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August 1998

Environmental Technology Verification Report

Electrochemical Technique/Ion Specific Electrode

Dexsil Corporation
L2000 PCB/Chloride Analyzer

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By

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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:	**L2000 PCB/CHLORIDE ANALYZER**
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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 Dexsil L2000 PCB/Chloride Analyzer.

PROGRAM OPERATION

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's) 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 were also 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, 1997. The study was conducted under two environmental conditions. The first site was outdoors, with naturally fluctuating temperatures 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: Electrochemical Technique/Ion Specific Electrode, Dexsil Corporation, L2000 PCB/Chloride Analyzer,* EPA/600/R-98/109.

TECHNOLOGY DESCRIPTION

The L2000 PCB/Chloride Analyzer (dimensions: 8" × 8" × 4.5") is a field-portable instrument, weighing approximately 3.5 lb, designed to quantify PCB concentration in soils, dielectric fluids, and surface wipes. Sample preparation consists of extraction and dehalogenation of the PCB. A 10-g sample of soil is weighed into a polyethylene test tube. The soil is extracted with a nonchlorinated solvent from a premeasured ampule. (Note that a newly developed hydrocarbon solvent system was used for the demonstration analyses.) The soil is allowed to settle, and the supernatant is decanted onto a Florisil column. The solution is passed through the column, where all of the water and inorganic chloride is removed. Five milliliters of the solution are collected in a polyethylene reaction tube. Two glass ampules contained in the reaction tube are broken, introducing metallic sodium to the extract solution. The sodium strips the covalently bound chlorine atoms off the PCB molecule. The mixture is then shaken for 10 s and allowed to react for a total of 1 min. An aqueous extraction solution is added to the reaction tube to adjust the pH, destroy the excess sodium, and extract and isolate the newly formed chloride ions in an aqueous buffered solution. The aqueous layer is decanted, filtered, and collected in an analysis vial. A chloride-ion-specific electrode is put into this aqueous solution to measure the millivolt potential of the chloride solution. The potential is then converted to a PCB concentration in terms of parts per million (ppm).

VERIFICATION OF PERFORMANCE

The following performance characteristics of the L2000 PCB/Chloride Analyzer 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. The MDL was calculated to be 7.1 ppm based on the performance evaluation sample analyses. By use of a line fitted to a plot of the L2000-measured PCB concentrations versus the certified PE values, bias in the L2000 data can be corrected. After compensation for bias, the resulting L2000 MDL agrees with Dexsil's specified MDL of 2 ppm.

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

Ease of Use: Two operators analyzed samples during the demonstration, but the technology can be run by a single trained operator. Minimal training (<1 hour) is required to operate the L2000, provided the user has a fundamental understanding of basic chemical techniques.

Completeness: The L2000 generated results for all 232 PCB samples for a completeness of 100%.

Blank results: PCBs were detected above the L2000's MDL for four of the eight blank samples. Therefore, the percentage of false positive results was 50%. These results were obtained for both soil and extract samples. The L2000 reported no false negative results.

Precision: The overall precision, based on average relative standard deviations (RSDs), was 23% for soil samples and 14% for extract samples. The L2000's precision was comparable to that of the reference laboratory (21% RSD for soils and 14% RSD for extracts). At higher concentrations (>125 ppm), the L2000 was more precise than the reference laboratory (4% versus 19% RSD).

Accuracy: Accuracy was assessed using PE soil and extract samples. The data showed that the L2000 exhibited a significantly high bias. The overall accuracy, based on average percent recoveries, was 208% for PE soil samples and

149% for extract samples. Evaluation of the data generated at each site indicated that there were no significant differences between the two data sets based on environmental conditions.

Comparability: This demonstration showed that the L2000 generated data that exhibited a linear 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 L2000 data, was 0.854 when all soil samples (0 to 700 ppm) were considered. For the concentration range from 0 to 125 ppm, the R^2 value was 0.781. Most of the percent difference values were greater than 100% when the L2000 results were compared directly with the reference laboratory results.

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 high (12% RSD), but the measured concentrations were biased high (147% recovery). For extract samples representing surface wipe sample concentrations of 100 µg/100cm^2 and 1000 µg/100cm^2 (assuming a 1000 cm^2 wipe sample), measurements were precise (14% RSD), but indicated a high bias (149% recovery), especially for the lower concentrations.

Data quality levels: Because the PCB data generated in this demonstration strongly correlated with the reference laboratory results, it may be possible for Dexsil's L2000 PCB/Chloride Analyzer to be used quantitatively, but the high bias must be considered. The overall performance was characterized as consistently biased but precise.

The results of the demonstration show that the Dexsil L2000 PCB/Chloride Analyzer can provide useful, cost-effective data for environmental problem-solving and decision-making. Undoubtedly, it will be employed in a variety of applications, ranging from serving as a complement to data generated in a fixed analytical laboratory to generating data that will stand alone in the decision-making process. As with any technology selection, the user must determine if this 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*.

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Director
National Exposure Research Laboratory
Office of Research and Development

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's) Environmental Management (EM) program has entered into active partnership with EPA, by 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 Dexsil's L2000 PCB/Chloride Analyzer. Separate ETVRs have been published for the other technologies demonstrated.

The L2000 PCB/Chloride Analyzer is a field-portable instrument, weighing approximately 3.5 lb, designed to quantify PCB concentration in soils, dielectric fluids, and surface wipes. The L2000 utilizes a chloride-specific electrode to determine the amount of chlorine in a sample after the sample has been digested to convert the bound chlorine into ionic chloride. The L2000 detects the total chloride content of the sample and then electronically converts total chloride content to PCB concentration in units of parts per million (ppm). The L2000 provides no information on Aroclor identification.

The L2000's quantitative results were based on site-specific calibrations that were temperature-dependent. Recalibration was required approximately every 15 min, or whenever there was an internal temperature change. 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. A field-based MDL was calculated from a linear line fit to all of the PE data. The calculated field-based MDL (2.0 ppm) was comparable to Dexsil's specified detection limit (2 ppm) when the instrument bias was mathematically corrected (MDL without bias correction was 7.1 ppm). In general, the L2000's results were biased high (208% recovery for soils and 149% for extracts). The overall precision, based on the relative standard deviation, for soil samples (23%) was comparable to that for the reference laboratory (21%) . The precision for extract samples was also comparable to that of the reference laboratory (both 14%). Comparability, based on coefficients of determination (R^2), was 0.854 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 L2000 results were compared directly with the reference laboratory results.

The demonstration found that the L2000 was simple to operate in the field, requiring less than 2 h for initial set-up and preparation for sample analysis. Once operational, the sample throughput of the L2000 during the demonstration was 5 to 10 samples/h. Two operators analyzed samples during the demonstration, but the technology can be run by a single trained person. Minimal training (<1 h) is required to operate the L2000, provided the user has a fundamental understanding of basic chemical techniques. Because the PCB data generated in this demonstration strongly correlated ($R^2 = 0.95$) with the reference laboratory results, it may be possible for Dexsil's L2000 PCB/Chloride Analyzer to be used quantitatively, but the high bias must be considered. No "site effects" were observed in the data generated by the L2000 based on the change in environmental conditions. The overall performance was characterized as consistently biased but precise.

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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 (ORNL)
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 (DOE)
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 (EPA)
NRC	Nuclear Regulatory Commission
ORD	Office of Research and Development (EPA)
ORNL	Oak Ridge National Laboratory
ORO	Oak Ridge Operations (DOE)
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	relative standard deviation (percent)
RT	regulatory threshold
S^2	variance for the measurement
SARA	Superfund Amendments and Reauthorization Act of 1986
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), 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, Dexsil's L2000 PCB/Chloride Analyzer. 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.

General Technology Description

The L2000 PCB/Chloride Analyzer (dimensions: 8" × 8" × 4.5") is a field-portable instrument, weighing approximately 3.5 lb, designed to quantify PCB concentration in soils, dielectric fluids, and surface wipes. The L2000 currently requires 120V AC power, but the next version of the instrument will be battery-operated. The instrument can quantify PCBs in soil over a range of 2 ppm to 2000 ppm and has the ability to extend the range to over 2000 ppm with the reduction of the sample size. For wipe samples, PCBs can be quantified over a range of 2 to 2000 µg/100 cm^2. The percent error rate is specified as 5% chlorine. The total time for analysis of soil is 10 min; for dielectric fluid, 5 min; and for surface wipes, 12 min.

Soil Sample Preparation

Sample preparation consists of extraction and dehalogenation of the PCB. A 10-g sample of soil is weighed into a polyethylene test tube. The soil is extracted with a nonchlorinated solvent from a premeasured ampule. (A newly developed hydrocarbon solvent system was used for the demonstration analyses.) The soil is allowed to settle, and the supernatant is decanted onto a Florisil cartridge. The soil extract is passed through the cartridge, where all of the water and inorganic chloride is removed. Five milliliters of the eluent is collected in a polyethylene reaction tube. Two glass ampules contained in the reaction tube are broken, introducing metallic sodium to the extract solution. The sodium strips the covalently bonded chlorine atoms off the PCB molecule. The mixture is then shaken for 10 s and allowed to react for a total of 1 min. An aqueous extraction solution is added to the reaction tube to adjust the pH, destroy the excess sodium, and extract and isolate the newly formed chloride ions in an aqueous buffered solution. The aqueous layer is decanted, filtered, and collected in an analysis vial. The ion-specific electrode is put into this aqueous solution to measure the millivolt potential. The potential is then converted to PCB concentration in terms of parts per million.

Instrument Calibration

A one-point calibration is analyzed prior to sample analysis. The analyst simply selects calibration mode and inserts the electrode into a 50 ppm chloride solution supplied with the reagents. A start button is pushed and a “wait light” illuminates for approximately 30 s. When a “read light” illuminates, the analyst calibrates the instrument by turning the calibration knob until the display reads 50 ppm. The instrument is now calibrated. Additional calibration is required when the recalibrate light illuminates. This occurs approximately every 20 min, or after the completion of 15 to 20 samples.

Sample Analysis

The analyst chooses between four different PCB settings—1242, 1260, Askarel A (60% Aroclor 1260/40% trichlorobenzene), and total chloride—depending on the percentage of chlorine in the PCBs expected in the samples as indicated by site information or history. If the Aroclor is not known or if there is a mixture of Aroclors, the 1242 setting should be employed for the most conservative results. Total chloride setting is used to quantify "odd" Aroclors (1221, 1248, etc.) or other chlorinated organics. To analyze the sample, the analyst places the electrode into the aqueous extract solution and pushes the start button. After approximately 30 s, the PCB concentration of the sample (in ppm) is displayed on the L2000 when the "read light" illuminates. Note that total chlorine results must be divided by the percent chlorine of the analyte and multiplied by 100 to calculate the PCB concentration of the sample.

Surface Wipe Sampling and Analysis

For this demonstration, simulated extract samples were provided for analysis. A sample collection and preparation kit for surface wipes is available from Dexsil for use with the L2000 PCB/Chloride Analyzer. The kit contains the following items for surface wipe sampling:

- chromatographic-grade hexane in 2-mL sealed glass ampules,
- disposable PCB-rated gloves,
- disposable forceps,
- goggles,
- gauze pads, and
- reagents and vials.

To collect a wipe sample, a 1000-cm^2 area is wiped with a gauze pad saturated with 2 mL of chromatographic-grade hexane. (A 100-cm^2 area must be wiped to obtain a low-level PCB concentration in µg/100cm^2.) After waiting approximately 30 seconds for the hexane to evaporate, the analyst extracts the gauze pad with 10 mL of isooctane. (Note that this is where the analysis of the demonstration extract samples began.) Five milliliters of the extract is introduced into the sodium reaction tube. Once the extract is in the reaction tube, the procedure is exactly the same as for the soil analysis. The PCB concentration is reported in terms of µg/100cm^2. The concentration range of the instrument is 2 to 2000 µg/100 cm^2.

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 descriptions of the environmental soil samples 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

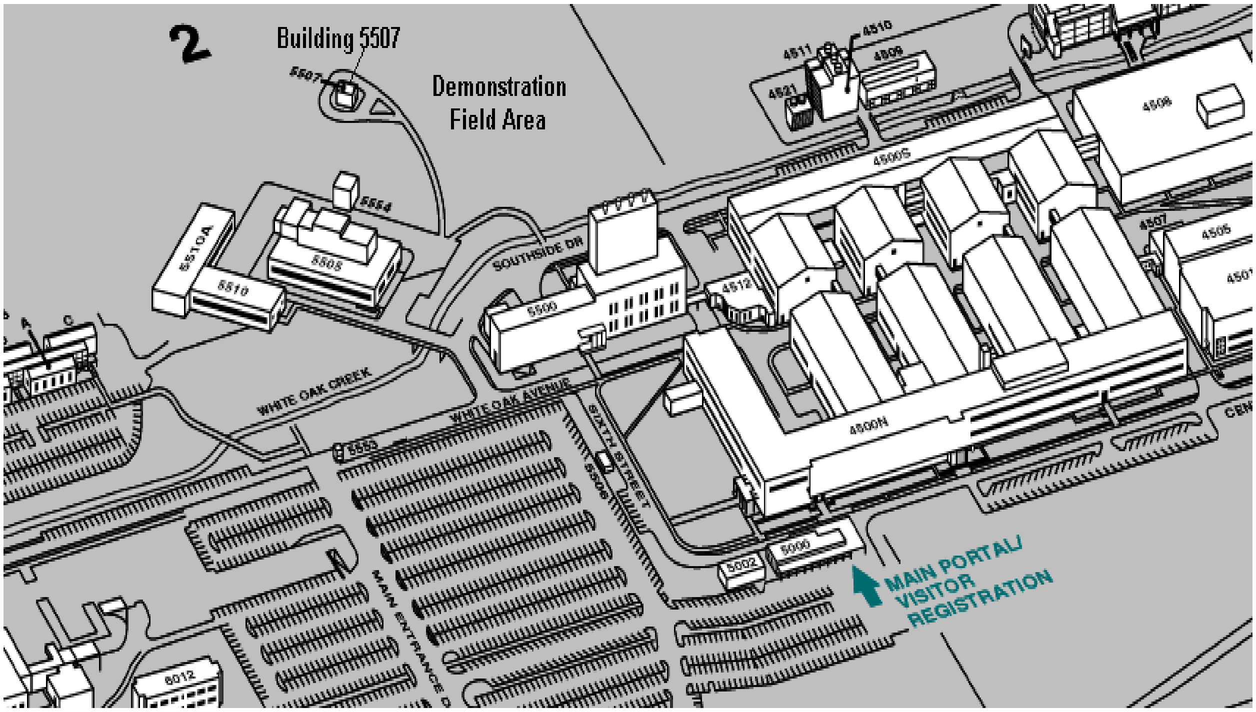

Figure 3-1. Schematic map of ORNL, indicating the demonstration area.

environmental soil) were analyzed. The ability to use environmental soils in the verification 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

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.

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.

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 Dexsil team worked outdoors July 22, 23, 24, 25, and 26, 1997, and in the chamber on July 26, 28, and 29, 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. Dexsil analyzed extracts prepared in iso-octane. 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., Dexsil 1001 through Dexsil 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. Dexsil received information pertaining to which Aroclors were in the samples. This was provided at the request of Dexsil to simulate the type of information that would be available during actual field testing. 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 L2000's results for the predemonstration samples. Results indicated that Dexsil's L2000 PCB/Chloride Analyzer was ready for field evaluation. The same analyst, instrument, and procedure were used in the field demonstration study.

Table 3-2. Summary of the L2000's predemonstration results

Sample Description	Matrix	Source	L2000[a]		Reference Laboratory	
			Result (ppm)	Duplicate result (ppm)	Result (ppm)	Duplicate result (ppm)
2 ppm of Aroclor 1260	Soil	ORNL	2.4	2.8	2.2	2.3
100 ppm (total) of Aroclors 1254 and 1260	Soil	ORNL	82.1	88.4	78.0	89.0
11 ppm of Aroclor 1260	Soil	EPA	8.8	7.7	11.0	9.5
50 ppm of Aroclor 1254	Soil	ERA	45.3	*b*	37.0	*b*
5 ppm of Aroclor 1242	Extract	ORNL	6.0	6.4	4.7	4.9

[a] No sample information was provided to Dexsil. All samples quantified as Aroclor 1260.
[b] Replicate was not analyzed because of lack of adequate sample for second analyses.

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 Dexsil team made two modifications to the procedure described in the technology demonstration plan [5]. On the first day of testing, the Dexsil field team realized the need for an additional pre-filter, prior to the Florisil column, to remove particulate matter. The Dexsil team attributed the filtering problems to fine particulate matter in the sample matrix that was somewhat different from the predemonstration study sample matrix. The second deviation from the demonstration plan was that Dexsil used iso-octane as the solvent for the extract samples and not hexane, as was listed.

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:

$$percent\ recovery = \frac{measured\ amount}{actual\ amount} \times 100\% \tag{4-1}$$

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:

$$RPD = \frac{|\ MS\ recovery\ -\ MSD\ recovery\ |}{average\ recovery} \times 100\% \tag{4-2}$$

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

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%).

samples, was 21% for the worst case (including the suspect result) and 18% for the best case (excluding the suspect result).

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.

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).

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 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 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 ≤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.

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	PE	63	18	101
	Environmental			
Best Case	< 125 ppm	107	23	n/a [b]
(excluding suspect data)	> 125 ppm	17	19	n/a [b]
	overall	187	21	101
Soil	PE	64	21	105
	Environmental			
Worst Case	< 125 ppm	108	26	n/a [b]
(including suspect data)	> 125 ppm	20	56	n/a [b]
	overall	192	28	105
Extract	10 ppm	16	19	104
	100 ppm	16	8	64
	overall	32	14	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.

Section 5
Technology Performance and Evaluation

Objective and Approach

This section presents the evaluation of data generated by Dexsil's L2000 PCB/Chloride Analyzer. 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 Dexsil's L2000 PCB/Chloride Analyzer through a statistical analysis of the data. PARCC parameters were used to evaluate the L2000'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 measurements made at each site indicated that there were no significant differences between the two data sets. All statistical tests were performed at the 5% significance level. Because environmental conditions did not appear to affect the results significantly, data from both sites were also combined for each parameter (precision and accuracy) to determine overall performance. Appendix D contains the raw data that were used to assess the performance of the L2000 PCB/Chloride Analyzer.

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 Equation 4-3). For comparative information on 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 L2000 PCB/Chloride Analyzer for the analysis of PE samples. RSDs ranged from 7 to 35% under the outdoor conditions, and from 5 to 46% under inside chamber conditions. In Table 5-1, the data generated under both environmental conditions are combined to

Table 5-1. Precision of the L2000 PCB/Chloride Analyzer 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]	2.1	1.0	48	226 [a]	1.8	1.3	72	1.9	1.1	58
118	6.5	1.0	15	218	5.0	2.3	46	5.8	1.8	31
124	6.2	1.9	31	224	8.3	3.6	43	7.2	2.9	40
120	12.2	4.3	35	220	7.8	1.8	23	10.0	3.9	39
122	18.1	4.5	25	222	15.1	6.0	40	16.6	5.2	31
119	47.8	12.9	27	219	41.6	6.2	15	44.7	9.9	22
125	72.3	5.2	7	225	73.3	3.9	5	72.9	4.3	6
121	66.2	5.9	9	221	73.4	5.6	8	69.8	6.6	9
123	78.7	6.1	8	223	75.4	7.8	10	77.0	6.7	9

[a] The L2000 detected PCBs in the blanks. The method detection limit (specified by Dexsil) was 2 ppm. The blank data were not included in the calculation of the overall average RSD.

provide an overall assessment of precision. The performance for the combined site data indicated RSDs ranging from 6 to 40%.

Environmental Soil Samples
The precision of the L2000 PCB/Chloride Analyzer for the analysis of environmental soil samples is reported in Table 5-2. RSDs ranged from 3 to 54% under the outdoor conditions, and from 2 to 51% under inside chamber conditions. For concentrations above 15 ppm, all RSDs were below 35%. Because the majority 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 26%, in contrast to that of the high concentration range, which was 4%.

The Paducah soils (indicated by bold sample IDs in Table 5-2) were analyzed at both sites to provide an assessment of the L2000'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. For the replicate Paducah soil sample sets, represented in bold at the bottom of the table, the 100 series were samples analyzed under the outdoor conditions and the 200 series were samples

Table 5-2. Precision of the L2000 PCB/Chloride Analyzer for environmental soil samples

Outdoor Site				Chamber Site				Combined Sites
Sample ID	Average Concentration (ppm)	SD (ppm)	RSD (%)	Sample ID	Average Concentration (ppm)	SD (ppm)	RSD (%)	RSD (%)
108	5.6	2	35	206	9.5	3.8	39	n/a [a]
109	5.9	2.5	42	207	31.7	0.8	3	n/a
102	6.3	3.2	50	208	64.2	7.0	11	n/a
107	6.9	2.4	34	209	80.5	27.7	35	n/a
103	10.3	3.8	36	210	105.0	5.0	5	n/a
101	10.6	5.7	54	211	437.1	7.9	2	n/a
104	13	3.1	24	212	14.1	6.1	43	n/a
111	49.4	11.9	24	213	15.4	3.5	23	n/a
105	72.9	10.9	15	214	50.6	5.5	11	n/a
106	430.6	26.1	6	215	52.6	7.0	13	n/a
110	432.7	108.1	25	216	86.7	9.7	11	n/a
112	473.3	134.5	28	217	445.7	10.6	2	n/a
113 [b]	6.7	1.4	21	**201**	8.7	4.4	51	42
114	7.7	3.1	40	**202**	5.5	2.2	40	41
115	38.2	4.5	12	**203**	31.3	5.9	19	17
116	100.9	3.3	3	**204**	108.7	8.6	8	7
117	513.9	35.3	7	**205**	477.1	25.2	5	7

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

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 this analysis showed that there were no significant differences in the data generated at each site. This indicated that different environmental conditions had no effect on the L2000's performance for this sample set, as illustrated in the following data. Under the outdoor conditions, the RSDs for the Paducah samples ranged from 3 to 40%, and under chamber conditions, from 5 to 51%. RSDs for the combined site data (eight replicates per paired Paducah sample IDs) ranged from 7 to 41%.

Extract Samples

Table 5-3 summarizes the L2000 PCB/Chloride Analyzer results for the extract samples which were used to simulate surface wipe samples. Refer to Section 3 under the heading "Extract Samples" for further clarification of this sample type. RSDs ranged from 3 to 11% under the outdoor conditions, and from 6 to 19% inside the chamber. In terms of concentration levels, the average RSD at the 10-µg/mL level was 9%, while the average RSD at the 100-µg/mL level was 18%.

Table 5-3. Precision of the L2000 PCB/Chloride Analyzer 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 (%)**
129 [a]	2.9	0.3	10	229 [a]	1.8	0.3	18	2.3	0.70	30
127	21.5	2.4	11	227	20.0	1.2	6	20.7	1.9	9
128	81.4	2.5	3	228	100.0	19.3	19	90.7	16.2	18

[a] The L2000 detected PCBs in the blanks. The method detection limit (specified by Dexsil) was 2 ppm. 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 overall precision of the L2000 PCB/Chloride Analyzer for the PE samples was a mean RSD of 22% and a median RSD of 19%; the 95th percentile of all individual RSDs was 45%. The environmental soil sample RSD results were a mean of 23%, a median of 22%, and a 95th percentile of 50%. The overall precision for all extract samples was a mean RSD of 14%. The 95th percentile and median data are not presented for extract samples because of the limited number of data points. Additionally, the precision of the solvent blanks from the extract data was comparable to the precision of the soil blanks from the environmental soil sample data (SD of 0.7 vs 1.1 ppm, respectively).

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 Equation 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 "Accuracy."

Table 5-4. Overall precision of the L2000 PCB/Chloride Analyzer for all sample types

Statistic	% RSD, PE Samples			% RSD, Environmental Soil Samples			% RSD, Extract Samples		
	Outdoor	Chamber	Combined	Outdoor	Chamber	Combined [a]	Outdoor	Chamber	Combined
Mean	20	24	22	27	19	23	7	13	14
Median	20	19	19	25	11	22	n/a [b]	n/a	n/a
95th percentile	34	46	45	51	45	50	n/a	n/a	n/a

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

Performance Evaluation Soil Samples

The performance of the L2000 PCB/Chloride Analyzer 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. All average concentrations determined by the L2000 were outside of the acceptance ranges and all were biased high. This was also reflected in the average percent recoveries, which were all greater than 100%. Average percent recoveries ranged from 132 to 325% under the outdoor conditions. Under chamber conditions, average percent recoveries ranged from 139 to 415%. When the data for the two sites were combined, the average percent recovery ranged from 132 to 360%. Additionally, some of the PE samples (sample IDs 118/218, 119/219, 120/220, 121/221, 122/222, 123/223) were spiked with pesticides (up to 15 ppm). The results for the pesticide-containing PE samples did not appear to be biased significantly higher than the nonpesticide PE samples (sample IDs 124/224 and 125/225). Pesticides are potential interferences for the L2000 because they contain organic chlorine. The results for the pesticide-containing PE samples did not appear to be biased significantly higher than the nonpesticide PE samples (sample IDs 124/224 and 125/225). It was speculated that the aliphatic pesticides were probably removed during sample preparation, and the aromatic pesticides were a minor contribution to the total chlorine concentration.

While the results were biased high, the L2000 data did correlate with the certified PE values. Because a mathematical relationship between the certified values and the biased results can be defined, it is possible to mathematically correct for the bias evident in this study. Although the correlation between the certified values and the L2000's results in this study was most accurately described by a quadratic equation (which draws a curved line through the data points), a simpler linear equation (which draws a straight line through the data points) can be used with minimal loss of predictive capability. A detailed description of how the L2000 data could be converted to compensate for the bias is presented in Appendix E.

Several factors may have contributed to the high bias of the L2000 results. First, PCBs were detected at concentrations that ranged from 2 to 4 ppm in four blank soil samples, and the results were not blank-corrected. Second, a multiplier of 1.25 was built into the circuitry of the L2000 analyzer to account for the extraction efficiencies typical of complex environmental soil samples. This multiplier ensured that a conservative estimate was reported. Third, as discussed in Section 3, Dexsil was provided information

Table 5-5. Accuracy of the L2000 PCB/Chloride Analyzer for PE soil samples

Certified Concentration (ppm) (Acceptance Range, ppm)	Outdoor Site			Chamber Site			Combined Sites	
	Sample ID	Average Conc (ppm)	Average Recovery (%)	Sample ID	Average Conc (ppm)	Average Recovery (%)	Average Conc (ppm)	Average Recovery (%)
0 [a] (n/a)	126	2.1	n/a	226	1.8	n/a	1.9	n/a
2.0 (0.7-2.2)	118	6.5	325	218	5.0	250	5.8	290
2.0 (0.9-2.5)	124	6.2	310	224	8.3	415	7.2	360
5.0 (2.1-6.2)	120	12.2	244	220	7.8	156	10.0	200
10.9 (4.0-12.8)	122	18.1	166	222	15.1	139	16.6	152
20.0 (11.4-32.4)	119	47.8	239	219	41.6	208	44.7	224
49.8 (23.0-60.8)	125	72.6	145	225	73.3	147	72.9	146
50.0 (19.7-63.0)	121	66.2	132	221	73.4	147	69.8	140
50.0 (11.9-75.9)	123	78.7	157	223	75.4	151	77.0	154

[a] The L2000 detected PCBs in the blanks. The method detection limit (specified by Dexsil) was 2 ppm. Average recovery calculations were not applicable to blank samples.

prior to the demonstration pertaining to which Aroclors were thought to be present in the samples. Dexsil used this sample information to convert the total chloride concentration detected by the L2000 to a PCB concentration. In some cases, the Aroclor suspected to be present did not match the Aroclor reported by the reference laboratory. It is difficult to quantify the impact that this discrepancy had on the L2000's bias, but it is thought to be minor.

Extract Samples

Percent recovery results for the extract samples are summarized in Table 5-6 for the L2000 PCB/ Chloride Analyzer. Under the outdoor conditions, the average percent recoveries for extract samples ranged from 81 to 215% and under indoor conditions from 100 to 200%. In terms of concentration levels (i.e., for the combined site data), the average recovery at the 10-µg/mL level was 207%, compared to

Table 5-6. Accuracy of the L2000 PCB/Chloride Analyzer for extract samples

Spike Concentration (µg/mL)	Outdoor Site			Chamber Site			Combined Sites	
	Sample ID	Average Conc (µg/mL)	Average Recovery (%)	Sample ID	Average Conc (µg/mL)	Average Recovery (%)	Average Conc (µg/mL)	Average Recovery (%)
0 [a]	129	2.9	n/a	229	1.8	n/a	2.3	n/a
10	127	21.5	215	227	20.0	200	20.7	207
100	128	81.4	81	228	100.0	100	90.7	91

[a] The L2000 detected PCBs in the blanks. The method detection limit (specified by Dexsil) was 2 ppm. Average recovery calculations were not applicable to blank samples.

91% at the 100-µg/mL level. Blank concentrations of 2.0 to 3.2 µg/mL may have contributed more significantly to the bias in the 10 µg/mL concentration results.

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 L2000 PCB/Chloride Analyzer can be characterized as biased high, with a mean percent recovery of 208%, a median of 168%, and a 95th percentile of 420%. The overall accuracy for all extract samples was a mean percent recovery of 149%. The 95th percentile and median data were not presented for extract samples because of the limited number of data points.

Table 5-7. Overall accuracy of the L2000 PCB/Chloride Analyzer for all sample types

Statistic	% Recovery, PE Samples			% Recovery, Extract Samples		
	Outdoor	Chamber	Combined	Outdoor	Chamber	Combined
Mean	215	201	208	148	150	149
Median	181	157	168	n/a[a]	n/a	n/a
95th percentile	355	420	420	n/a	n/a	n/a

[a] Median and 95th percentile statistics were not applicable to extract samples because of the limited number of data points.

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 PCBs actually are present. Both fp and fn results are influenced by the method detection limit of the technology. Of the eight blank soil samples analyzed, four were reported as having detectable levels of PCBs (i.e., fp = 50%). Of the 192 non-blank soil samples analyzed, none were reported as non-detects. Therefore, the percentage of fn results was 0%. The results were the same for the extract samples (fp = 50% and fn = 0%).

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 L2000 PCB/Chloride Analyzer was capable of analyzing diverse sample types (PE, simulated surface wipe extract, and actual field environmental soil samples) under multiple environmental conditions. When this technology is used, quality control samples should be analyzed to assess the performance of the L2000 under the testing conditions.

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 by the technology for all 232 samples. Therefore, the completeness of the L2000 PCB/Chloride Analyzer was 100%.

Comparability

Comparability refers to the confidence with which one data set can be compared to 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 L2000 measured values vs the reference laboratory results. Additional statistical analysis of the PCB soil concentrations for paired samples showed no significant difference between the L2000 and reference laboratory results for the higher concentrations (i.e., >125 ppm). In contrast, for the lower concentrations (i.e., <125 ppm), the L2000 reported PCB concentrations that were significantly higher than those reported by the reference laboratory. This is illustrated in Figure 5-1, which is a plot of the L2000-measured PCB soil concentrations vs the corresponding reference laboratory–measured concentrations (excluding the suspect values listed in Table 4-1). Figure 5-1(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. The diagonal lines in Figure 5-1 represent the line of theoretically perfect correlation ($R^2 = 1.0$) between the reference laboratory data set (plotted along the *x*-axis) and the L2000 data set (plotted along the *y*-axis). A value above the diagonal line indicated that the L2000'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 L2000 PCB concentrations vs the reference laboratory PCB concentrations. Excluding the reference laboratory's suspect measurements, the coefficient of determination (R^2) was 0.854 when all soil samples (0 to 700 ppm) were considered. As shown in Figure 5-1(b), the majority of the soil samples were in the concentration range of 0 to 125 ppm. The R^2 value for this concentration range was 0.781.

A direct comparison between the L2000 and reference laboratory data was performed by evaluating the percent difference (%D) between the measured concentrations, defined as

$$\% D = \frac{[L2000] - [Ref\ Lab]}{[Ref\ Lab]} \ x\ 100\% \qquad (5\text{-}1)$$

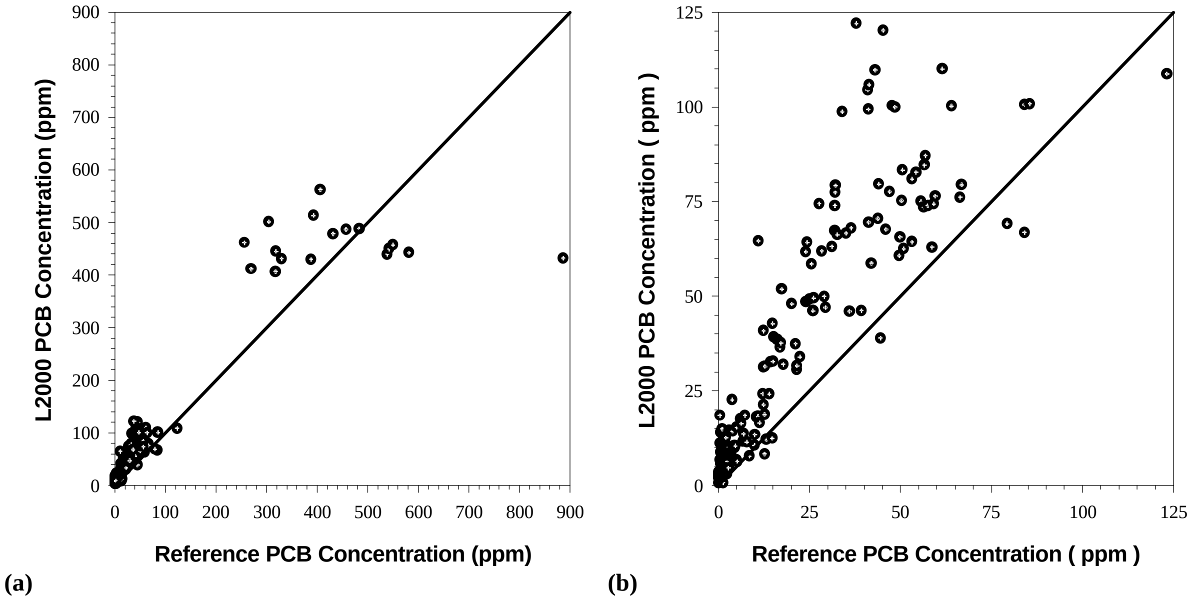

Figure 5-1. Paired PCB measurements for the L2000 and reference laboratory for (a) all soil samples and (b) soil samples where the reference laboratory results were less than or equal to 125 ppm. Lines denote perfect correlation.

Figure 5-2 provides a summary of the range of percent difference values for the soil samples, as calculated using Equation 5-1. The graph represents the percentage of samples that fall within each range of percent difference values, but 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 these samples. As shown in Figure 5-2, the majority of the percent difference values were greater than 100%. Fewer than 10% of the samples were biased low (%D ≤ −1%) relative to the reference laboratory. Approximately 14% of the soil sample results had percent difference values within the range of ±25%.

Comparability was also assessed for the extract samples. Analysis of the reference laboratory extract results vs the L2000 results indicated a high bias for the L2000's extract PCB concentrations. The coefficient of determination (R^2) for a line fitted to this data was 0.954. The correlation was near perfect (i.e., $R^2 = 1.0$) primarily because of the precision at the two concentration levels (10 and 100 ppm) that were analyzed. The percent difference values for the extract samples were also assessed. Percent differences were evenly distributed around the 76%D range (e.g., 8 of 16 samples had percent differences >76%, while 8 of 16 samples were between 0 and 75%D). None of the extract samples analyzed by the L2000 had a negative percent difference relative to the reference laboratory.

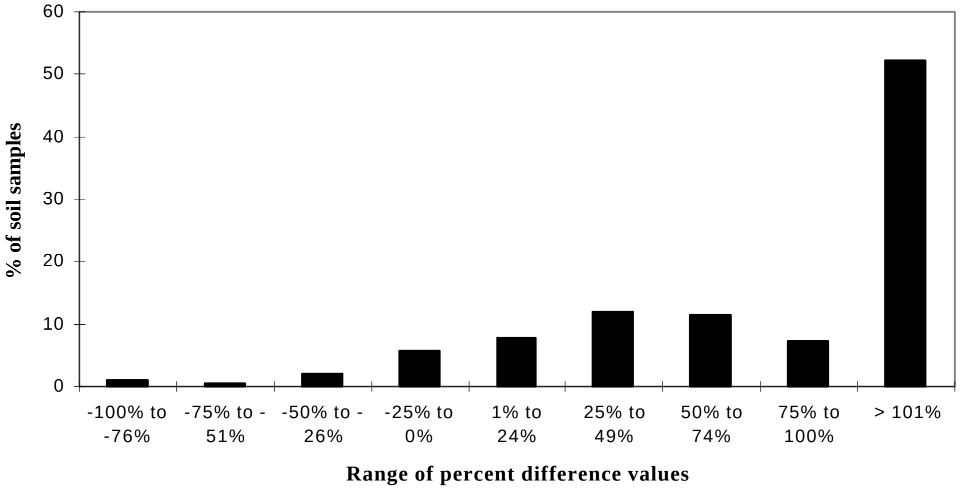

Figure 5-2. Range of percent difference values for the comparisons of the L2000 soil sample results with the reference laboratory results.

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 L2000's matching results. For sample IDs 110 and 112, the reference laboratory obtained qualitative results only, while Dexsil reported quantitative PCB concentrations for the four replicates that were precise. 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 L2000 generated results for all four replicates that were consistent and that were comparable with the reference laboratory's replicate means that excluded the suspect value. These comparisons demonstrate the L2000's ability to analyze successfully samples that were troublesome for the reference laboratory.

Summary of PARCC Observations

Table 5-9 provides a summary of the performance of Dexsil's L2000 PCB/Chloride Analyzer for the analysis of all sample types used in this demonstration. 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 L2000, weighted for the number of samples, was 23% for the soil samples. This is comparable to the reference laboratory's overall RSD of 21%. For the extract samples, the overall average RSD was the same (at 14%) for both the L2000 and the reference laboratory.

In terms of accuracy, the L2000's soil measurements were generally biased high by approximately a factor of 2 for PE PCB concentrations less than the regulatory limit of 50 ppm [2]. In comparison, the reference laboratory reported unbiased PCB concentrations for these PE soil samples. Extract

Table 5-8. Comparison of the reference laboratory's suspect data to the L2000 PCB/Chloride Analyzer data

Sample ID	Reference Laboratory Method		L2000 PCB/Chloride Analyzer	
	Suspect Measurement (ppm)	Replicate Mean [a] (ppm)	Suspect-matching Measurement (ppm)	Replicate Mean (ppm)
110	≤RDL [b]	≤RDL [b]	n/a	432.7
112	≤RDL [b]	≤RDL [b]	n/a	473.3
106	649.6	281.0	442.2	430.6
205	3305.0	493.0	493.6	477.1
216	151.6	55.1	86.4	86.7
217	1913.3	659.8	444.1	445.7
225	146.0	41.7	74.4	73.3

[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.

Table 5-9. Summary of PARCC observations for the L2000 PCB/Chloride Analyzer

Sample Matrix	Sample Type	L2000 Number of Samples	Precision (Average % RSD)		Accuracy (Average % Recovery)	
			L2000	Reference Laboratory	L2000	Reference Laboratory
Blank	Soil Extract	8 8	58 30	n/a	PCB levels in blanks were 2–4 ppm	All reported as non-detects
Soil	PE	64	22	18 [a]	208	101 [a]
	Environmental					
	<125 ppm [b]	108	26	23 [a]		
	>125 ppm [c]	20	4	19 [a]		
	Sample ID 110	4	25	Not quantified		
	Sample ID 112	4	28	Not quantified		
	Overall	200	23	21 [a]	208	101 [a]
Extract	10 ppm	8	9	19	207	104
	100 ppm	8	18	8	91	64
	Overall	16	14	14	149	84

[a] Average result excluding the suspect measurements.

[b] Samples for which the reference laboratory values were < 125 ppm.

[c] Samples for which the reference laboratory values were > 125 ppm.

measurements by the L2000 were also biased high at 10 ppm (207% recovery), but were unbiased at 100 ppm (91% recovery). In contrast, the reference laboratory results were unbiased at 10 ppm (104% recovery), but were biased low at 100 ppm (64% recovery) for extract samples.

The L2000 detected PCBs in four blanks (i.e., 50% fp results), while the reference laboratory correctly reported all blank samples as non-detects. No fn results were reported by the L2000. Thirteen suspect measurements that the reference laboratory had difficulty in analyzing were reported precisely by the L2000. Overall, the performance of the L2000 PCB/Chloride Analyzer for the PCB demonstration samples was characterized as biased but precise.

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/100cm^2 for surface wipes. The L2000's performance for soil samples (both PE and environmental) ranging in concentration from 40 to 60 ppm can be used to assess this ability, and the data are provided in Table 5-10. The performance of the L2000 for this concentration range showed a slightly lower RSD and percent recovery compared to the entire PE and environmental soil sample data set. In general, the variability of the measurements was low (the mean RSD was 12%), but the bias was still high by almost a factor of 2 (147% mean percent recovery). The mean percent difference value was 83% when the L2000 results were compared to the corresponding reference laboratory results for the 40- to 60-ppm concentration range.

Table 5-10. Performance of the L2000 PCB/Chloride Analyzer for soil samples between 40 and 60 ppm

Statistic	Precision (% RSD)	Accuracy (% Recovery)	Comparability (% Difference)
Mean	12	147	83
Median	8	148	53
95th percentile	29	168	188

The L2000 PCB/Chloride Analyzer's performance on extract samples is shown 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/100cm^2. For the simulated wipe extract samples, the L2000 was precise (14% average RSD), but had a high bias (149% average percent recovery) overall. For the L2000, a 1000 cm^2 sample is collected, and the results are reported in µg/100 cm^2 according to a conversion algorithm built into the instrument's software. Note that the manufacturer recommends the collection of 1000 cm^2 samples to ensure that detection limits are exceeded.

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]. The reported

MDL for the L2000 was 2 ppm. An MDL, calculated from a linear line fitted to all PE data, was 7.1 ppm. As previously discussed above (under the heading "Accuracy"), the use of a plot of the L2000 values for the PE samples vs the certified PE values permits compensation for the bias in the L2000 results. By this method, the calculated MDL (7.1 ppm) can be corrected to an unbiased result of 2.0 ppm, which then agrees with the L2000's specified MDL of 2 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. Dexsil's sample throughput rate was consistently around 5 samples/hour under the outdoor conditions but improved to nearly 10 samples/hour under the chamber conditions. This increased sample throughput may be attributed to (1) the analysis order (Dexsil may have gained experience by analyzing samples under the outdoor conditions first); (2) difficulty with the sample matrices that were analyzed only under the outdoor conditions (i.e., filtering problems, as noted in Section 3 under "Deviations from the Demonstration Plan"); or (3) the reduced need for recalibration when operating in the controlled temperature environment of the chamber.

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 L2000 PCB/Chloride Analyzer and a conventional analytical reference laboratory method. The analysis was based on the results and experience gained from this demonstration, costs provided by Dexsil Corporation, and representative costs provided by the reference analytical laboratories who offered to analyze these 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 L2000 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, and
- waste disposal costs.

Each of these cost factors is defined and discussed below and serves as the basis for the estimated cost ranges presented in Table 5-11. This analysis assumed that the individuals performing the analyses were fully trained to operate the technology. Dexsil does not offer a specific training course on the use of the L2000, but does provide free assistance, on an as-needed basis, through its technical service department.

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

L2000 PCB/Chloride Analyzer **Dexsil Corporation**		**EPA SW-846 Method 8080/8081/8082** **Reference Laboratory**	
Sample throughput rate:	**5 samples per hour (outdoors)** **10 samples per hour (chamber)**	**Typical turnaround 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	15–1000 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
L2000 rental fee	500 per month	Rental/purchase of system	Included
L2000 purchase price	3500	Reagents/supplies	Included
Reagents/supplies	8–10 per sample		
Waste Disposal	35–470	**Waste Disposal**	Included

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

Sample acquisition and pre-analytical sample preparation, which were tasks common to both methods, are costs that were not included here.

L2000 PCB/Chloride Analyzer Costs

- **Sample shipment costs.** Because the samples were analyzed on-site, no sample shipment charges were associated with the cost of operating the L2000.

- **Labor costs.** 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 hours, at a rate of $50 per hour.
  - 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 ($1000) included the cost of airline travel and rental car fees.

  - Per diem: This cost element included food, lodging, and incidental expenses. Estimates ranged from zero (for a local site) to $150/day per analyst.
  - Rate: The cost of the on-site labor was estimated at a rate of $30 to $75 per hour, 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.** Equipment costs included mobilization/demobilization, rental fees or purchase of equipment, 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 is local, the cost would be zero. For this demonstration, the cost of shipping equipment and supplies was estimated at $150.
  - Rental/purchase: The fee to rent the L2000 at the time of the demonstration study was $500 per month. At the time of the demonstration, the cost of purchasing the equipment was $3500. The purchase price included the L2000 PCB/Chloride Analyzer, chloride specific electrode, power cube, portable electronic balance, 5-mL pipettor, carrying case, vial rack, timer, instructions, and 20 soil test reagents.
  - 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 L2000 was $8 to $10 per sample. The price may be reduced if large quantities are purchased.

- **Waste disposal costs.** Waste disposal costs were estimated based on the 1997 regulations for disposal of PCB-contaminated waste. Using the L2000, Dexsil generated approximately 10 lb of liquid PCB waste and approximately 20 lb of solid PCB waste. The disposal costs for the PCB waste by incineration at a commercial facility was estimated at $0.25/lb for liquids and $1.50/lb for solids. For comparison, the cost for PCB waste disposal at ETTP was estimated at $11/lb for liquids and $18/lb for solids.

Reference Laboratory Costs

- **Sample shipment 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.
  - Overnight shipping: The overnight express shipping service cost was estimated to be $50 for one 50-lb cooler of samples.
  - Labor: This cost element included 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 hours at $50 per hour.

- **Labor, equipment, and waste disposal costs.** The labor bids from commercial analytical reference laboratories who 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 workload 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 that included labor, equipment, waste disposal, and report preparation.

Cost Assessment Summary

An overall cost estimate for the L2000 vs the reference laboratory was not made due to 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 vs the reference laboratory.

General Observations

The following are general observations regarding the field operation and performance of the L2000:

- The system was light, easily transportable, and rugged. It took less than 2 h for the Dexsil team to prepare to analyze samples on the first day of testing. While working at the outdoor site, the Dexsil team completely disassembled their work station and brought everything inside at the close of each day. It took the Dexsil team less than 1 h each morning to prepare for sample analysis.

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

- Operators generally require less than an hour of training and should have a basic knowledge of chemistry and lab techniques.

- Reagent handling was minimized by the use of premeasured, breakable glass ampules.

- The system required 120-V AC power. A battery-operated L2000 system is expected to be commercially available in 1998.

- The L2000 has a temperature setting adjustment. The Dexsil team monitored the temperature during the technology demonstration and adjusted the setting accordingly. This procedure increased sample throughput time during the outdoor site activities because adjustment of the temperature setting required recalibration of the instrument.

- The system required calibration approximately every 15 min. It also was recalibrated whenever there was an internal temperature change. Typically, a calibration standard was analyzed approximately every 12 samples. Calibration seemed to be more frequent when the

Dexsil team was working outdoors, presumably because the outdoor temperature fluctuated throughout the day.

- The Dexsil team usually analyzed three reagent blanks with each batch of 12 samples. Reagent blanks were analyzed to establish a baseline correction for the system. On average, the correction was less than 1 ppm. The blank results also provided Dexsil with information concerning the daily temperature fluctuations.

- The Dexsil analysts used the L2000 in the “total chloride” mode. Using the sample information provided at their request [i.e., which Aroclor(s) was in each sample; see Section 3 for more details], Dexsil calculated the most conservative (highest) PCB concentration. In cases where no Aroclor information is known, Dexsil advises that the sample should be quantified as Aroclor 1242.

- Approximately 20 lb of solid waste (used and unused soil, gloves, paper towels, ampules, etc.) were generated from the analysis of the technology demonstration samples. In addition, approximately 10 lb of liquid hazardous waste were generated.

Performance Summary

A summary of the performance characteristics of Dexsil’s L2000 PCB/Chloride Analyzer, presented previously in this chapter, is shown in Table 5-12. Because the PCB data generated by the technology could be correlated with the reference laboratory results, it may be possible for the L2000 to be used quantitatively, but the high bias must be considered. The overall performance of the L2000 PCB/Chloride Analyzer was characterized as consistently biased but precise.

Table 5-12. Performance summary for the L2000 PCB/Chloride Analyzer

Feature/Parameter	Performance Summary
Blank Samples	**Soils:** PCBs detected in 4 of 8 blanks at 2 to 4 ppm **Extracts:** PCBs detected in 4 of 8 blanks at 2 to 3 ppm
Method Detection Limit	Dexsil specified: 2 ppm Calculated: 7.1 ppm (corrected: 2.0 ppm)
Precision	**Average RSD** PE soils: 22% Environmental soils: 23% Extracts: 14%
Accuracy	**Average Percent Recovery** PE soils: 208% Extracts: 149%
False Positive Results	**Blank Soils:** 50% (4 of 8 samples) **Blank Extracts:** 50% (4 of 8 samples)
False Negative Results	**PE and Environmental Soils**: 0% (0 of 192 samples) **Spiked Extracts**: 0% (0 of 16 samples)
Comparison with Reference Laboratory Results	**PE and Environmental Soil Samples** Percent Difference: 52% of samples were > 100% D Coefficients of determination (R^2): 0.854 (all data), 0.781 (<125 ppm) **Extract Samples** Percent Difference: 50% of samples were > 76% D Coefficient of determination (R^2): 0.954
Regulatory Decision-Making Applicability	**40 to 60 ppm PE and Environmental Soil Samples** Precision: 12% average RSD Accuracy: 147% average recovery Comparability: 83% average difference **100 µg/100cm^2 and 1000 µg/100cm^2 Extract Samples** Precision: 14% average RSD Accuracy : 149% average recovery Comparability: 70% average difference
Sample Throughput	5 samples/hour (outdoors) 10 samples/hour (chamber)
Power Requirements	120V AC
Operator Requirements	Basic knowledge of chemical techniques; <1 hour technology-specific training
Cost	Equipment purchase: $3500 $5 to $16 per sample (matrix-dependent)
Hazardous Waste Generation	Approximately 10 lb liquid waste Approximately 20 lb solid waste

Section 6
Technology Update and Representative Applications

Objective

In this section, Dexsil describes new technology developments that have occurred since the demonstration activities. In addition, the developer has provided a list of representative applications where the L2000 has been or is currently being utilized.

Technology Update

A new version of the L2000 will be on the market in 1998. The L2000 DX Analyzer comes equipped with an LCD (2-in. by 16-in.) backlit display. The display is easy to read in all lighting situations. Pertinent information regarding the program in use, blank subtraction values, reporting units, and concentration values are visible on the display.

L2000 DX is preprogrammed with conversion factors for all major Aroclors and most chlorinated pesticides and solvents. The built-in methods include corrections for extraction efficiencies, dilution factors, and blank contributions. Programs are easily selected from a menu to perform routine analyses of common chlorinated organic compounds. For less common analytes or for custom measurement protocols, user-defined methods can be easily built and stored using the method development menus.

Analysis results can either be stored electronically, using the parallel port or uploading to a PC via the RS-232 serial port, or can be printed directly to the on-board 40-column thermal printer. The analyzer itself utilizes rechargeable batteries, which allow fully mobile operation in remote locations without access to power.

In addition, Dexsil has developed a new solvent system that provides extraction efficiency for PCBs from all soils tested that is equal to or better than the traditional extraction solvent. This new solvent system, which was the system used in the demonstration, is presently available for purchase. Over the next year, the traditional solvent system will be phased out and replaced by the more universal extraction solvent.

Representative Applications

The L2000 PCB/Chloride Analyzer is designed to provide quick quantitative results for PCB concentrations in soils, in dielectric fluids, and on surfaces. The analyzer operates on the principle of total organic chlorine detection. Co-contamination of the matrices with hydrocarbons such as transformer oil does not affect the quantification of the PCB. Water and salt content also has no effect on the test.

The insensitivity of the L2000 analyzer to common test interferences makes the technology ideal for a wide range of environmental applications. Numerous field applications have benefitted from the use of the L2000. Due to our policy to protect client confidentiality, Dexsil will not name specific projects. The following four companies regularly use the L2000 analyzer for a variety of applications and may assist a potential user in verifying they would benefit from the use of this technology.

1. GZA GeoEnvironmental, Inc.
   N4140 Duplainville Road
   Pewaukee, WI 53072
   Contact: Mark Krumenacher
   414-691-2662
   (PCB Soil Analyses)

2. Public Electric and Gas
   150 Circle Ave
   Cliffton, NJ 07011
   Contact: Joe Fink
   201-365-2901
   (Transformer Oil Analyses)

3. Phoenix Soil
   P.O. Box 1750
   Waterbury, CT 06723
   Contact: Dave Green
   203-759-0053
   (PCB Soil Analyses)

4. Long Island Lighting
   175 East Old Country Road
   Hickesville, NY 11801
   Contact: Bart Polizotti
   516-545-5511
   (Transformer Oil Analyses)

Data Quality Objective Example

This application of Dexsil's L2000 PCB/Chloride Analyzer is based on data quality objective (DQO) methods for project planning advocated by the American Society for Testing and Materials (ASTM) [12, 13] and EPA [14]. A DQO example was derived by ORNL from the performance results in Section 5. This example, which is presented in Appendix E, illustrates the use of the L2000'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

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[11] "Definition and Procedure for the Determination of the Method Detection Limit," *Code of Federal Regulations,* 40 CFR, pt. 136, appendix B, rev. 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, EPA, Washington, D.C., 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.

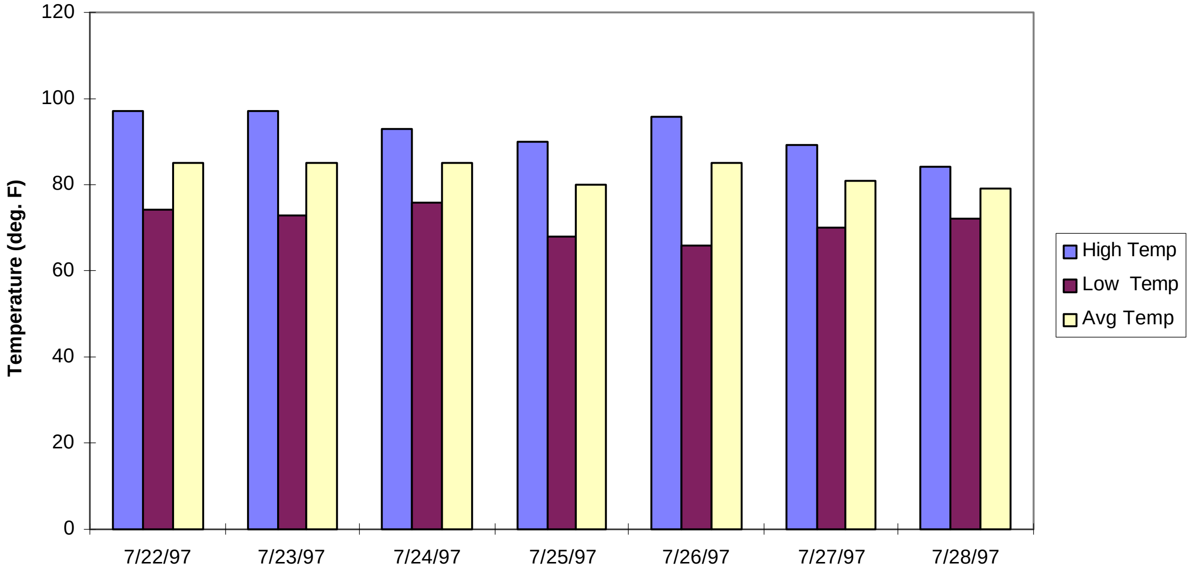

Figure C-1. Summary of temperature conditions for outdoor site.

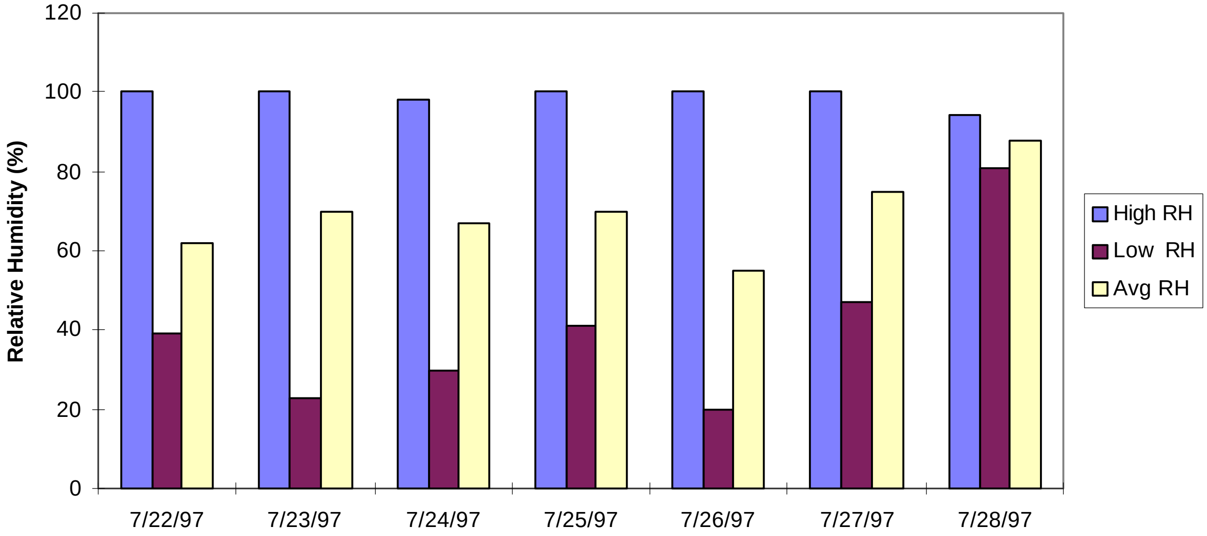

Figure C-2. Summary of relative humidity conditions for the outdoor site.

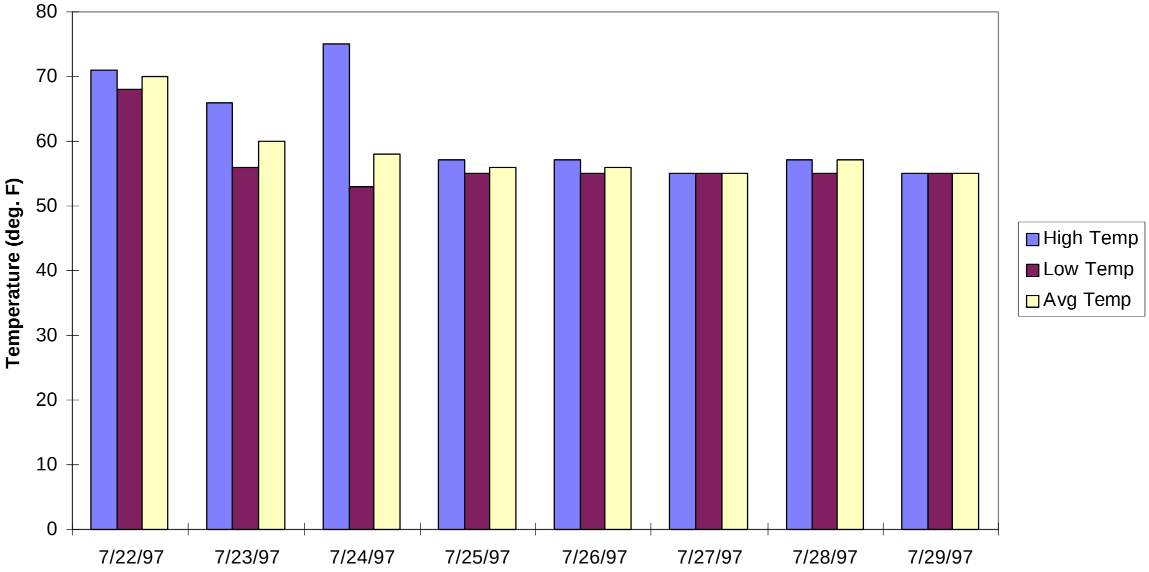

Figure C-3. Summary of temperature conditions for chamber site.

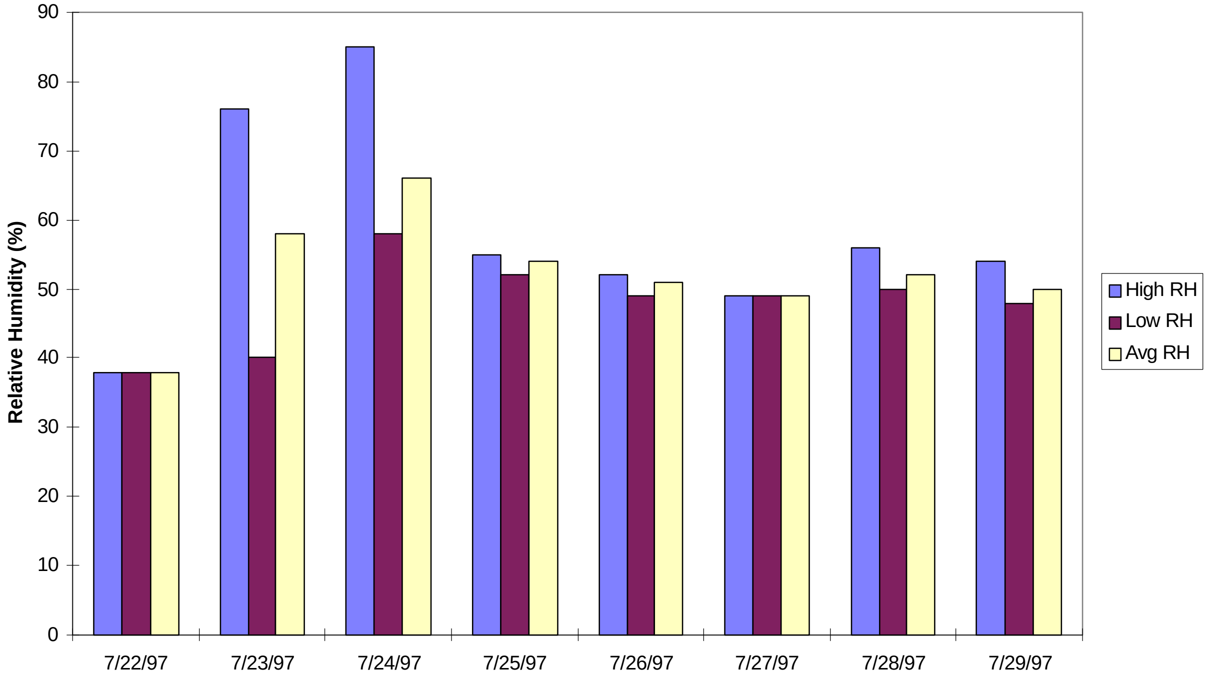

Figure C-4. Summary of relative humidity conditions for chamber site.

Appendix D
Dexsil’s L2000 PCB/Chloride Analyzer
PCB Technology Demonstration Sample Data

Legend for Appendix D Tables

Table Heading	Definition
Obs	Observation
Sample ID	Sample identification 101 to 126 = outdoor site soil samples 127 to 130 = outdoor site extract samples 201 to 226 = chamber site soil samples 227 to 230 = chamber site extract samples
Rep	Replicate of sample ID (1 through 4)
L2000 Result	L2000'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 = environmental soil 1242, 1248, 1254, 1260 = Aroclor in PE samples Blank = non-PCB-contaminated sample
Order	Order of sample analysis (started with 1001–1116, then 2001–2116)

Table D-1. L2000 PCB technology demonstration soil sample data

Obs	Sample ID	Rep	L2000 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
1	101	1	6.1	0.6	1254	Sample	1012
2	101	2	18.5	0.4	1254	Sample	1077
3	101	3	11.2	0.5	1254	Sample	1098
4	101	4	6.7	0.5	1254	Sample	1071
5	102	1	5.1	2.2	1254	Sample	1068
6	102	2	11.0	2.1	1254	Sample	1042
7	102	3	3.9	1.7	1260	Sample	1063
8	102	4	5.3	2.5	1260	Sample	1086
9	103	1	14.5	3.0	1254	Sample	1078
10	103	2	7.9	2.4	1254	Sample	1070
11	103	3	6.5	2.0	1260	Sample	1058
12	103	4	12.4	1.6	1260	Sample	1100
13	104	1	11.6	6.8	1260	Sample	1029
14	104	2	17.5	6.0	1254	Sample	1079
15	104	3	12.4	14.8	1254	Sample	1088
16	104	4	10.6	9.9	1254	Sample	1002
17	105	1	60.7	49.7	1260	Sample	1003
18	105	2	66.8	84.1	1260	Sample	1019
19	105	3	83.3	50.6	1260	Sample	1033
20	105	4	80.9	53.2	1260	Sample	1031
21	106	1	411.7	269.6	1254	Sample	1041
22	106	2	461.8	255.9	1254	Sample	1056
23	106	3	406.6	317.6	1254	Sample	1104
24	106	4	442.2	649.6	1254	Sample	1044
25	107	1	6.1	1.0	1254	Sample	1089
26	107	2	10.4	1.6	1254	Sample	1075
27	107	3	5.1	1.2	1254	Sample	1016
28	107	4	6.1	1.2	1254	Sample	1072
29	108	1	7.5	1.7	1254	Sample	1023
30	108	2	3.1	2.0	1254	Sample	1062
31	108	3	6.7	1.7	1254	Sample	1092
32	108	4	4.9	1.9	1254	Sample	1085
33	109	1	4.5	1.5	1254	Sample	1067
34	109	2	4.5	2.1	1254	Sample	1013
35	109	3	5.1	1.8	1254	Sample	1051
36	109	4	9.6	2.4	1254	Sample	1035
37	110	1	582.5	≤490.0	Non-Detect	Sample	1007
38	110	2	327.4	≤99.0	Non-Detect	Sample	1006
39	110	3	394.0	≤66.0	Non-Detect	Sample	1005
40	110	4	427.0	≤98.0	Non-Detect	Sample	1022

Obs	Sample ID	Rep	L2000 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
41	111	1	38.9	44.5	1254	Sample	1052
42	111	2	46.0	36.0	1254	Sample	1054
43	111	3	46.2	39.3	1254	Sample	1026
44	111	4	66.6	35.1	1254	Sample	1048
45	112	1	443.5	≤66.0	Non-Detect	Sample	1032
46	112	2	346.5	≤200.0	Non-Detect	Sample	1011
47	112	3	663.5	≤130.0	Non-Detect	Sample	1034
48	112	4	439.8	≤200.0	Non-Detect	Sample	1073
49	113	1	5.7	0.7	1260	Sample	1037
50	113	2	6.2	1.1	1260	Sample	1015
51	113	3	8.7	0.6	1260	Sample	1059
52	113	4	6.0	1.9	1248/1260	Sample	1004
53	114	1	6.7	1.1	1260	Sample	1021
54	114	2	4.1	1.2	1260	Sample	1055
55	114	3	11.4	1.3	1260	Sample	1099
56	114	4	8.4	1.7	1260	Sample	1069
57	115	1	42.7	14.9	1248	Sample	1043
58	115	2	40.8	12.4	1016	Sample	1045
59	115	3	32.7	15.0	1248	Sample	1097
60	115	4	36.4	16.9	1248	Sample	1093
61	116	1	105.8	41.4	1248	Sample	1074
62	116	2	99.3	41.2	1016	Sample	1080
63	116	3	99.9	48.5	1248	Sample	1083
64	116	4	98.7	34.0	1016	Sample	1101
65	117	1	478.7	431.6	1016	Sample	1082
66	117	2	562.4	406.3	1016	Sample	1024
67	117	3	501.4	304.7	1016	Sample	1090
68	117	4	513.1	392.8	1016	Sample	1076
69	118	1	6.4	2.1	1248	1248	1050
70	118	2	5.5	1.9	1016	1248	1057
71	118	3	6.4	0.7	1248	1248	1018
72	118	4	7.8	1.6	1248	1248	1030
73	119	1	37.4	21.2	1016	1248	1010
74	119	2	37.6	17.2	1248	1248	1066
75	119	3	51.8	17.4	1248	1248	1046
76	119	4	64.2	24.4	1248	1248	1047
77	120	1	10.0	4.5	1254	1254	1091
78	120	2	7.3	4.0	1254	1254	1017
79	120	3	16.3	6.3	1254	1254	1036
80	120	4	15.3	5.0	1254	1254	1081

Obs	Sample ID	Rep	L2000 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
81	121	1	62.9	58.7	1254	1254	1049
82	121	2	75.0	55.7	1254	1254	1096
83	121	3	64.3	53.2	1254	1254	1053
84	121	4	62.5	50.9	1254	1254	1020
85	122	1	24.2	12.2	1260	1260	1084
86	122	2	18.2	10.9	1260	1260	1103
87	122	3	16.5	11.3	1260	1260	1094
88	122	4	13.4	10.0	1260	1260	1064
89	123	1	74.3	59.2	1260	1260	1087
90	123	2	87.1	56.9	1260	1260	1039
91	123	3	79.4	66.8	1260	1260	1028
92	123	4	73.9	57.5	1260	1260	1025
93	124	1	9.0	1.8	1254	1254/1260	1095
94	124	2	5.1	1.4	1260	1254/1260	1001
95	124	3	5.5	1.9	1254	1254/1260	1008
96	124	4	5.1	1.8	1254	1254/1260	1014
97	125	1	73.9	32.0	1254	1254/1260	1060
98	125	2	69.5	41.3	1254	1254/1260	1027
99	125	3	67.6	46.0	1254	1254/1260	1009
100	125	4	79.2	32.2	1260	1254/1260	1040
101	126	1	3.1	≤0.1	Non-Detect	Blank	1102
102	126	2	2.1	≤0.1	Non-Detect	Blank	1065
103	126	3	2.3	≤0.2	Non-Detect	Blank	1038
104	126	4	0.7	≤1.3	Non-Detect	Blank	1061
105	201	1	6.9	1.0	1016/1260	Sample	2008
106	201	2	3.7	1.0	1016/1260	Sample	2023
107	201	3	10.1	1.1	1016/1260	Sample	2050
108	201	4	14.0	0.6	1260	Sample	2057
109	202	1	5.1	1.4	1260	Sample	2063
110	202	2	8.8	1.6	1260	Sample	2079
111	202	3	4.1	1.2	1260	Sample	2039
112	202	4	4.1	1.5	1260	Sample	2046
113	203	1	24.1	14.0	1248	Sample	2041
114	203	2	31.4	12.8	1248	Sample	2084
115	203	3	38.5	16.2	1248	Sample	2058
116	203	4	31.2	12.4	1248	Sample	2065
117	204	1	109.7	43.1	1248	Sample	2053
118	204	2	120.2	45.3	1248	Sample	2091
119	204	3	104.5	41.0	1248	Sample	2018
120	204	4	100.3	47.7	1248	Sample	2029

Obs	Sample ID	Rep	L2000 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
121	205	1	493.6	3305.0	1016/1260	Sample	2033
122	205	2	439.5	538.7	1016	Sample	2076
123	205	3	487.0	457.0	1016	Sample	2102
124	205	4	488.1	483.3	1016	Sample	2104
125	206	1	7.9	2.9	1260	Sample	2070
126	206	2	9.0	1.1	1260	Sample	2083
127	206	3	14.9	1.1	1016/1260	Sample	2077
128	206	4	6.3	2.5	1260	Sample	2035
129	207	1	32.0	17.8	1260	Sample	2019
130	207	2	32.6	14.3	1260	Sample	2080
131	207	3	30.6	21.6	1260	Sample	2073
132	207	4	31.6	21.6	1254	Sample	2074
133	208	1	58.7	42.0	1260	Sample	2081
134	208	2	74.4	27.7	1016/1260	Sample	2025
135	208	3	61.7	24.0	1254	Sample	2016
136	208	4	61.9	28.4	1260	Sample	2012
137	209	1	66.2	32.7	1260	Sample	2048
138	209	2	69.1	79.3	1260	Sample	2062
139	209	3	64.6	11.0	1260	Sample	2092
140	209	4	122.0	37.9	1260	Sample	2032
141	210	1	108.7	123.2	1260	Sample	2005
142	210	2	110.0	61.5	1260	Sample	2055
143	210	3	100.6	84.1	1260	Sample	2097
144	210	4	100.8	85.5	1260	Sample	2071
145	211	1	429.8	387.8	1254	Sample	2098
146	211	2	442.4	581.4	1254	Sample	2082
147	211	3	431.0	330.0	1254	Sample	2061
148	211	4	445.3	318.7	1254	Sample	2068
149	212	1	22.6	3.8	1260	Sample	2056
150	212	2	14.3	3.9	1260	Sample	2072
151	212	3	10.4	4.3	1260	Sample	2004
152	212	4	9.0	0.8	1260	Sample	2020
153	213	1	13.6	6.9	1260	Sample	2047
154	213	2	18.5	7.3	1260	Sample	2049
155	213	3	11.4	7.8	1260	Sample	2026
156	213	4	18.1	10.5	1260	Sample	2015
157	214	1	46.2	26.0	1260	Sample	2001
158	214	2	58.5	25.6	1260	Sample	2011
159	214	3	49.9	29.1	1260	Sample	2043
160	214	4	47.9	20.2	1260	Sample	2028

Obs	Sample ID	Rep	L2000 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
161	215	1	49.1	25.1	1260	Sample	2009
162	215	2	48.5	24.1	1260	Sample	2103
163	215	3	49.5	26.2	1260	Sample	2040
164	215	4	63.1	31.2	1016/1260	Sample	2060
165	216	1	86.4	151.6	1260	Sample	2067
166	216	2	77.6	47.0	1260	Sample	2086
167	216	3	82.7	54.3	1260	Sample	2027
168	216	4	100.2	64.0	1260	Sample	2006
169	217	1	431.9	886.7	1254	Sample	2087
170	217	2	457.1	549.8	1254	Sample	2059
171	217	3	449.6	542.8	1254	Sample	2013
172	217	4	444.1	1913.3	1016/1260	Sample	2085
173	218	1	4.6	2.8	1248	1248	2042
174	218	2	3.0	2.4	1248	1248	2021
175	218	3	4.1	2.6	1248	1248	2044
176	218	4	8.4	2.6	1248	1248	2094
177	219	1	33.9	22.4	1248	1248	2038
178	219	2	46.1	26.0	1016	1248	2051
179	219	3	47.0	29.4	1248	1248	2017
180	219	4	39.2	15.2	1248	1248	2078
181	220	1	7.7	8.5	1254	1254	2034
182	220	2	6.7	4.9	1254	1254	2088
183	220	3	10.4	4.7	1254	1254	2100
184	220	4	6.3	5.2	1254	1254	2045
185	221	1	67.2	32.0	1016/1260	1254	2064
186	221	2	79.6	44.1	1016/1260	1254	2095
187	221	3	70.5	43.8	1254	1254	2096
188	221	4	76.4	59.6	1254	1254	2054
189	222	1	12.1	13.2	1260	1260	2022
190	222	2	21.3	12.4	1260	1260	2093
191	222	3	8.3	12.7	1260	1260	2037
192	222	4	18.7	12.7	1260	1260	2010
193	223	1	84.6	56.6	1260	1260	2090
194	223	2	75.2	50.3	1260	1260	2089
195	223	3	65.6	49.9	1260	1260	2002
196	223	4	76.1	66.4	1260	1260	2036
197	224	1	8.4	2.2	1254	1254/1260	2101
198	224	2	3.7	1.2	1260	1254/1260	2024
199	224	3	8.4	1.4	1260	1254/1260	2069
200	224	4	12.6	2.1	1254	1254/1260	2052

Obs	Sample ID	Rep	L2000 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Order
201	225	1	73.5	56.4	1260	1254/1260	2003
202	225	2	68.0	36.5	1016/1260	1254/1260	2075
203	225	3	77.4	32.1	1260	1254/1260	2007
204	225	4	74.4	146.0	1254	1254/1260	2066
205	226	1	0.7	≤0.1	Non-Detect	Blank	2030
206	226	2	1.0	≤0.8	Non-Detect	Blank	2014
207	226	3	3.6	≤0.1	Non-Detect	Blank	2099
208	226	4	1.9	≤0.1	Non-Detect	Blank	2031

Table D-2. L2000 technology demonstration extract sample data

OBS	Sample ID	Rep	L2000 Result (ppm)	Ref Lab Result (ppm)	Reference Aroclor	Type	Spike[a] (ppm)	Order
1	127	1	21.0	10.9	1016	1242	10	1105
2	127	2	18.3	11.4	1016	1242	10	1112
3	127	3	22.9	10.9	1016	1242	10	1114
4	127	4	23.6	10.4	1016	1242	10	1115
5	128	1	79.6	66.9	1254	1254	100	1111
6	128	2	78.9	70.7	1254	1254	100	1113
7	128	3	82.6	66.5	1254	1254	100	1116
8	128	4	84.3	65.6	1254	1254	100	1107
9	129	1	3.2	≤0.1	Non-Detect	blank	0	1106
10	129	2	3.0	≤0.1	Non-Detect	blank	0	1109
11	129	3	2.7	≤0.1	Non-Detect	blank	0	1108
12	129	4	2.6	≤0.1	Non-Detect	blank	0	1110
13	227	1	18.8	9.2	1016	1242	10	2105
14	227	2	20.5	10.7	1016	1242	10	2108
15	227	3	21.4	8.9	1016	1242	10	2111
16	227	4	19.3	9.7	1016	1242	10	2112
17	228	1	127.8	72.8	1254	1254	100	2113
18	228	2	97.0	62.0	1254	1254	100	2115
19	228	3	83.9	63.8	1254	1254	100	2109
20	228	4	91.3	62.2	1254	1254	100	2114
21	229	1	1.8	≤0.1	Non-Detect	blank	0	2106
22	229	2	1.9	≤0.1	Non-Detect	blank	0	2116
23	229	3	2.0	≤0.1	Non-Detect	blank	0	2107
24	229	4	1.3	≤0.1	Non-Detect	blank	0	2110

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

Table D-3. Corrected reference laboratory data

Error	Sample ID	Reported Result (ppm)	Corrected Result (ppm)
Transcription	106	≤490	255.9
	130	5.6	10.3
	205	32,000	3,305.0
	207	180	17.8
	210	160	123.2
Calculation	118	3.6	2.1
	119	4.3	17.4
	209	2.3	37.9
	214	43.0	26.0
	219	29.0	22.4
Interpretation	101[a]	≤0.7	0.5
	101[a]	≤0.7	0.6
	107	≤1.3	1.2
	109	18.0	1.5
	113[b]	≤0.9	0.6
	113[b]	≤1.0	0.7
	119	18.0	21.2
	127	7.2	10.9
	201	≤ 1.0	0.6
	219	21.0	26.0

[a] Two of four measurements in sample ID 101 were corrected.
[b] Two of four measurements in sample ID 113 were corrected.

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 which 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 Dexsil's L2000 PCB/Chloride Analyzer 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 average PCB concentration < than action level, then send the soil drum to the landfill.

If average PCB concentration action level, then send the soil drum to the incinerator.

DQO Goals

EPA's *Guidance for Data Quality Assessment* [14] states 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 landfill (i.e., the false positive error rate for the decision) could not be more than 5%. Therefore, a 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 sending a drum containing 50 ppm or more of PCBs to the landfill.

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 made when it is concluded that a drum is “hot” (i.e., the null hypothesis is not rejected), when in actuality, 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] for developing limits on decision errors, the team selected the false negative decision error rate (FN) to be 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 was 40 ppm.

Permissible FP and FN Error Rates and Critical Decision Points

FP: Pr[Take Drum to Landfill] $\leq$ 0.05 when true PCB concentration = 50 ppm

FN: Pr[Take Drum to Incinerator] $\leq$ 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 produce data of sufficient quality to support the site decision. Because the DQO team is considering the use of the L2000 PCB/Chloride Analyzer, the performance of this technology (as reported in this ETV report) was used to assess its applicability to this project. Two questions arise:

1. *How many samples are needed* from a single drum to permit a valid estimation of the true average concentration of PCBs in the drum to the specified certainty? Recall that the simplifying 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 variability, then, to be considered in this example is the variability in the L2000’s analytical method, which is determined by precision studies.

2 *What is the appropriate action level (AL)* for using the Dexsil L2000 to make decisions in the field? After the required number of samples have been collected from a drum and analyzed, the results are averaged together to get an estimate of the “true” PCB concentration of the drum. When using the L2000, what is the value (here called “the action level for the decision rule”) to which that average is compared to decide if 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 quality control regimen.

L2000 PCB/Chloride Analyzer Accuracy

The ETV demonstration results indicated that the PCB concentrations determined by the L2000 were biased high when compared with reference concentration values. However, the L2000 data had a strong linear correlation ($R^2 = 0.95$) with the certified values for the performance evaluation samples. This correlation is represented by a line fitted to the data that predicts the expected PCB concentration from the certified PE value. Figure E-1 shows this linear relationship with the L2000's average PCB concentrations plotted against the certified PCB values for the PE samples, which were in the concentration range of 0 to 50 ppm. The arrows on the plot in Figure E-1 demonstrate a method to quickly estimate a corrected PCB concentration from a L2000 PCB measurement. The equation for the PCB prediction line is

L2000 result = 4.33 + 1.41 × (*Certified PE value*) *(E-1)*

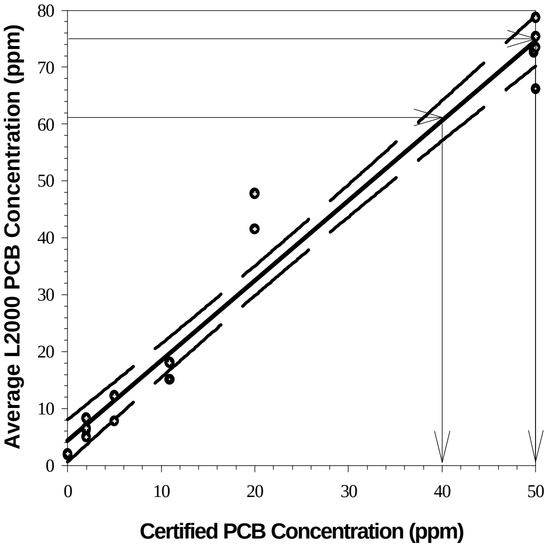

Figure E-1. A linear model for predicting L2000 PCB concentrations from certified PCB concentrations with 95% confidence intervals (dashed lines).

Both Figure E-1 and the equation of the PCB prediction line (E-1) can be used to correct an L2000 result for bias. As shown in Figure E-1, an L2000 result (i.e., the *y*-axis) can be projected over to the prediction line. Then, a perpendicular line can be dropped to the certified PCB concentration axis (i.e., the *x*-axis). Two examples are illustrated by the arrows drawn on Figure E-1. The first arrow projects an L2000 result of 61 ppm to the certified PCB concentration of 40 ppm, and the second arrow projects an L2000 result of 75 ppm to the certified PCB concentration of 50 ppm.

Compensation for bias may also be performed mathematically, by solving the linear PCB prediction line (Eq. E-1) for the certified PE value (a "true" unbiased result). The resulting equation is Equation E-2:

Corrected result = (*L2000 result* − 4.33) ÷ 1.41 *(E-2)*

For example, if the L2000 Result = 61 ppm the corrected result would be:

Corrected result = (61.0 - 4.33) ÷ 1.41 = 40.2 ppm.

The DQO team discussed the two options available to them to deal with the bias in the L2000 results. One option was to use the L2000 results as they were and accept the positive bias inherent in the L2000 results as a conservative margin of safety. The other option was to compensate for the positive bias. If the DQO team decided to correct for the bias, compensation could be performed by the graphical method discussed above, where a result of 61 ppm obtained by the L2000 corresponds to a corrected result estimated to be 40 ppm.

Based on their site-specific circumstances, the team decided to compensate for the bias. They would design an appropriate quality control regimen, which became part of the Sampling and Analysis Plan, to use with the L2000 during their site work. This quality control program would enable them to adequately document the site-specific performance of the L2000, and to prepare site-specific performance graphs (which would resemble

Figure E-1), from which they would produce verifiable and defensible site-specific unbiased data. Since unbiased data would be produced, the critical decision points of 40 ppm and 50 ppm (which correspond to C_{FN} and RT in Eq. E-3 below) were selected for use with the L2000 in calculating the sample size and action level to meet the project's DQO goals.

Determining the Number of Samples

With the critical decision points selected, the team could then determine the number of samples needed from each drum to calculate the drum's "true" average PCB concentration. For a homogeneous matrix, the number of samples required depends on the precision of the analytical method.

The L2000's results from the ETV demonstration established that the standard deviation for PE samples was approximately 6.2 ppm within the concentration range of 20 to 50 ppm (see Figure E-2). This estimate of analytical variability (precision) is used to calculate the number of soil samples required to be analyzed from each drum to achieve the DQOs for the project. A formula provided in EPA's *Guidance for Data Quality Assessment* [14] (pp. 3.2-3, Box 3.2-1) can be adapted to this example for calculating the number of samples required to meet the FN and the FP requirements:

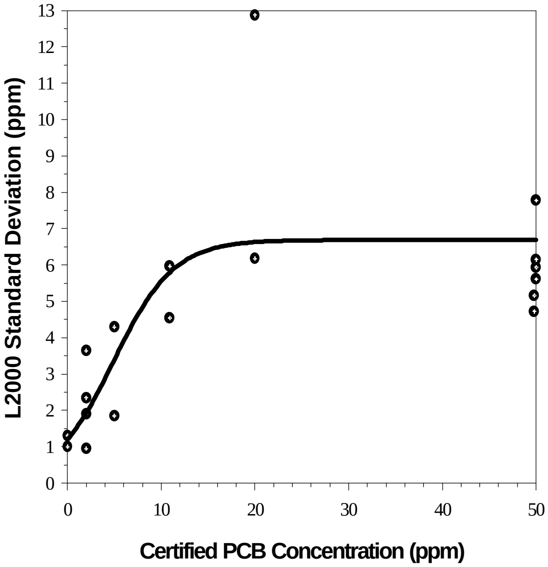

Figure E-2. L2000 standard deviations versus certified PCB concentrations.

$$n = \frac{(SD)^2 \; (\, Z_{1-FP} \; + \; Z_{1-FN} \,)^2}{(RT \; - \; C_{FN})^2} \; + \; (0.5) Z^2_{1-FP} \qquad (E\text{-}3)$$

where

n = number of samples from a drum to be measured,

$(SD)^2$ = variance for the measurement [e.g., $(SD)^2 = (6.2)^2$],

RT = regulatory threshold (e.g., RT = 50 ppm),

C_{FN} = concentration at which the FN is specified (e.g., C_{FN} = 40 ppm),

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 [14], Table A-1 of Appendix A). Example: $Z_{(1-FP)} = Z_{0.95} = 1.645$.

Incorporating the appropriate values for the L2000 into Equation E-3 gives

$$n = \frac{(6.2)^2 \; (1.645 + 1.282)^2}{(50-40)^2} + (0.5)(1.645)^2 = 4.65 \qquad 5 \quad .$$

Therefore, five samples from each drum would be analyzed by Dexsil's L2000 PCB/Chloride Analyzer to meet the criteria established by the DQO process. Note that, to be conservative, the sample size was rounded up to the next integer. These five samples are averaged (by taking the arithmetic mean) to produce an L2000 value for a drum's PCB concentration. As discussed earlier, this L2000 value can then be converted to a corrected average drum concentration by using a graph such as Figure E-1 or an equation for the PCB prediction line (such as Eq. E-2).

Determining the Action Level

Now that the number of samples that need to be analyzed from each drum to meet the DQO goals has been determined, the action level (AL) can be calculated. The action level is the decision criterion (or cutoff value) that will be compared to the unbiased average PCB concentration determined for each drum. The AL for the decision rule is calculated on the basis of regulation-driven requirements (the TSCA regulatory threshold of 50 ppm), and on controlling the FP established in the DQO process. Recall that the team set the permissible FP error rate at 5%.

The formula [14] to compute the AL is

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

Computing the AL in this instance we find the following:

$$AL = 50\,ppm - (1.645) \times \frac{6.2}{\sqrt{5}} = 45.4\,ppm \quad .$$

To summarize, five random samples from each drum are analyzed, and the biased results are corrected. The five corrected results are averaged to produce the average PCB concentration for the drum, which is then compared to the AL for the decision rule (45.4 ppm). Therefore, the decision rule using Dexsil's L2000 PCB/Chloride Analyzer to satisfy a 5% FP and a 10% FN (after correcting the L2000 results for bias) is as follows:

Decision Rule for 5% FP and 10% FN

If the corrected average PCB concentration of 5 random soil samples on a drum < 45.4 ppm, then send the drum to the landfill.

If the corrected average PCB concentration of 5 random soil samples on a drum 45.4 ppm, then send the drum to the incinerator.

The decision performance curve (see EPA QC/G9, pp. 34–36) calculates the probability of sending a drum to the incinerator for different values of true PCB concentration in a drum. Figure E-3 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] = 0.03 for True = 40 ppm, which is better (at 3%) than the FN of 10% that the DQO team had originally 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.

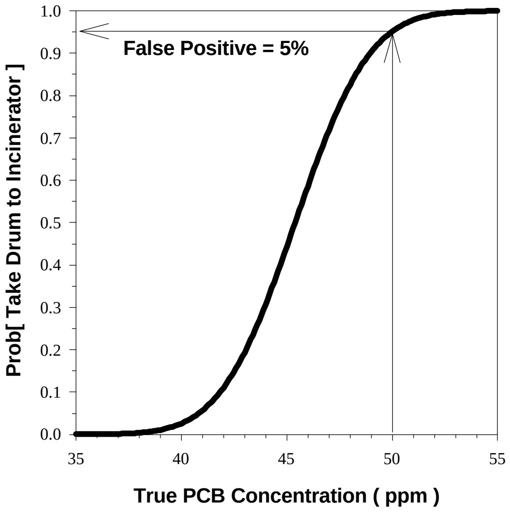

Figure E-3. Decision performance curve for PCB drum example.

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 8 and the action level is calculated to be 44.9 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 the DQO team'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 as shown below.

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

If the corrected average PCB concentration of 8 random soil samples on a drum < 44.9 ppm, then send the drum to the landfill.

If the corrected average PCB concentration of 8 random soil samples on a drum 44.9 ppm, then send the drum to the incinerator.