of concentration levels (i.e., for the combined site data), the average recovery at the 10-µg/mL level was 267%, compared with 54% at the 100-µg/mL level. Of the eight blank samples analyzed, five were reported as non-detects, two as <1 ppm, and one as 133 µg/mL. Note that the one anomalous blank result was obtained after the

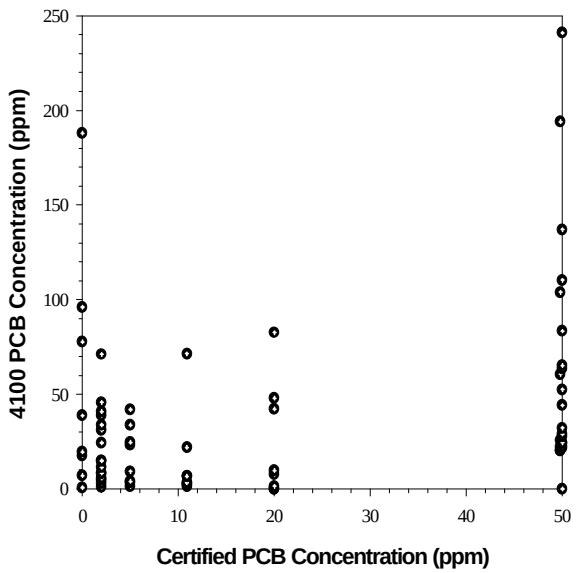

Figure 5-1. The 4100 Vapor Detector's results versus the certified PCB concentration for PE soil samples.

analysis of a 100-µg/mL sample; it may have resulted from carryover if insufficient instrument blanks were not analyzed. Refer to Section 2 under the heading of "Sample Preparation and Analysis Procedures" for more information on the technology's requirements for the analysis of instrument blanks.

Accuracy Summary

The overall accuracy was characterized by three summary values for the percent recovery: mean, median, and 95th percentile. These values are summarized in Table 5-7 for the PE and extract samples. For the PE samples, the overall accuracy of the 4100 Vapor Detector can be characterized as biased with a significant influence based on environmental conditions. The mean percent recovery of the 4100 operating under outdoor conditions was 177% with a median of 53% a and 95th percentile of 693%. Under chamber conditions, the overall accuracy was a mean percent recovery of 631%, a median of 257%, and a 95th percentile of 2,150%. The overall accuracy for all extract samples was a mean percent recovery of 161%; the 95th percentile and median data were not presented because the number of data points was limited.

Table 5-5. Accuracy of the 4100 Vapor Detector for PE soils samples

Certified Concentration (ppm) (Acceptance Range, ppm)	Outdoor Site			Chamber Site		
	Sample ID	Average (ppm)	Recovery (%)	Sample ID	Average (ppm)	Recovery (%)
0 [a] (n/a)	126	33.5	n/a	226	77.8	n/a
2.0 (0.7-2.2)	118	9.2	460	218	39.8	1,990
2.0 (0.9-2.5)	124	8.3	415	224	32.1	1,605
5.0 (2.1-6.2)	120	8.2	164	220	27.0	540
10.9 (4.0-12.8)	122	20.9	192	222	8.1	74
20.0 (11.4-32.4)	119	2.3	12	219	45.6	228
49.8 (23.0-60.8)	125	30.9	62	225	120.1	241
50.0 (19.7-63.0)	121	39.1	78	221	142.9	286
50.0 (11.9-75.9)	123	18.4	37	223	44.3	89

[a] The 4100 Vapor Detector detected PCBs in the blanks. Average recovery calculations were not applicable to blank samples.

Table 5-6. Accuracy of the 4100 Vapor Detector for extract samples

Spike Concentration (µg/mL)	Outdoor Site			Chamber Site			Combined Sites	
	Sample ID	Average Conc (µg/mL)	Recovery (%)	Sample ID	Average Conc (µg/mL)	Recovery (%)	Average Conc (µg/mL)	Recovery (%)
0 [a]	132	0.2	n/a	232	33.3	n/a	16.7	n/a
10	130	14.1	141	230	39.3	393	26.7	267
100	131	40.5	41	231	68.3	68	54.4	54

[a] The 4100 Vapor Detector detected PCBs in the blanks. Average recovery calculations were not applicable to blank samples.

Table 5-7. Overall accuracy of the 4100 Vapor Detector for all sample types

Statistic	PE Samples %Recovery			Extract Samples %Recovery		
	Outdoor	Chamber	Combined	Outdoor	Chamber	Combined
Mean	177	631	n/a [a]	91	231	161
Median	53	257	n/a	n/a [b]	n/a	n/a
95th percentile	693	2,150	n/a	n/a	n/a	n/a

[a] Combined site results are not applicable because of significant site-specific differences.
[b] Median and 95th percentile statistics were not applicable to extract samples.

False Positive/False Negative Results

A false positive (fp) result [10] is one in which the technology detects PCBs in the sample when there actually are none. A false negative (fn) result [10] is one in which the technology indicates that there are no PCBs present in the sample, when there actually are. Both fp and fn results are influenced by the method detection limit of the technology. Because EST did not specify a method detection limit prior to the demonstration, any PCB concentration that was detected was considered real. Of the blank soil samples analyzed, PCBs were reported in all eight (fp = 100%). Of the 192 non-blank soil samples analyzed, ten were reported as non-detects (i.e., fn = 5%). For the extract samples, the percentage of fp results was 38% (three of eight blank samples were reported as containing PCBs), with 0% fn results.

Representativeness

Representativeness expresses the degree to which the sample data accurately and precisely represent the capability of the technology. The performance data were accepted as being representative of the technology because the 4100 Vapor Detector was capable of analyzing diverse sample types (PE, simulated surface wipe extract, and actual environmental soil samples) under multiple environmental conditions. When this technology is used, independent quality control samples should be analyzed to assess the performance of the 4100 under the testing conditions.

Completeness
Completeness is defined as the percentage of measurements that are judged to be useable (i.e., the result was not rejected). Useable results were obtained by the technology for all 232 samples. Therefore, the completeness of the 4100 Vapor Detector was 100%.

Comparability
Comparability refers to the confidence with which one data set can be compared with another. A one-to-one sample comparison was performed to assess the comparability of the PCB concentrations found in all soil samples (PE and environmental) for the 4100 measured values versus the reference laboratory results. Additional statistical analysis of the PCB soil concentrations for paired samples showed that the 4100 measured values were significantly different from the reference laboratory results. This is illustrated in Figure 5-2, which is a plot of the 4100 measured PCB soil concentrations versus the corresponding reference laboratory measured concentrations (excluding the suspect values listed in Table 4-1). Figure 5-2 (a) is a plot of all of the soil data, while (b) is a plot of the concentration region from 0 to 125 ppm, where most of the variation can be viewed. Note that the diagonal lines drawn in Figure 5-2 represent the line of theoretically perfect correlation ($R^2 = 1.0$) between the reference laboratory data set (plotted along the *x*-axis) and the 4100 data set (plotted along the *y*-axis). A value above the diagonal line indicated that the 4100's measurement was higher than the reference laboratory's measurement, while those below the diagonal line indicated a lower result. Coefficients of determination (R^2) [9] were computed using a linear model fitted to the plot of the 4100 PCB concentrations versus the reference laboratory PCB concentrations. Excluding the reference laboratory's suspect measurements, the coefficient of determination (R^2) was 0.177 when all soil samples (0 to 700 ppm) were considered. As shown in Figure 5-2(b), most of the soil samples were in the concentration range of 0 to 125 ppm. The R^2 value for this concentration range was 0.115.

A direct comparison between the 4100 and reference laboratory data was performed by evaluating the percent difference (% D) between the measured concentrations, defined as:

$$\% D = \frac{[4100] - [Ref\ Lab]}{[Ref\ Lab]} \times 100\% \qquad (5\text{-}1)$$

Figure 5-3 provides a summary of the range of percent difference values for the soil samples, as calculated using Eq. 5-1. The graph represents the percentage of samples that fall within each range of percent difference values; however, the graph does not reflect any grouping according to the actual concentrations of the replicate sets. Results for sample IDs 110, 112, 126, and 226 were not included because the reference laboratory did not report quantitative results for them. As shown in Figure 5-3, most of the percent difference values were greater than 100%, and 40% of the samples had a negative bias (< −1%) relative to the reference laboratory results. Approximately 10% of the soil sample results had %D values within the range of ± 25%.

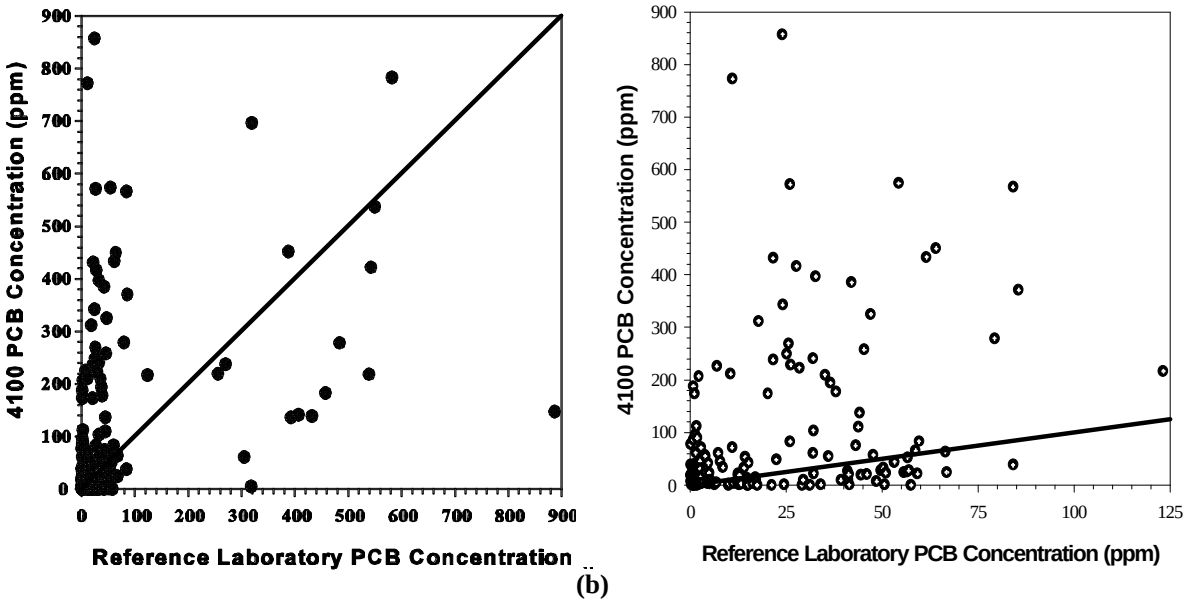

Figure 5-2. Paired PCB measurements for 4100 and reference measurements for (a) all soil samples and (b) soil samples where the reference laboratory result was less than or equal to 125 ppm. Lines denote perfect correlation.

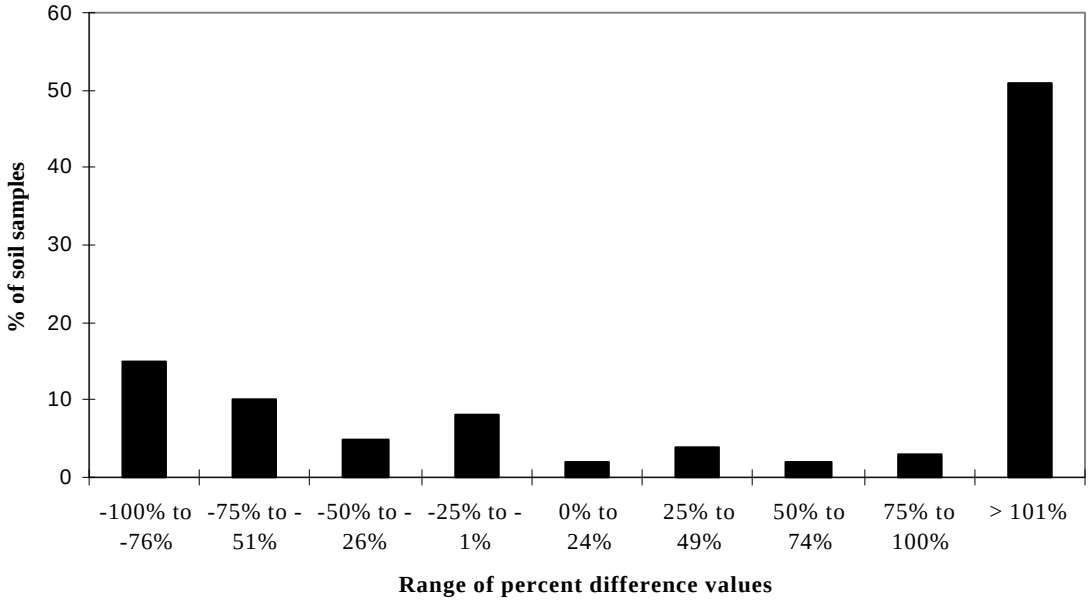

Figure 5-3. Range of percent difference values for the comparison of the 4100 Vapor Detector soil sample results with the reference laboratory results.

Comparability was also assessed for the extract samples. Figure 5-4 is a plot of the 4100 measured extract concentrations versus the reference laboratory results. The coefficient of determination (R^2) was 0.187 for a line fit to the data, indicating a low correlation between the 4100 extract values and the reference laboratory results. The percent difference values for the extract samples were also assessed, and are shown in Figure 5-5. The bias in the 4100 results was evenly distributed (positive and negative) compared with that of the reference laboratory results. Approximately 19% of the extract results had %D values within the range of ± 25%.

The soil data not included in previous comparability evaluations (because the replicate data for the reference laboratory were considered suspect) are shown in Table 5-8. Refer to Section 4, in particular Table 4-1, for more information on the reference laboratory's suspect measurements. The reference laboratory's suspect data were compared with the 4100's matching results. For sample IDs 110 and 112, the reference laboratory obtained qualitative results only, while EST reported quantitative PCB concentrations. For the other five suspect reference laboratory measurements, quantitative results were obtained; however, one of the four replicates was considered suspect. For those samples, the 4100 generated quantitative results that were not always consistent with the replicate means or comparable with the reference laboratory's corresponding suspect value.

Table 5-8. Comparison of the reference laboratory's suspect data to the 4100 Vapor Detector data

Sample ID	Reference Laboratory		4100 Vapor Detector	
	Suspect Measurement (ppm)	Replicate Mean [a] (ppm)	Suspect-matching Measurement (ppm)	Replicate Mean (ppm)
110	≤RDL [b]	≤RDL [b]	n/a	53.5
112	≤RDL [b]	≤RDL [b]	n/a	693.3
106	649.6	281.0	142.3	151.3
205	3,305.0	493.0	500.0	295.1
216	151.6	55.1	372.1	430.3
217	1,913.3	659.8	1,045.0	537.8
225	146.0	41.7	156.9	120.1

[a] Mean result excluding the suspect measurement.
[b] Measurement reported qualitatively as less than or equal to the reporting detection limit (≤RDL) for all replicates.

Summary of PARCC Observations

Table 5-9 provides a summary of the performance of EST's 4100 Vapor Detector for the analysis of all sample types used in this demonstration study. The reference laboratory's performance (excluding suspect data) is also presented in this table for comparison. In terms of precision, the overall average RSD for the 4100, weighted for the number of samples, was 87% for the soil samples. This is in

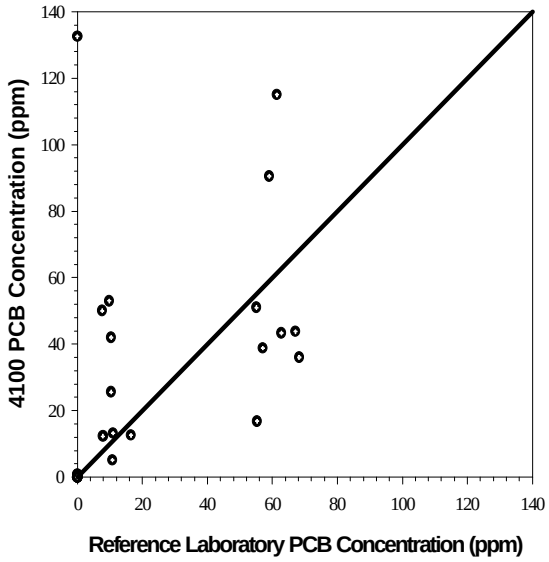

Figure 5-4. Paired PCB extract measurements for the 4100 Vapor Detector and reference laboratory.

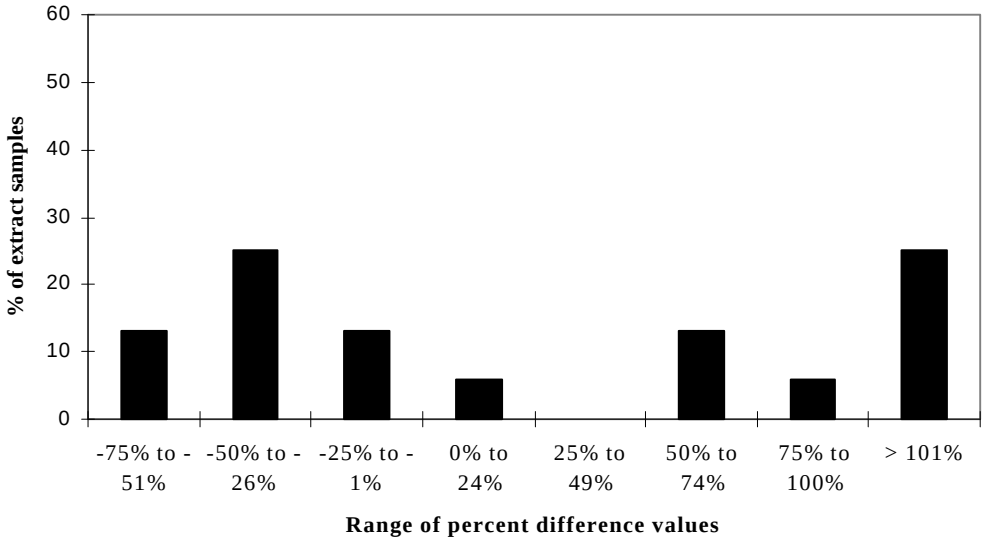

Figure 5-5. Range of percent difference values for the comparison of the 4100 Vapor Detector extract sample results with the reference laboratory results.

Table 5-9. Summary of PARCC observations for the 4100 Vapor Detector

Sample Matrix	Sample Type	4100's Number of Samples	Precision (Average % RSD)		Accuracy (Average %Recovery)	
			4100	Reference Laboratory	4100	Reference Laboratory
Blank	Soil Extract	8 8	114 280	n/a	Background contributions were detected.	All reported as non-detects.
Soil	PE	64	81	18 [a]	177 (outdoors) 631 (chamber)	101 [a]
	Environmental					
	< 125 ppm [b]	108	93	23 [a]		
	> 125 ppm [c]	20	50	19 [a]		
	Sample ID 110	4	187	not quantified		
	Sample ID 112	4	129	not quantified		
	overall	200	87	21 [a]	177 (outdoors) 631 (chamber)	101 [a]
Extract	10 ppm	8	71	19	267	104
	100 ppm	8	59	8	54	64
	overall	16	65	14	161	84

[a] Average result excluding the suspect measurements.
[b] Samples where the reference laboratory values were < 125 ppm.
[c] Samples where the reference laboratory values were > 125 ppm.

comparison with the reference laboratory's overall RSD of 21%. For the extract samples, the overall average RSD for the 4100 was 65%, compared with that of the reference laboratory, which was 14%.

In terms of accuracy, the 4100's PE soil measurements were generally biased high. The results also indicated significant differences in the percent recoveries of the measurements performed outdoors (177% recovery) and those performed inside the chamber (631% recovery). In comparison, the reference laboratory reported unbiased PCB concentrations for these PE soil samples. Extract measurements by the 4100 were also biased high at 10 ppm (267% recovery), but were biased low at 100 ppm (54% recovery). In contrast, the reference laboratory results were unbiased at 10 ppm (104% recovery), but were biased low at 100 ppm (64% recovery).

The 4100 detected PCBs in all soil blanks (i.e., 100% false positive results), while the reference laboratory correctly reported all blank samples as non-detects. For the 4100, the percentage of false negative results was 5%. Overall, the performance of the 4100 Vapor Detector for the PCB demonstration samples was characterized as biased and imprecise.

Regulatory Decision-Making Applicability

One of the objectives of this demonstration was to assess the technology's ability to perform at regulatory decision-making levels for PCBs, specifically 50 ppm for soils and 100 µg/100 cm^2 for surface wipes. To

assess this, the 4100's performance for soil samples (PE and environmental soils) ranging in concentration from 40 to 60 ppm can be used, and the data are provided in Table 5-10. The performance of the 4100 for this concentration range was consistent with the conclusions outlined above (which found the technology to provide results that were biased both high and low, and that were imprecise). Additionally, most of the percent difference values were greater than 100% when compared with the corresponding reference laboratory result.

The 4100 Vapor Detector's performance on extract samples was provided in Tables 5-4 and 5-7. Assuming a 10-mL extract volume, extract samples (at 10 and 100 µg/mL) represented surface wipe sample concentrations of 100 and 1000 µg/100 cm^2. For the simulated wipe extract samples, the 4100's precision was 65% RSD with a high bias (267% recovery) on the lower concentration samples, and a low bias (54% recovery) on the higher concentration samples.

Table 5-10. Performance of the 4100 Vapor Detector for soil samples between 40 and 60 ppm

Overall Performance	Precision (% RSD)	Accuracy (% Recovery)	Comparability (% Difference)
Mean	72	132	296
Median	64	76	60
95th percentile	114	377	630

Additional Performance Factors

Detection Limits

The method detection limit (MDL) is often defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. An MDL is determined from repeated analyses of a sample in a given matrix containing the analyte [11]. EST did not specify a method detection limit prior to the demonstration study. An MDL was calculated from the data for the PE samples. Because there was a significant "site effect" (i.e., differences in performance due to environmental conditions) inherent to the PE samples, separate MDLs were calculated for both the outdoor and chamber conditions. The MDL calculated for the outdoor conditions was 26 ppm, while the MDL for the chamber conditions was 62 ppm.

Sample Throughput

Sample throughput is representative of the average amount of time required to extract the PCBs, to perform appropriate reactions, and to analyze the sample. Operating under the outdoor conditions, EST's sample throughput rate was approximately 5 to 6 samples/h, but improved to 10 samples/h under the chamber conditions. This increased sample throughput may be attributed to the analysis order (EST may have gained experience by analyzing samples under the outdoor conditions first), or difficulty with the sample matrices that were analyzed only under the outdoor conditions.

Cost Assessment

The purpose of this economic analysis is to provide an estimation of the range of costs for an analysis of PCB-contaminated soil samples using the 4100 Vapor Detector and a conventional analytical reference

laboratory method. The analysis was based on the results and experience gained from this demonstration, costs provided by EST, and representative costs provided by the reference analytical laboratories that offered to analyze the samples. To account for the variability in cost data and assumptions, the economic analysis was presented as a list of cost elements and a range of costs for sample analysis by the 4100 and by the reference laboratory.

Several factors affected the cost of analysis. Where possible, these factors were addressed so that decision makers can independently complete a site-specific economic analysis to suit their needs. The following categories were considered in the estimate:

- sample shipment costs,
- labor costs,
- equipment costs,
- waste disposal costs.

Each of these cost factors is defined and discussed in the following section; the cost factors compose the basis for the estimated cost ranges presented in Table 5-11. Sample acquisition and preanalytical sample preparation, which were tasks common to both methods, are costs that were not included here.

4100 Vapor Detector Costs

Because the samples were analyzed on site, no sample shipment charges were associated with the cost of operating the 4100. Labor costs included mobilization/demobilization, travel, per diem, and on-site labor.

- Labor mobilization/demobilization: This cost element included the time for one person to prepare for and travel to each site. The estimate ranged from 5 to 8 h, at a rate of $50/h
- Travel: This element was the cost for the analyst(s) to travel to the site. If the analyst is located near the site, the cost of commuting to the site (estimated to be 50 miles at $0.30 per mile) would be minimal ($15). The estimated cost of an analyst traveling to the site for this demonstration ($1,000) included the cost of airline travel and rental car fees.
- Per diem: This cost element included food, lodging, and incidental expenses, and was estimated ranging from zero (for a local site) to $150 per day per analyst.
- Rate: The cost of the on-site labor was estimated at a rate of $30 to $75/h, depending on the required expertise level of the analyst. This cost element included the labor involved with the entire analytical process, comprising sample preparation, sample management, analysis, and reporting.

Equipment costs included mobilization/demobilization, purchase of equipment, training, and the reagents and other consumable supplies necessary to complete the analysis.

- Equipment mobilization/demobilization: This included the cost of shipping the equipment to the test site. If the site were local, the cost would be zero. For this demonstration, the cost of shipping equipment and supplies was estimated at $150.

- Purchase: At the time of the demonstration study, the cost of purchasing the 4100 Vapor Detector was $24,950. The SAW detector is sold separately for $1,500.

- Training: EST offers a 3-d training course on the use of the 4100 Vapor Detector at a cost of $2,400.

- Reagents/supplies: These items are consumable and are purchased on a per-sample basis. At the time of the demonstration, the cost of the reagents and supplies needed to prepare and analyze PCB soil samples using the 4100 was $1 to $2 per sample.

Waste disposal costs were estimated based on the 1997 regulations for disposal of PCB-contaminated waste. Using the 4100, EST generated approximately 27 lb of solid PCB waste that could be incinerated (i.e., vials containing soils and liquid solvents) and approximately 20 lb of solid PCB waste (i.e., used and unused soil, gloves, paper towels, and ampules). The disposal costs for solid PCB wastes by incineration at a commercial facility was estimated at $1.50 per pound. The cost for solid PCB waste disposal at ETTP was estimated at $18 per pound.

Table 5-11. Estimated analytical costs for PCB soil samples

4100 Vapor Detector Electronic Sensor Technology **Sample throughput rate: 5-6 samples per hour (outdoors) 10 samples per hour (chamber)**		**EPA SW-846 Method 8080/8081/8082 Reference Laboratory** **Typical turn-around time: 14 - 30 days**	
Cost Category	**Cost ($)**	**Cost Category**	**Cost ($)**
Sample Shipment	0	**Sample Shipment**	
		Labor	100 - 200
		Overnight shipping charges	50 - 150
Labor		**Labor**	
Mobilization/demobilization	250 - 400	Mobilization/demobilization	included [a]
Travel	15 - 1,000 per analyst	Travel	included
Per diem	0 - 150 per day per analyst	Per diem	included
Rate	30 - 75 per hour per analyst	Rate	44 - 239 per sample
Equipment		**Equipment**	
Mobilization/demobilization	0 - 150	Mobilization/demobilization	included
4100 Vapor Detector price	24,950	Purchase of equipment	included
SAW detector price	1,500	Reagents/supplies	included
3-Day Training	2,400		
Reagents/supplies	1 - 2 per sample		
Waste Disposal	70 - 850	**Waste Disposal**	included

[a] "Included" indicates that the cost is included in the labor rate.

Reference Laboratory Costs
Sample shipment costs to the reference laboratory included overnight shipping charges as well as labor charges associated with the various organizations involved in the shipping process.

- Labor: This cost element includes all of the tasks associated with the shipment of the samples to the reference laboratory. Tasks included packing the shipping coolers, completing the chain-of-custody documentation, and completing the shipping forms. Because the samples contained PCBs, the coolers were inspected by qualified personnel to ensure acceptance with the U.S. Department of Transportation's shipping regulations for PCBs. The estimate to complete this task ranged from 2 to 4 h at $50/h.

- Overnight Shipping: The overnight express shipping service cost was estimated to be $50 for one 50-lb cooler of samples.

The labor bids from commercial analytical reference laboratories that offered to perform the PCB analysis for this demonstration ranged from $44 per sample to $239 per sample. The bid was dependent on many factors, including the perceived difficulty of the sample matrix, the current work-load of the laboratory, and the competitiveness of the market. In this case, the wide variation in bids may also be related to the cost of PCB waste disposal in a particular laboratory's state. LAS Laboratories was awarded the contract to complete the analysis as the lowest qualified bidder ($44 per sample). This rate was a fully loaded analytical cost, including equipment, labor, waste disposal, and report preparation.

Cost Assessment Summary
An overall cost estimate for the 4100 versus the reference laboratory was not made because of the extent of variation in the different cost factors, as outlined in Table 5-11. The overall costs for the application of each technology will also be based on the number of samples requiring analysis, the sample type, and the site location and characteristics. Decision-making factors, such as turnaround time for results, must also be weighed against the cost estimate to determine the value of the field technology versus the reference laboratory.

General Observations
The following are general observations regarding the field operation of the 4100 Vapor Detector:

- The system was light (approximately 35 lb), easily transportable, and rugged. The system was shock mounted into a rugged field-portable fiberglass shipping case that could be checked as airplane baggage. It took the EST team less than 1 h to prepare to analyze samples on the first day of testing.

- Two operators were used for the demonstration because of the number of samples and working conditions, but the technology can be run by a single person.

- Operators generally require several hours of training and should have a basic knowledge of gas chromatographic techniques. These methods should be used by, or under the supervision of, analysts experienced in the use of sampling techniques and gas

chromatography. The analysts should also be skilled in the interpretation of gas chromatograms and in the use of chromatography as a quantitative tool.

- The system requires 120 VAC or battery power. Also, the system requires high-purity helium for the chromatographic column.

- The data acquisition system ran under a Windows 95 operating system.

- EST generated approximately 20 lb of PCB-contaminated solid hazardous waste (i.e., used and unused soil, gloves, paper towels, and ampules) using the 4100 Vapor Detector. In addition, approximately 27 lb of small sample vials (containing less than 1 g soil, methanol, water, and/or hexane) were also generated as hazardous waste.

Performance Summary

The performance characteristics of EST's 4100 Vapor Detector presented previously in this chapter are summarized in Table 5-12. The overall performance of the 4100 Vapor Detector was characterized as biased and imprecise.

Table 5-12. Performance summary for the 4100 Vapor Detector

Feature/Parameter	Performance Summary
Blank Samples	**Soils:** PCBs detected in all 8 blanks (0.7 to 188 ppm) **Extracts:** PCBs detected in 3 of 8 blanks (0.5 to 133 µg/mL)
Method Detection Limit	EST specified: none Calculated: 26 ppm (outdoors); 62 ppm (chamber)
Precision	**Average RSD** PE Soils: 81% (range: 51 to 165%) Environmental Soils: 90% (range: 25 top 187%) Extracts: 65% (range: 9 to 60%)
Accuracy	**Average Percent Recovery** PE Soils: 177% recovery (outdoors, range: 12 to 460%)); 631% recovery (chamber, range: 74 to 1,990%) Extracts: 161% recovery (range: 41 to 393%)
False Positive Results	**Blank Soils:** 100% (8 of 8 samples) **Blank Extracts:** 38% (3 of 8 samples)
False Negative Results	**PE and Environmental Soils:** 5% (10 of 192 samples) **Spiked Extracts:** 0% (0 of 16 samples)
Comparison with Reference Laboratory Results	**PE and Environmental Soil Samples** Percent Difference: 51% of samples were > 100% D Coefficients of determination (R^2): 0. 177 (all data) 0.115 (< 125 ppm) **Extract Samples** Percent Difference: 44% of samples were > 50% D Coefficient of determination (R^2): 0.187
Regulatory Decision-Making Applicability	**40 to 60 ppm PE and Environmental Soil Samples** precision: 72% average RSD (range: 37 to 127%) accuracy: 132% average recovery (range: 0 to 482%) comparability: 296% average difference (range: -100 to 6,922%) **100 µg/100cm^2 and 1000 µg/100cm^2 Extract Samples** precision: 65% average RSD (range: 59 to 71%) accuracy : 161% average recovery (range: 54 to 267%) comparability: 124% average difference (range: -69 to 558%)
Sample Throughput	5-6 samples/hour (outdoor) 10 samples/hour (chamber)
Power Requirements	120V AC or battery-operated
Operator Requirements	Basic knowledge of chromatographic techniques; optional 3-day training course for $2,400
Cost	Equipment purchase: $24,950 (GC); $1,500 (SAW) $1 to 2 per sample
Hazardous Waste Generation	approximately 27 lb of vials with soils/solvents (solid) approximately 20 lb solid waste (gloves, pipettes, etc.)

Section 6
Technology Update and Representative Applications

Objective
In this section, EST describes new technology developments that have occurred since the demonstration activities. In addition, the developer has provided a list of representative applications where the 4100 Vapor Detector has been or is currently being utilized.

Technology Update
A field-portable chromatography system equipped with an SAW detector has been used to speciate and quantify PCB contamination in soil and flyash with a 10-s analysis time. Measurement speed and accuracy make the instrument well suited to rapid screening of soil samples. The technology participated in a performance demonstration study under EPA's ETV program in August 1997. In the three months following the study, a number of improvements have been made in the GC method as well as in the instrument hardware. These improvements are as follows:

- Pipette filtering has been eliminated as part of the liquid extraction method. The use of a portable centrifuge to separate particulate materials improves the speed of the method and reduces the amount of waste produced (disposable pipettes).

- A new temperature program for the GC column has been developed that doubles the resolving power of the instrument and improves the separation and identification of different Aroclor mixtures.

- An improved open tubular desorption (OTD) apparatus has been engineered and is now in production. The new OTD is capable of reaching 300 °C (previous units were limited to 200 °C) and can be temperature-programmed to reduce interference from high-boiling-point compounds (oils).

- Software provided with the instrument now contains a full manual and mpeg movies with sound describing the PCB/dioxin measurement method. Additional mpeg files provide the user with a graphic description of instrument maintenance procedures and a fully illustrated manual.

Representative Applications
Full-scale production of GC/SAW instruments began in July 1997. Since then, a number of users have reported on their performance. The following is a short list of relevant user sites as representative applications.

Savannah River DOE Site
Joe Rossabi, (803) 725-5220
(EPA-ETV program for VOCs in water matrices)

Hanford DOE Site
Marcus Stauffer, (509) 373-9928
(Tank farm, headspace analysis—VOC-PCB)

Lawrence Livermore National Laboratory
Paula Kato, (510) 423-6241
(Volatile organic screening)

Idaho National Engineering and Environmenetal Laboratory (INEEL)
Rod Shurtliff, (208) 526-3325
(Volatile organic screening)

Japan, Nissho Engineering
Yoshinobu Inoue, 011-033-952-0261
(Dioxin monitoring— incinerators)

Data Quality Objective Example

This application of EST's 4100 Vapor Detector is based on data quality objective (DQO) methods for project planning advocated by the American Society of Testing and Materials (ASTM) [12, 13] and EPA [14]. ORNL derived a DQO example from the performance results in Section 5. This example, which is presented in Appendix E, illustrates the use of the 4100's performance data from the ETV demonstration in the DQO process to select the number of samples and to quantify the action level for the decision rule.

Section 7
References

[1] M. D Erickson, *Analytical Chemistry of PCBs*, 2nd ed. CRC Press/Lewis Publishers, Boca Raton, Fla., 1997.

[2] "Polychlorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions, *Code of Federal Regulations*, 40 CFR Part 761, rev. 7, December 1994.

[3] M. P. Maskarinec et al., *Stability of Volatile Organics in Environmental Soil Samples: Final Report*, ORNL/TM-12128, Oak Ridge Natl. Lab., November 1992.

[4] U.S. Environmental Protection Agency, "Organochlorine Pesticides and PCBs as Aroclors by Gas Chromatography: Capillary Column Technique," *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. EPA SW846, Final Update II, Method 8081*, September 1994.

[5] Oak Ridge National Laboratory, *Technology Demonstration Plan: Evaluation of Polychlorinated Biphenyl (PCB) Field Analytical Techniques*, July 1997.

[6] U.S. Environmental Protection Agency, *Data Quality Objectives for Remedial Response Activities*, EPA 540/G-87/003, Washington D.C., March 1987.

[7] Lothar Sachs, *Applied Statistics: A Handbook of Techniques*, 2nd ed., Springer-Verlag, New York, 1984.

[8] G. W. Snedecor and William G. Cochran, *Statistical Methods*, The Iowa State University Press, Ames, Iowa, 1967.

[9] N. R. Draper and H. Smith, *Applied Regression Analysis*, 2nd ed., John Wiley & Sons Inc., New York, 1981.

[10] Walter Berger, Harry McCarty, and Roy-Keith Smith, *Environmental Laboratory Data Evaluation*, Genium Publishing Corporation, Schenectady, N.Y., 1996.

[11] "Definition and Procedure for the Determination of the Method Detection Limit," Code of Federal Regulations, CFR 40 Part 136, Appendix B, Revision 1.11.

[12] American Society for Testing and Materials (ASTM), *Standard Practice for Generation of Environmental Data Related to Waste Management Activities Quality Assurance and Quality Control Planning and Implementation*, D5283-92, 1997.

[13] American Society for Testing and Materials (ASTM), *Standard Practice for Generation of Environmental Data Related to Waste Management Activities Development of Data Quality Objectives*, D5792-95, 1997.

[14] U.S. Environmental Protection Agency, *Guidance for Data Quality Assessment*, EPA QA/G-9; EPA/600/R-96/084, July 1996.

Appendix A
Description of Environmental Soil Samples

Table A-1. Summary of soil sample descriptions

Location	Request for Disposal (RFD) #	Drum #	Description
Oak Ridge	40022	02	Soil from spill cleanup at the Y-12 Plant in Oak Ridge, Tennessee. This soil is PCB-contaminated soil excavated in 1992.
Oak Ridge	40267	01 02 03 04	Soil from the Elza Gate area, a DOE Formerly Utilized Sites Remedial Action Program site in Oak Ridge, Tennessee. This soil is PCB-contaminated soil that was excavated in 1992.
Oak Ridge	24375	01 02 03	Catch-basin sediment from the K-711 area (old Powerhouse Area) at the DOE East Tennessee Technology Park (formerly known as Oak Ridge Gaseous Diffusion Plant) in Oak Ridge, Tennessee. This soil is PCB-contaminated storm drain sediment that was excavated in 1991.
Oak Ridge	43275	01 02	Soil from the K-25 Building area at the DOE East Tennessee Technology Park (formerly known as Oak Ridge Gaseous Diffusion Plant) in Oak Ridge, Tennessee. This soil is PCB-contaminated soil that was excavated in 1993.
Oak Ridge	134555	03	Soil from the K-707 area at the DOE East Tennessee Technology Park (formerly known as Oak Ridge Gaseous Diffusion Plant) in Oak Ridge, Tennessee. This soil is PCB-contaminated soil from a dike spillage that was excavated in 1995.
Paducah	97002	01 02 03 04	Soil from the DOE Paducah Gaseous Diffusion Plant in Kentucky. This soil is PCB-contaminated soil from a spill cleanup at the C-746-R (Organic Waste Storage Area) that was excavated in 1989.
Portsmouth	7515	858 1069 1096 1898 2143 2528 3281 538 940 4096	Soil from the DOE Portsmouth Gaseous Diffusion Plant in Ohio. This soil is PCB-contaminated soil from a probable PCB oil spill into the East Drainage Ditch that was excavated in 1986.
Tennessee Reference Soil	n/a	n/a	Captina silt loam from Roane County, Tennessee; used as a blank in this study (i.e., not contaminated with PCBs)

Appendix B
Characterization of Environmental Soil Samples

Table B-1. Summary of environmental soil characterization

Location	Sample ID	RFD Drum # [a]	Composition			Total Organic Carbon (mg/kg)	pH
			% gravel	% sand	% silt + clay		
Oak Ridge	101	40022-02	0	91.8	8.2	5384	7.12
	102	40267-03	0.5	99.3	0.2	13170	7.30
	103	40267-01	0.2	96.7	3.1	13503	7.21
	104	40267-04	0.6	98.2	1.2	15723	7.07
	105	40267-01S [b]	0.5	94.8	4.7	14533	7.28
	106	24375-03	0.5	87.8	11.7	19643	7.36
	107	24375-01	2.5	92.5	5.0	1196	7.26
	108	40267-02	0.4	94.2	5.4	9007	7.30
	109	24375-02	0.3	93.1	6.6	1116	7.48
	110	43275-01	0	89.2	10.8	14250	7.57
	111	134555-03S [b]	0.5	88.1	11.4	10422	7.41
	112	43275-02	0.1	91.4	8.5	38907	7.66
	126, 226	non-PCB soil	0	85.6	14.4	9249	7.33
Paducah	113, 201	97002-04	0	92.4	7.6	1296	7.71
	114, 202	97002-01	0.2	87.6	12.2	6097	7.64
	115, 203	97002-03	0.1	83.6	16.3	3649	7.59
	116, 204 117, 205	97002-02 97002-02S [b]	0.4	93.7	5.8	4075	7.43
Portsmouth	206	7515-4096	0	87.1	12.9	3465	7.72
	207	7515-1898	0.2	78.0	21.8	3721	7.66
	208	7515-1096	0.4	74.4	25.2	3856	7.77
	209	7515-2143	0	74.3	25.7	10687	7.71
	210	7515-0940	0.3	73.0	26.7	7345	7.78
	216 211 217	7515-0538 7515-0538S [b] 7515-0538S [b]	0.5	73.3	26.3	1328	7.78
	212	7515-2528	0.5	70.4	29.1	5231	7.92
	213	7515-3281	0.5	72.6	26.8	5862	7.67
	214	7515-0858	0	65.8	34.2	6776	7.85
	215	7515-1069	1.3	75.0	23.7	4875	7.56

[a] Request for disposal drum number (see Table A-1).
[b] "S" indicates that the environmental soil was spiked with additional PCBs.

Appendix C
Temperature and Relative Humidity Conditions

Table C-1. Average temperature and relative humidity conditions during testing periods

Date	Outdoor Site		Chamber Site	
	Average Temperature (°F)	Average Relative Humidity (%)	Average Temperature (°F)	Average Relative Humidity (%)
7/22/97	85	62	70 [a]	38 [a]
7/23/97	85	70	60 [a]	58 [a]
7/24/97	85	67	58	66
7/25/97	80	70	56	54
7/26/97	85	55	57	51
7/27/97	80	75	55	49
7/28/97	79	88	57	52
7/29/97	**b**	**b**	55	50

[a] The chamber was not operating properly on this day. See discussion in Section 3.
[b] No developers were working outdoors on this day.

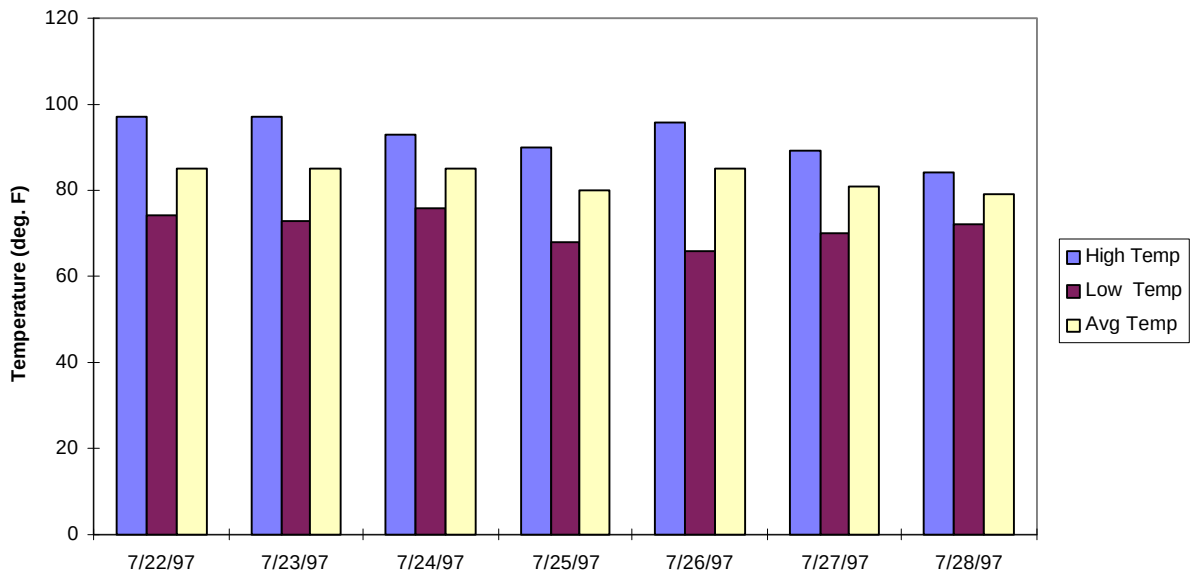

Figure C-1. Summary of temperature conditions for outdoor site.

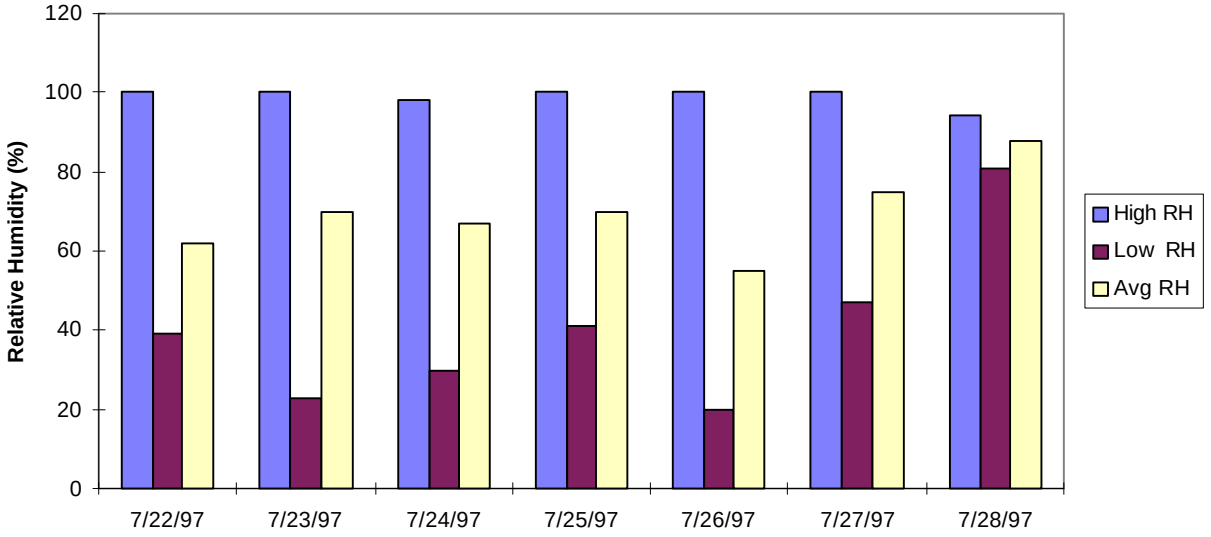

Figure C-2. Summary of relative humidity conditions for the outdoor site.

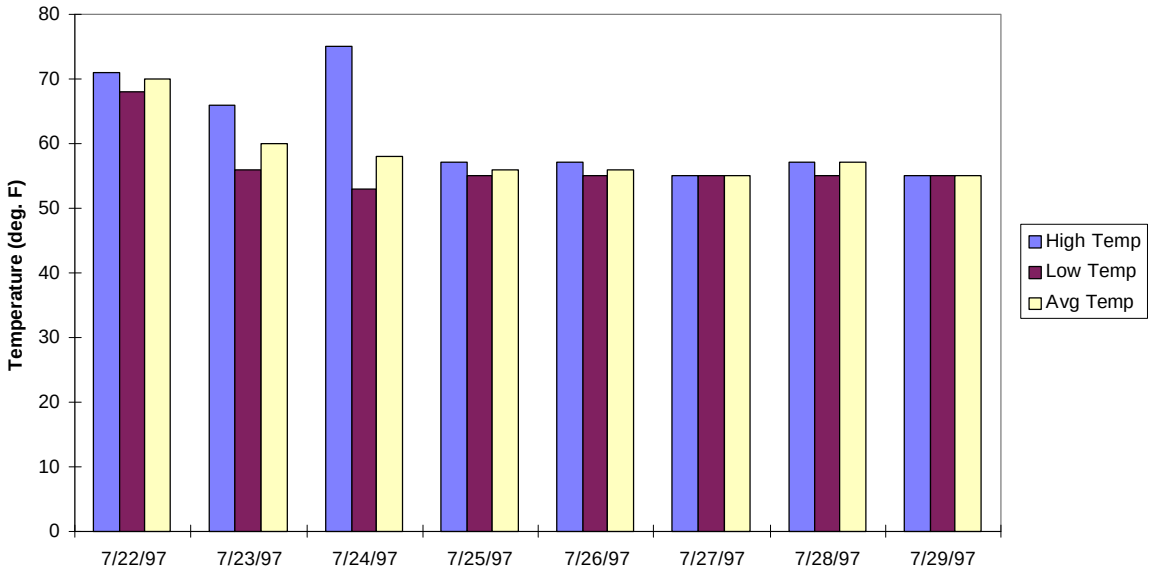

Figure C-3. Summary of temperature conditions for chamber site.

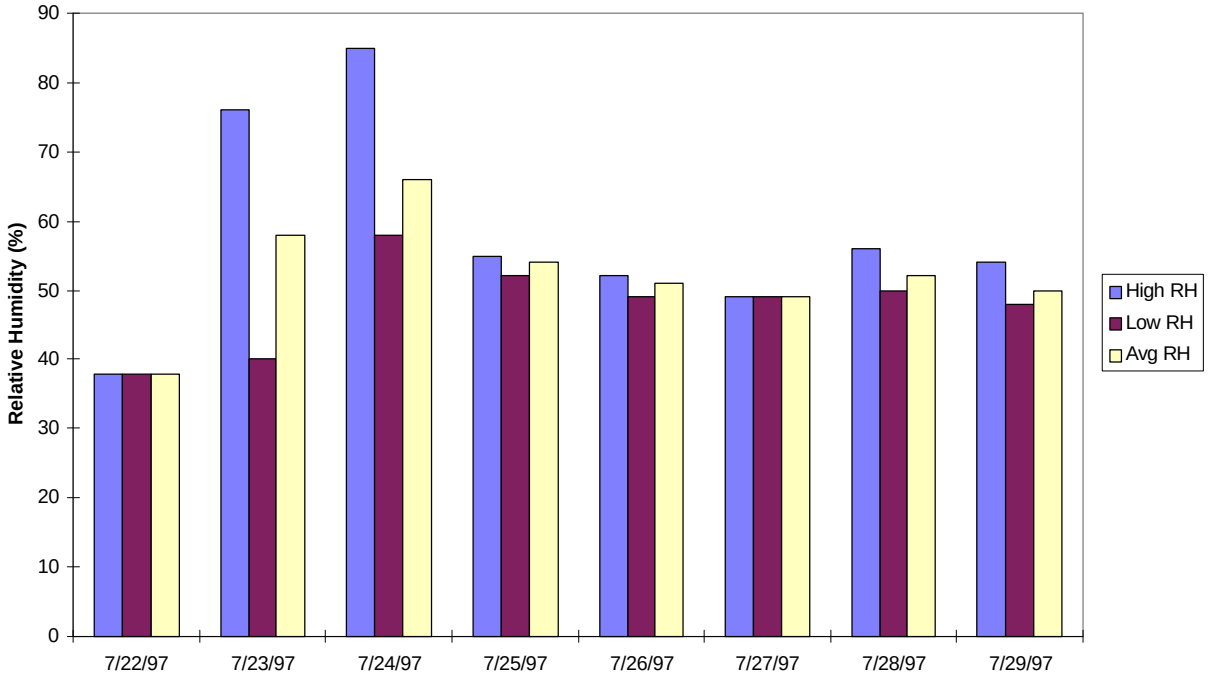

Figure C-4. Summary of relative humidity conditions for chamber site.

Appendix D
EST's 4100 Vapor Detector
PCB Technology Demonstration Sample Data

Legend for Appendix D Tables

Obs	=	Observation
Sample ID	=	Sample identification 101 to 126 for Outdoor Site soil samples 127 to 130 for Outdoor Site extract samples 201 to 226 for Chamber Site soil samples 227 to 230 for Chamber Site extract samples
Rep	=	Replicate of Sample ID (1 through 4)
4100 Result	=	4100's measured PCB concentration (ppm).
Ref Lab Result	=	LAS reference laboratory measured PCB concentration (ppm). Values with "≤" are samples that the reference laboratory reported as "≤ reporting detection limit"
Reference Aroclor	=	Aroclor(s) identified by the reference laboratory
Type	=	"sample" indicates environmental soil; "1242", "1248", "1254", "1260" indicates Aroclor in the PE samples;"blank" indicates non-PCB contaminated sample
Order	=	Order of sample analysis by EST (started with 1001 through 1116, then 2001 through 2116)

Table D-1. EST's 4100 Vapor Detector PCB technology demonstration soil sample data

Obs	Sample ID	Rep	4100 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
1	101	1	14.5	0.6	1254	Sample	1078
2	101	2	2.5	0.4	1254	Sample	1103
3	101	3	34.6	0.5	1254	Sample	1063
4	101	4	6.2	0.5	1254	Sample	1022
5	102	1	206.8	2.2	1254	Sample	1013
6	102	2	3.1	2.1	1254	Sample	1015
7	102	3	6.9	1.7	1260	Sample	1006
8	102	4	4	2.5	1260	Sample	1014
9	103	1	4.1	3.0	1254	Sample	1055
10	103	2	12.1	2.4	1254	Sample	1048
11	103	3	38.6	2.0	1260	Sample	1064
12	103	4	112.3	1.6	1260	Sample	1069
13	104	1	4.4	6.8	1260	Sample	1037
14	104	2	4.9	6.0	1254	Sample	1077
15	104	3	13	14.8	1254	Sample	1016
16	104	4	0.2	9.9	1254	Sample	1011
17	105	1	27.8	49.7	1260	Sample	1035
18	105	2	38.3	84.1	1260	Sample	1020
19	105	3	1.3	50.6	1260	Sample	1034
20	105	4	43.6	53.2	1260	Sample	1073
21	106	1	237.3	269.6	1254	Sample	1074
22	106	2	220	255.9	1254	Sample	1050
23	106	3	5.4	317.6	1254	Sample	1017
24	106	4	142.3	649.6	1254	Sample	1039
25	107	1	3.6	1.0	1254	Sample	1041
26	107	2	3.4	1.6	1254	Sample	1018
27	107	3	1.1	1.2	1254	Sample	1003
28	107	4	6.7	1.2	1254	Sample	1090
29	108	1	2.6	1.7	1254	Sample	1026
30	108	2	0.9	2.0	1254	Sample	1001
31	108	3	23.5	1.7	1254	Sample	1030
32	108	4	2.0	1.9	1254	Sample	1102
33	109	1	15.8	1.5	1254	Sample	1080
34	109	2	20.8	2.1	1254	Sample	1083
35	109	3	89.6	1.8	1254	Sample	1100
36	109	4	14.5	2.4	1254	Sample	1038
37	110	1	0	≤490.0	Non-Detect	Sample	1008
38	110	2	8	≤99.0	Non-Detect	Sample	1019
39	110	3	203.4	≤66.0	Non-Detect	Sample	1085
40	110	4	2.7	≤98.0	Non-Detect	Sample	1005

Obs	Sample ID	Rep	4100 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
41	111	1	19.1	44.5	1254	Sample	1065
42	111	2	54.7	36.0	1254	Sample	1070
43	111	3	9.4	39.3	1254	Sample	1044
44	111	4	209.8	35.1	1254	Sample	1021
45	112	1	102.6	≤66.0	Non-Detect	Sample	1051
46	112	2	548.7	≤200.0	Non-Detect	Sample	1060
47	112	3	1995.4	≤130.0	Non-Detect	Sample	1082
48	112	4	126.5	≤200.0	Non-Detect	Sample	1081
49	113	1	0	0.7	1260	Sample	1054
50	113	2	6.3	1.1	1260	Sample	1010
51	113	3	6.1	0.6	1260	Sample	1092
52	113	4	11	1.9	1248/1260	Sample	1086
53	114	1	35.8	1.1	1260	Sample	1097
54	114	2	3.3	1.2	1260	Sample	1093
55	114	3	25	1.3	1260	Sample	1094
56	114	4	0	1.7	1260	Sample	1042
57	115	1	0	14.9	1248	Sample	1012
58	115	2	18.5	12.4	1016	Sample	1088
59	115	3	0.2	15.0	1248	Sample	1031
60	115	4	14.1	16.9	1248	Sample	1068
61	116	1	0.5	41.4	1248	Sample	1028
62	116	2	9.4	41.2	1016	Sample	1024
63	116	3	6.7	48.5	1248	Sample	1075
64	116	4	0.8	34.0	1016	Sample	1056
65	117	1	139.3	431.6	1016	Sample	1098
66	117	2	141.1	406.3	1016	Sample	1071
67	117	3	60.9	304.7	1016	Sample	1032
68	117	4	136.5	392.8	1016	Sample	1087
69	118	1	8.3	2.1	1248	1248	1049
70	118	2	24.3	1.9	1016	1248	1033
71	118	3	1	0.7	1248	1248	1057
72	118	4	3.1	1.6	1248	1248	1104
73	119	1	0	21.2	1016	1248	1067
74	119	2	7.8	17.2	1248	1248	1099
75	119	3	0	17.4	1248	1248	1072
76	119	4	1.4	24.4	1248	1248	1076
77	120	1	3.2	4.5	1254	1254	1036
78	120	2	24.6	4.0	1254	1254	1052
79	120	3	1.2	6.3	1254	1254	1002
80	120	4	3.9	5.0	1254	1254	1059

Obs	Sample ID	Rep	4100 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
81	121	1	65.2	58.7	1254	1254	1096
82	121	2	24.4	55.7	1254	1254	1047
83	121	3	44.1	53.2	1254	1254	1101
84	121	4	22.5	50.9	1254	1254	1029
85	122	1	6.6	12.2	1260	1260	1058
86	122	2	71.4	10.9	1260	1260	1007
87	122	3	3.3	11.3	1260	1260	1004
88	122	4	2.3	10	1260	1260	1095
89	123	1	21.5	59.2	1260	1260	1066
90	123	2	27.6	56.9	1260	1260	1084
91	123	3	24.3	66.8	1260	1260	1040
92	123	4	0	57.5	1260	1260	1009
93	124	1	14.8	1.8	1254	1254/1260	1062
94	124	2	5.7	1.4	1260	1254/1254	1023
95	124	3	8	1.9	1254	1254/1260	1079
96	124	4	4.8	1.8	1254	1254/1260	1043
97	125	1	60.6	32.0	1254	1254/1260	1091
98	125	2	20.3	41.3	1254	1254/1260	1053
99	125	3	20.2	46.0	1254	1254/1260	1046
100	125	4	22.3	32.2	1260	1254/1260	1025
101	126	1	17.7	≤0.1	Non-Detect	Blank	1045
102	126	2	19.5	≤0.1	Non-Detect	Blank	1061
103	126	3	0.7	≤0.2	Non-Detect	Blank	1027
104	126	4	96.0	≤1.3	Non-Detect	Blank	1089
105	201	1	0	1.0	1016/1260	Sample	2021
106	201	2	0	1.0	1016/1260	Sample	2015
107	201	3	20.3	1.1	1016/1260	Sample	2083
108	201	4	24.3	0.6	1260	Sample	2072
109	202	1	61.4	1.4	1260	Sample	2037
110	202	2	3.3	1.6	1260	Sample	2062
111	202	3	13.6	1.2	1260	Sample	2049
112	202	4	13.6	1.5	1260	Sample	2092
113	203	1	32.9	14.0	1248	Sample	2095
114	203	2	18.3	12.8	1248	Sample	2042
115	203	3	3.3	16.2	1248	Sample	2026
116	203	4	2.1	12.4	1248	Sample	2008
117	204	1	75	43.1	1248	Sample	2089
118	204	2	257.9	45.3	1248	Sample	2033
119	204	3	26.3	41	1248	Sample	2017
120	204	4	57.1	47.7	1248	Sample	2093

Obs	Sample ID	Rep	4100 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
121	205	1	500	3305	1016/1260	Sample	2047
122	205	2	218.6	538.7	1016	Sample	2057
123	205	3	183.3	457	1016	Sample	2029
124	205	4	278.3	483.3	1016	Sample	2103
125	206	1	16.7	2.9	1260	Sample	2022
126	206	2	173.6	1.1	1260	Sample	2031
127	206	3	21.2	1.1	1016/1260	Sample	2079
128	206	4	2.4	2.5	1260	Sample	2025
129	207	1	311.9	17.8	1260	Sample	2085
130	207	2.0	52.9	14.3	1260	Sample	2098
131	207	3.0	238	21.6	1260	Sample	2005
132	207	4	431.3	21.6	1254	Sample	2081
133	208	1	385.1	42	1260	Sample	2001
134	208	2	416.2	27.7	1016/1260	Sample	2045
135	208	3	857.1	24	1254	Sample	2086
136	208	4	223.1	28.4	1260	Sample	2096
137	209	1	396.7	32.7	1260	Sample	2055
138	209	2	278.8	79.3	1260	Sample	2009
139	209	3	772.4	11.0	1260	Sample	2078
140	209	4	177.6	37.9	1260	Sample	2052
141	210	1	216.7	123.2	1260	Sample	2048
142	210	2	433.3	61.5	1260	Sample	2038
143	210	3	566.7	84.1	1260	Sample	2082
144	210	4	370.7	85.5	1260	Sample	2070
145	211	1	451.6	387.8	1254	Sample	2027
146	211	2	783.3	581.4	1254	Sample	2091
147	211	3	940.0	330.0	1254	Sample	2061
148	211	4	696.6	318.7	1254	Sample	2035
149	212	1	56.6	3.8	1260	Sample	2074
150	212	2	55.0	3.9	1260	Sample	2019
151	212	3	37.9	4.3	1260	Sample	2063
152	212	4	85.9	0.8	1260	Sample	2068
153	213	1	226	6.9	1260	Sample	2020
154	213	2	60.5	7.3	1260	Sample	2002
155	213	3	45.5	7.8	1260	Sample	2023
156	213	4	211.4	10.5	1260	Sample	2071
157	214	1	571.4	26.0	1260	Sample	2065
158	214	2	269	25.6	1260	Sample	2030
159	214	3	0	29.1	1260	Sample	2016
160	214	4	173.6	20.2	1260	Sample	2011

Obs	Sample ID	Rep	4100 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
161	215	1	249.3	25.1	1260	Sample	2060
162	215	2	342.9	24.1	1260	Sample	2084
163	215	3	228.9	26.2	1260	Sample	2059
164	215	4	0	31.2	1016/1260	Sample	2013
165	216	1	372.1	151.6	1260	Sample	2028
166	216	2	325	47.0	1260	Sample	2094
167	216	3	573.9	54.3	1260	Sample	2104
168	216	4	450	64.0	1260	Sample	2043
169	217	1	146.9	886.7	1254	Sample	2058
170	217	2	537.1	549.8	1254	Sample	2010
171	217	3	422.2	542.8	1254	Sample	2051
172	217	4	1045	1913.3	1016/1260	Sample	2069
173	218	1	71.1	2.8	1248	1248	2088
174	218	2	11.3	2.4	1248	1248	2101
175	218	3	45.7	2.6	1248	1248	2004
176	218	4	31.0	2.6	1248	1248	2075
177	219	1	47.9	22.4	1248	1248	2090
178	219	2	82.6	26.0	1016	1248	2034
179	219	3	9.7	29.4	1248	1248	2056
180	219	4	42.2	15.2	1248	1248	2066
181	220	1	33.7	8.5	1254	1254	2012
182	220	2	23.1	4.9	1254	1254	2076
183	220	3	41.9	4.7	1254	1254	2039
184	220	4	9.2	5.2	1254	1254	2050
185	221	1	240.9	32.0	1016/1260	1254	2087
186	221	2	137	44.1	1016/1260	1254	2032
187	221	3	110.3	43.8	1254	1254	2073
188	221	4	83.3	59.6	1254	1254	2064
189	222	1	2.8	13.2	1260	1260	2003
190	222	2	21.8	12.4	1260	1260	2036
191	222	3	1.2	12.7	1260	1260	2053
192	222	4	6.6	12.7	1260	1260	2018
193	223	1	52.5	56.6	1260	1260	2080
194	223	2	32.2	50.3	1260	1260	2006
195	223	3	28.9	49.9	1260	1260	2097
196	223	4	63.4	66.4	1260	1260	2102
197	224	1	33.8	2.2	1254	1254/1260	2007
198	224	2	39.0	1.2	1260	1254/1260	2067
199	224	3	40.8	1.4	1260	1254/1260	2044
200	224	4	14.8	2.1	1254	1254/1260	2024

Obs	Sample ID	Rep	4100 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
201	225	1	25.6	56.4	1260	1254/1260	2014
202	225	2	194	36.5	1016/1260	1254/1260	2077
203	225	3	103.8	32.1	1260	1254/1260	2041
204	225	4	156.9	146.0	1254	1254/1260	2040
205	226	1	77.6	≤0.1	Non-Detect	Blank	2100
206	226	2	187.9	≤0.8	Non-Detect	Blank	2099
207	226	3	38.7	≤0.1	Non-Detect	Blank	2046
208	226	4	7	≤0.1	Non-Detect	Blank	2054

Table D-2. EST's 4100 Vapor Detector technology demonstration extract sample data

OBS	Sample ID	Rep	4100 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Spike[a] (ppm)	Type	Order
1	130	1	12.6	16.0	1016	10	1242	1111
2	130	2	13.2	11.0	1016	10	1242	1114
3	130	3	25.6	10.3	1248	10	1242	1113
4	130	4	5.1	11.0	1016	10	1242	1105
5	131	1	43.8	67.0	1254	100	1254	1110
6	131	2	38.8	57.0	1254	100	1254	1109
7	131	3	43.3	63.0	1254	100	1254	1116
8	131	4	36.0	68.0	1254	100	1254	1107
9	132	1	0.0	≤0.1	Non-Detect	0	Blank	1115
10	132	2	0.8	≤0.1	Non-Detect	0	Blank	1106
11	132	3	0.0	≤0.1	Non-Detect	0	Blank	1108
12	132	4	0.0	≤0.1	Non-Detect	0	Blank	1112
13	230	1	53.0	9.8	1016	10	1242	2108
14	230	2	42.0	10.0	1016	10	1242	2111
15	230	3	50.0	7.6	1016	10	1242	2112
16	230	4	12.3	7.9	1016	10	1242	2109
17	231	1	16.8	55.0	1254	100	1254	2115
18	231	2	51.0	55.0	1254	100	1254	2107
19	231	3	115.0	61.0	1254	100	1254	2113
20	231	4	90.5	59.0	1254	100	1254	2105
21	232	1	0.0	≤0.1	Non-Detect	0	Blank	2110
22	232	2	0.0	≤0.1	Non-Detect	0	Blank	2116
23	232	3	132.5	≤0.1	Non-Detect	0	Blank	2106
24	232	4	0.5	≤0.1	Non-Detect	0	Blank	2114

[a]Nominal spike concentration of the extract sample prepared by ORNL.

Error	Sample ID	(ppm)	Corrected Result
Transcription	106	≤ 490	
	130		10.3
		32,000	
	207		17.8
		160	
Calculation		3.6	
	119		17.4
		2.3	
	214		26.0
		29.0	
Interpretation	[a]	≤	0.5
	101 [a]	0.7	
		≤	1.2
		18.0	
	113 [b]	0.9	
		≤	0.7
	119		21.2
		7.2	
	201	1.0	
	219		26.0

Two of four measurements in Sample ID 101 were corrected.

[b]

Appendix E
Data Quality Objective Example

Disclaimer
The following hypothetical example serves to demonstrate how the information provided in this report may be used in the data quality objectives (DQO) process. This example serves to illustrate the application of quantitative DQOs to a decision process but cannot attempt to provide a thorough education in this topic. Please refer to other educational or technical resources for further details. In addition, since the focus of this report is on the analytical technology, this example makes the simplifying assumption that the contents of these drums will be homogeneous. In the real world, however, this assumption is seldom valid, and matrix heterogeneity constitutes a source of considerable uncertainty that must be adequately evaluated if the overall certainty of a site decision is to be quantified.

Background and Problem Statement
An industrial company discovered a land area contaminated with PCBs from an unknown source. The contaminated soil was excavated into waste drums. Preliminary characterization determined that the PCB concentration in a single drum was homogenous, but PCB concentrations varied greatly from drum to drum. The company's DQO team was considering the use of EST's 4100 Vapor Detector to measure the PCB concentration in each drum. The DQO team decided that drums will be disposed of by incineration if the PCB concentration is greater than or equal to 50 ppm ("hot"). A concentration of 50 ppm is the Toxic Substances Control Act (TSCA) regulatory threshold (RT) for this environmental problem. Those drums with PCB concentrations less than 50 ppm will be put into a landfill because incineration of soil is very expensive. With regulator agreement, the DQO team determined that a decision rule for disposal would be based on the average concentration of PCBs in each drum.

General Decision Rule

If the average PCB concentration is less than the action level, then send the soil drum to the landfill.

If the average PCB concentration is greater than or equal to the action level, then send the soil drum to the incinerator.

DQO Goals
EPA's *Guidance for Data Quality Assessment* [14] states the following in Section 1.2: "The true condition that occurs with the more severe decision error . . . should be defined as the null hypothesis." The team decided that the more severe decision error would be for a drum to be erroneously sent to a landfill if the drum's PCB concentration actually exceeded 50 ppm. Therefore, the null hypothesis is constructed to assume that a drum's true PCB concentration is greater than 50 ppm; and as a "hot" drum, it would be sent to an incinerator. Drums would be sent to the landfill only if the null hypothesis is rejected and it is concluded that the "true" average PCB concentration is less than 50 ppm.

With the null hypothesis defined in this way, a false positive decision is made when it is concluded that a drum contains less than 50 ppm PCBs (i.e., the null hypothesis is rejected), when actually the drum is "hot"

(i.e., the null hypothesis is true). The team required that the error rate for sending a “hot” drum to the

sufficient number of samples must be taken from each drum so that the false positive decision error rate (FP) is 0.05 (or less) if the true drum concentration is 50 ppm. This scenario represents a 5% chance of

The DQO team did not want to send an excessive number of drums to the incinerator if the average PCB concentration was less than 50 ppm because of the expense. In this situation, a false negative decision is

the drum contains soil with less than 50 ppm PCBs (i.e., the null hypothesis is actually false). After considering the guidelines presented in Section 1.1 of EPA’s Guidance for Data Quality Assessment [14]

0.10 if the true drum concentration was 40 ppm. That is, there would be a 10% probability of sending a drum to the incinerator (denoted as Pr[Take Drum to Incinerator]) if the true PCB concentration for a drum

Permissible FP and FN Error Rates and Critical Decision Points	
FP: Pr[Take Drum to Landfill]	0.05 when true PCB concentration = 50 ppm
FN: Pr[Take Drum to Incinerator]	0.10 when true PCB concentration = 40 ppm

Use of Technology Performance Information to Implement the Decision Rule

Technology performance information is used to evaluate whether a particular analytical technology can

of the 4100 Vapor Detector, the performance of this technology (as reported in this ETV report) was used to assess its applicability to this project. Two questions arise:

How many samples are needed from a single drum to permit a valid estimation of the true average

assumption was made that the PCB distribution throughout the soil within a single drum is homogeneous, and thus, matrix heterogeneity will not contribute to overall variability. The only

analytical method, which is determined by precision studies.

2 for using the 4100 Vapor Detector to make decisions in the field? After the required number of samples have been collected from a drum and analyzed, the

using the 4100 Vapor Detector, what is the value (here called “the action level for the decision rule”) with which that average is compared to decide whether the drum is “hot” or not? This

method-specific or site-specific action level is derived from evaluations of the method's accuracy using an appropriate QC regimen.

4100 Vapor Detector Accuracy

The ETV demonstration indicated that the results from EST's 4100 Vapor Detector were biased and sensitive to environmental conditions. In addition, average PCB measurements on blank PE samples were 33.5 ppm and 77.8 ppm for outdoor and chamber conditions, respectively. These results from blank samples were near or greater than the regulatory threshold of 50 ppm. The DQO Team decided to review the PE data for the outdoor conditions with no blanks. These conditions were the best match for their application. Figure E-1 is a plot of a fitted line to the average concentration for the data. EST's measurements have a weak correlation ($R^2 = 0.57$) with certified PCB values for the performance evaluation samples.

Figure E-1 shows that the predicted results from the 4100 Vapor Detector would likely be biased low when compared with certified PE values. For example, at PE values of 40 and 50 ppm, the 4100 Vapor Detector could be expected to produce an average result of about 24 and 28 ppm, respectively. The DQO Team knew that if they selected the 4100 Vapor Detector for their project they would have to compensate for this negative bias. They decided to apply a correction factor to every result obtained from the 4100 Vapor Detector to obtain a conservative, unbiased result. Based on the information from the ETV study, the Team expected that they would need to multiply each 4100 Vapor Detector result by a correction factor. The exact value of the correction factor would be determined after detailed examination of a rigorous site-specific QC program.

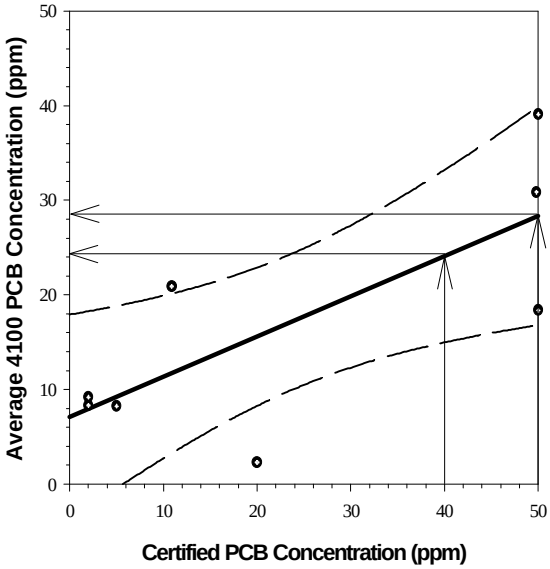

Figure E-1. A line fitted to the average concentrations of outdoor PE soil samples (no blanks) with 95% confidence intervals (dashed lines).

The DQO Team decided they would need to be very careful about interpreting the PCB results generated using EST's 4100 Vapor Detector. They would use the site-specific QC samples to assess the performance of the 4100 Vapor Detector under their site-specific conditions. The Team would have to design an extensive QC regimen (which included PE samples, matrix spikes, split samples sent for confirmatory laboratory analysis, and duplicates) that would verify whether the 4100 Vapor Detector was performing as expected under their site-specific conditions. Additionally, to address the possibility that these QC samples would reveal that the kit was performing differently from what they expected, the Team would have to create a backup plan (which would become part of the Sampling and Analysis Plan) that would permit them to document and account for deviations in expected performance. The backup plan would lay out the courses of action to follow if the kit's performance did not meet their expectations so that verifiable and defensible data could be produced to support decision-making at the site without the need for extensive resampling at a future time.

Determining the Number of Samples

With the critical decision points (which correspond to C_{FN} and RT in the following equations) selected for use with the kit, the Team could determine the number of samples needed from each drum to calculate its "true" average PCB concentration. For a homogeneous matrix, the number of samples required depends on the precision of the analytical method.

The ETV demonstration results indicated that the 4100 Vapor Detector's SD increased with concentration level, so the RSD would be a more appropriate precision measurement than the standard deviation (SD). The DQO Team used the precision value determined from the ETV demonstration (average RSD of 101%) as a consistent RSD for outdoor PE samples. This estimate of measurement variability was used to calculate the number of soil samples required to be measured on each drum to achieve the DQO objectives. A formula (Eq. E-1) is provided in EPA's *Guidance for Data Quality Assessment* [14] (pp. 3.2-3, Box 3.2-1) that can be adapted to this example for calculating the number of samples required to meet the FP and FP requirements. This formula uses a constant SD for the analytical method's precision, but can be modified to use RSD by dividing the numerator and denominator by $(RT)^2$ and multiplying by $(100\%)^2$, as shown in E-2. The final form of the formula appears as Eq. E-3.

$$n = \frac{(SD)^2\,(Z_{1-FP} + Z_{1-FN})^2}{(RT - C_{FN})^2} + (0.5)Z_{1-FP}^2 \qquad (E-1)$$

$$n = \frac{(100\% \times SD/RT)^2\,(Z_{1-FP} + Z_{1-FN})^2}{[100\% \times (RT - C_{FN})/RT]^2} + (0.5)Z_{1-FP}^2 \qquad (E-2)$$

$$n = \frac{RSD^2\,(Z_{1-FP} + Z_{1-FN})^2}{(\%D)^2} + (0.5)Z_{1-FP}^2 \qquad (E-3)$$

where

n	=	number of samples from a drum to be measured,
RSD	=	RSD at the regulatory threshold [e.g., $RSD^2 = (101\%)^2$],
RT	=	regulatory threshold (e.g., RT = 50 ppm),
C_{FN}	=	concentration at which the FN is specified (e.g., C_{FN} = 40 ppm),
$\%D$	=	percent difference of C_{FN} relative to RT [e.g., $(\%D)^2 = (20\%)^2$]
FP	=	false positive decision error rate (e.g., FP = 0.05),
FN	=	false negative decision error rate (e.g., FN = 0.10), and
Z_{1-p}	=	the (1- p)th percentile of the standard normal distribution (see EPA QA/G-9, Table A-1 of Appendix A). Example $Z_{(1-FP)} = Z_{0.95} = 1.645$.

Equation E-3 is then used to determine the number of samples to be analyzed from each drum (n):

$$n = \frac{(101\%)^2\ (1.645 + 1.282)^2}{(20\%)^2} + (0.5)(1.645)^2 = 219.8 \quad 220 \quad .$$

Therefore, 220 samples would need to be analyzed from each drum by EST's 4100 Vapor Detector to meet the criteria established by the DQO process. The AL for the decision rule can then be calculated based on a sample size (n) of 220 samples from each drum.

Determining the Action Level

The results from the 220 samples from each drum will be corrected for bias based on the site-specific QC sample analyses. These 220 unbiased estimates (of the PCB concentration in each sample) will be averaged (arithmetic mean) to generate an unbiased PCB concentration for the drum. This unbiased estimate of the "true" PCB concentration in each drum will be compared with the AL. The AL for the decision rule is calculated based on regulation-driven requirements (the TSCA regulatory threshold of 50 ppm), and on controlling the FP requirement established in the DQO process. Recall that the Team set the permissible FP at 5%.

ASTM D5283-92 [12] provides the formula for the action level based on a constant SD over the concentration range (Eq. E-4). Since the 4100 Vapor Detector did not produce data with a constant SD, this formula can be adapted to this example by using the relationship between SD and RSD, which is SD = (Concentration) × RSD/100%. Thus Eq. E-4 becomes Eq. E-5, and the regulatory threshold (RT = 50 ppm) is the concentration used in the formula.

$$AL = RT - Z_{1-FP} \times \frac{SD}{\sqrt{n}} \qquad (E-4)$$

$$AL = RT - Z_{1-FP} \times \frac{RT \times RSD}{100\% \times \sqrt{n}} \qquad (E-5)$$

Decision Rule for 5% FP and 10% FN

If the corrected average PCB concentration of 220 random soil samples from a drum is less than 44.4 ppm, then send the drum to the landfill.

If the corrected average PCB concentration of 220 random soil samples from a drum is greater than or equal to 44.4 ppm, then send the drum to the incinerator.

$$AL = 50\,ppm - (1.645) \times \frac{50\,ppm \times 101\%}{100\% \times \sqrt{220}} = 44.4\,ppm \quad .$$

The average PCB concentration for a single drum will be calculated from the 220 samples from that drum. The results would be corrected for bias and the average of the corrected results would be compared with an AL = 44.4 ppm. The decision rule using EST's 4100 Vapor Detector to satisfy a 5% FP and a 10% FN thus becomes:

A decision performance curve for this environmental problem [14] calculates the probability of sending a drum to the incinerator for different values of true PCB concentration in a drum. Figure E-2 shows that the decision performance curve has the value of Pr[Take Drum to Incinerator] = 0.95 for True = 50 ppm. This indicates that the decision rule meets the DQO Team's FP of 5%. The Pr[Take Drum to Incinerator] = 0.05 for True = 40 ppm which is better than the FN of 10% that the DQO Team had specified. This improved performance is due to rounding up the number of samples to the next integer in the calculation of number of samples required.

Alternative FP Parameter

Because of random sampling and analysis error, there is always some chance that analytical results will not accurately reflect the true nature of a decision unit (such as a drum, in this example). Often, 95% certainty (a 5% FP) is customary and sufficient to meet stakeholder comfort. But suppose that the DQO Team wanted to be even more cautious about limiting the possibility that a drum might be sent to a landfill when its true value is 50 ppm. If the Team wanted to be 99% certain that a drum was correctly sent to a landfill, the following describes how changing the FP requirement from 5% to 1% would affect the decision rule. Using FP = 0.01, the sample size is calculated to be 333 and the action level is calculated to be 43.6 ppm. The decision performance curve has the value of Pr[Take Drum to Incinerator] = 0.99 for True = 50 ppm. This indicates that the decision rule meets EPA's FP of 1%. The Pr[Take Drum to Incinerator] = 0.01 for True = 40 ppm is better than the FN of 10% that the DQO Team had specified. This improved performance is due to rounding up the number of samples to the next integer in the calculation of number of samples required. The decision rule for the lower FP would be:

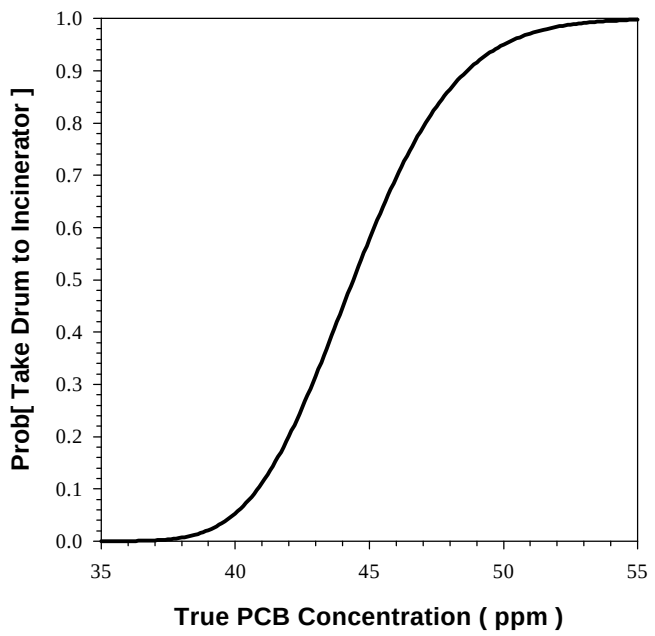

Figure E-2. Decision performance curve for PCB drum example.

Decision Rule for FP = 1% and FN = 10%

If the corrected average PCB concentration of 333 random soil samples on a drum is less than 43.6 ppm, then send the drum to the landfill.

If the corrected average PCB concentration of 333 random soil samples on a drum is greater than or equal to 43.6 ppm, then send the drum to the incinerator.