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Environmental Technology Verification Report

PCB Detection Technology

Hybrizyme
DELFIA™ PCB Assay

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THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

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Joint Verification Statement

TECHNOLOGY TYPE:	**IMMUNOASSAY**	
APPLICATION:	**MEASUREMENT OF PCBs IN CONTAMINATED SOIL AND SOLVENT EXTRACTS**	
TECHNOLOGY NAME:	**DELFIA™ PCB Assay**	
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The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification Program (ETV) to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations and stakeholder groups consisting of regulators, buyers, and vendor organizations, with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

Oak Ridge National Laboratory (ORNL) is one of the verification organizations operating under the Site Characterization and Monitoring Technologies (SCMT) program. SCMT, which is administered by EPA's National Exposure Research Laboratory, is one of six technology centers under ETV. In this verification test, ORNL evaluated the performance of polychlorinated biphenyl (PCB) detection technologies. This verification statement provides a summary of the test results for Hybrizyme's DELFIA™ PCB Assay.

VERIFICATION TEST DESCRIPTION

This verification test was designed to evaluate technologies that detect and measure PCBs in soil and solvent extracts. The test was conducted at ORNL in Oak Ridge, Tennessee, from August 21 through 24, 2000. Spiked samples of known concentration were used to assess the accuracy of the technology. Environmentally contaminated soil samples collected from U.S. Department of Energy sites in Ohio, Kentucky, and Tennessee and ranging in concentration from 0 to approximately 700 parts per million (ppm) were used to assess several performance characteristics. Tests were 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. Solutions of PCBs were also analyzed to simulate extracted surface wipe samples. The extracts were not analyzed by the reference laboratory. The results of the soil analyses conducted by the technology were compared with results from analyses of homogeneous replicate samples conducted by conventional EPA SW-846 methodology in a reference laboratory. Details of the test, including a data summary and discussion of results, may be found in the report entitled *Environmental Technology Verification Report: PCB Detection Technology—Hybrizyme, DELFIA™ PCB Assay,* EPA/600/R-01/052.

TECHNOLOGY DESCRIPTION

The DELFIA PCB Assay is a solid-phase time-resolved fluoroimmunoassay based on the sequential addition of sample extract and europium-labeled PCB tracer to a monoclonal antibody reagent specific for PCBs. In this assay, the antibody reagent and sample extract are added to a strip of microtiter plate wells and allowed to react. The strips have been specially treated to trap the antibody reagent or antibody-PCB complexes that may have formed. A wash step removes sample matrix from the captured antibody. This step significantly reduces any potential matrix interferences before the addition of the PCB tracer, resulting in an unusually robust assay system. The PCB tracer is then added and allowed to bind to the antibodies that are not complexed with sample PCBs. A wash step is used to separate antibody-bound tracer from the tracer free in solution. The addition of an enhancement solution forms highly fluorescent chelates with the bound europium ions. The amount of fluorescence measured is inversely proportional to the concentration of PCBs in the sample. The lowest reporting level is typically 0.5 ppm.

VERIFICATION OF PERFORMANCE

The following performance characteristics of the DELFIA PCB Assay were observed:

Precision: The mean relative standard deviations (RSDs) for the soil and extract samples were 20% and 15%, respectively, indicating that the analyses for both matrices were precise.

Accuracy: Accuracy was assessed using the nominal concentrations of the spiked soils. The percentages of recovery were significantly different for data generated under the outdoor and the chamber conditions. The results were biased slightly high under the outdoor conditions (mean % recovery = 124%), and biased slightly low under the chamber conditions (mean % recovery = 72%). Additional testing of the data demonstrated that the results generated under the outdoor and the chamber conditions were statistically different, indicating that the DELFIA PCB Assay performed differently under different environmental conditions. For the extracts, all samples were biased high, with larger bias observed under the outdoor conditions.

False positive/false negative results: No false positives were reported for the soil and extract blanks. In addition, false positive and false negative results were determined by comparing the DELFIA PCB Assay result to the reference laboratory result for the environmental and the spiked samples. None of the results were reported as false positives, but 2% (4 of 192 samples) were false negatives relative to the reference laboratory.

Completeness: The DELFIA PCB Assay generated results for all 208 soil samples and 24 extract samples, for a completeness of 100%.

Comparability: A one-to-one sample comparison of the DELFIA PCB Assay results and the reference laboratory results was performed for all samples (spiked and environmental) that were reported as detections. The correlation coefficient (r) for the comparison of the entire soil data set was 0.50 [slope (m) = 0.20]. If six justifiably suspect values are excluded from the data set, the r value improves to 0.89, with a slope of 0.78. As stated in the Accuracy section, the DELFIA PCB Assay's performance was different under the outdoor and the chamber conditions. When the performance of the field technology is compared with the results from the reference laboratory (rather than with the nominal concentrations, as was used in the accuracy assessment), there is no statistical difference between the data sets generated outdoors and in the chamber. The comparison with the reference laboratory results did not show statistical differences because of the uncertainty (i.e., variability) in the two data sets.

Sample Throughput: Operating both in the field and in the chamber, the Hybrizyme team accomplished a sample throughput rate of approximately six samples per hour for the soil and extract analyses. Two operators were used for the PCB analyses, but the technology can be run by a single trained operator.

Regulatory Decision-Making: One objective of this verification test was to assess the technology's ability to perform at regulatory decision-making levels for PCBs—specifically, 50 ppm for soils, including both performance evaluation and environmental samples. The performance of the DELFIA PCB Assay for this concentration range was precise (mean RSD = 14%), unbiased (mean % recovery = 94%), and comparable to the reference laboratory (mean % difference = 27%).

Overall Evaluation: The verification team found that the DELFIA PCB Assay was relatively simple for the trained analyst to operate in the field, requiring less than an hour for initial setup. The overall performance of the DELFIA PCB Assay for the analysis of PCBs in soil and extract samples was characterized as biased (dependent on environmental conditions) but precise. 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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Environmental Technology Verification Report

PCB Detection Technology

Hybrizyme DELFIA™ PCB Assay

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Notice

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Abbreviations and Acronyms

AL	action level
BHC	benzenehexachloride
DOE	U.S. Department of Energy
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
ERA	Environmental Resource Associates
ETTP	East Tennessee Technology Park
ETV	Environmental Technology Verification (Program, EPA)
FA	false acceptance decision error rate
fn	false negative result
fp	false positive result
FR	false rejection decision error rate
HEPA	high-efficiency particulate air
ID	inner diameter
N	number of samples
NERL	National Exposure Research Laboratory (EPA)
ORD	Office of Research and Development (EPA)
ORNL	Oak Ridge National Laboratory
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
RH	relative humidity
RSD	relative standard deviation (percentage)
RT	regulatory threshold
SCMT	Site Characterization and Monitoring Technologies
SD	standard deviation
SSM	synthetic soil matrix
TSCA	Toxic Substances Control Act
%D	percent difference

Section 1 — Introduction

The U.S. Environmental Protection Agency (EPA) created the Environmental Technology Verification Program (ETV) to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

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ETV is a voluntary program that seeks to provide objective performance information to all of the participants in the environmental marketplace and to assist them in making informed technology decisions. ETV does not rank technologies or compare their performance, label or list technologies as acceptable or unacceptable, seek to determine "best available technology," or approve or disapprove technologies. The program does not evaluate technologies at the bench or pilot scale and does not conduct or support research. Rather, it conducts and reports on testing designed to describe the performance of technologies under a range of environmental conditions and matrices.

The program now operates six centers covering a broad range of environmental areas. ETV began with a 5-year pilot phase (1995–2000) to test a wide range of partner and procedural alternatives in various technology areas, as well as the true market demand for and response to such a program. In these centers, EPA utilizes the expertise of partner "verification organizations" to design efficient processes for conducting performance tests of innovative technologies. These expert partners are both public and private organizations, including federal laboratories, states, industry consortia, and private sector entities. Verification organizations oversee and report verification activities based on testing and QA protocols developed with input from all major stakeholder/customer groups associated with the technology area. The verification described in this report was administered by the Site Characterization and Monitoring Technologies (SCMT) Center, with Oak Ridge National Laboratory (ORNL) serving as the verification organization. (To learn more about ETV, visit ETV's Web site at http://www.epa.gov/etv.) The SCMT Center is administered by EPA's National Exposure Research Laboratory (NERL), Environmental Sciences Division, in Las Vegas, Nevada.

The verification of a field analytical technology for polychlorinated biphenyls (PCBs) detection is described in this report. The verification test was conducted at ORNL in Oak Ridge, Tennessee, from August 21 through August 24, 2000. The performance of Hybrizyme's DELFIA™ PCB Assay was determined under both field and controlled atmosphere (i.e., chamber) conditions. The technology was evaluated by comparing its results with those obtained using an approved reference method, EPA SW-846 Method 8081. The verification was designed to evaluate the field technology's ability to detect and measure PCBs in soil and solvent extracts.

Section 2 — Technology Description

In this section, the vendor (with minimal editorial changes by ORNL) provides a description of the technology and the analytical procedure used during the verification testing activities.

Principle of the Assay

The Hybrizyme DELFIA PCB immunoassay system has been designed for the quantitative or qualitative detection of PCBs in sample extracts. The DELFIA technology is based on time-resolved fluorometry of lanthanide compounds, such as europium. Lanthanide ions exhibit a unique fluorescence that is characterized by narrow band emission lines, long decay times, and large Stoke's shifts. The specific fluorescence of the lanthanide label is measured after a certain time delay following an activation pulse. The delay eliminates essentially all of the nonspecific background, resulting in an ultra-sensitive assay system. Hybrizyme's DELFIA products incorporate many components and instrumentation manufactured by Perkin Elmer® that are used in hospitals worldwide for clinical analysis.

The DELFIA PCB assay is a solid-phase time-resolved fluoroimmunoassay based on the sequential addition of sample extract and europium-labeled PCB tracer to a monoclonal antibody reagent specific for PCBs. In this assay, the antibody reagent and sample extract are added to a strip of microtiter plate wells and allowed to react. The strips have been specially treated to trap the antibody reagent or antibody-PCB complexes that may have formed. A wash step removes the remaining sample from the captured antibody. This step significantly reduces any potential matrix interferences prior to the addition of the PCB tracer, resulting in an unusually robust assay system. The PCB tracer is then added and allowed to bind to the antibodies that are not complexed with sample PCBs. Another wash step is used to separate antibody-bound tracer from the tracer free in solution. The addition of an enhancement solution forms highly fluorescent chelates with the bound europium ions. The amount of fluorescence measured is inversely proportional to the concentration of PCBs in the sample.

Calculation of Results

The DELFIA PCB assay system was developed for use in fixed or mobile laboratories for high-throughput PCB analysis. Normal batch sizes range from 5 to 20 samples per run. Results are generated from stored calibration curves, eliminating the need to run calibrators with each assay. For characterized sites, the data-reduction package automatically generates a spreadsheet of results for Aroclors 1260, 1254, 1248, and 1242. The user can easily add custom calibration curves for any mixture of PCB congener to the instrumentation at any time. For uncharacterized sites, the cross-reactivity of the DELFIA PCB assay to various Aroclors can be used to develop qualitative screening strategies.

Sensitivity and Quality Control

Hybrizyme reports that the immunoassay can detect <100 parts per billion (ppb) PCBs in methanol. The sensitivity of the assay can be adjusted to higher detection levels by altering sample dilution protocols. Values that lie outside the detection range of the assay are automatically flagged as low or high. Results are calculated from the duplicate analysis of each extract. If the values between the duplicates are outside the acceptable range of variation, the result will automatically be flagged for review. A PCB standard is available from Hybrizyme for verification purposes. The ability of the assay to detect various Aroclors is shown in Table 1. If the Aroclor is known, the sample results can be adjusted based on cross-reactively.

Test Kit Components

Each Hybrizyme DELFIA PCB Test Kit (see Table 2) contains reagents for testing a maximum of 40 samples in duplicate. The reagents must be stored

Table 1. Summary of DELFIA PCB Assay's Cross-Reactivity [a]

Aroclor	% Reactivity
1262	110
1260	130
1254	160
1248	100
1242	40
1016	25
1232	20

[a] Cross-reactivity represents the amount of response to the various Aroclors.

Table 2. Test Kit Components

Component	Description	Quantity
Europium-labeled PCB tracer	The tracer is lyophilized in a Tris-buffered salt solution with bovine serum albumin, glycine, and <0.1 % sodium azide. It is reconstituted with 0.6 mL of deionized water and should be used within 2 weeks after reconstitution	1 vial
PCB monoclonal antibody	The antibody is in a Tris-buffered salt solution with casein and <0.1 % sodium azide	1 vial (0.6 mL)
Wash concentrate	A 25-fold concentration of Tris-buffered (pH 7.8) salt solution with Tween 20 and <0.1 % sodium azide. It is prepared for use by mixing entire contents with 960 mL of deionized water and placing in platewasher WASH bottle	1 bottle (40 mL)
Assay buffer	Ready-to-use Tris-buffered (pH 7.8) salt solution with casein and <0.1 % sodium azide	1 bottle (50 mL)
Enhancement solution	Ready-to-use reagent with Triton X-100, acetic acid, and chelators	1 bottle (50 mL)
Microtitration strips	Unused strips must be kept sealed and in the plastic tray	1 plate (8 × 12 wells)

between 2°C and 8°C when not in use. The expiration date of an unopened test kit is stated on the outer label. All analyses must be conducted within 2 weeks of tracer reconstitution.

Soil Sample Processing

The following is an example of the extraction procedure if the user is interested in a 1-ppm PCB detection level; this is the procedure that was used in the verification test.

1. Place 5.0 g of soil sample in a 40-mL glass vial.
2. Add 25 mL of methanol.
3. Cap vial and vortex (or shake) for 3 min.
4. Remove vial from vortex and allow soil to settle for 10 min.
5. Transfer a 4-µL aliquot of the extract to the PCB test.

The detection level of the test can be varied by changing the amount of soil, the volume of methanol, and the volume of extract added to the PCB test. The lowest reported concentration in the verification test was 0.5 ppm.

Quantitative Assay Procedure

The quantitative detection of PCBs in sample extracts is performed by comparing the test response of sample extracts to the test response of a control.

Research-grade methanol is used as the control. Each determination is performed in duplicate for the both the control and samples. All sample extracts must be in methanol for analysis. All reagents and samples must be brought to room temperature prior to use.

1. Prepare the PCB tracer solution by diluting 50 µL of PCB tracer stock solution in 1.5 mL of PCB assay buffer for each strip of wells used. For example, if three strips of wells will be used, dilute 150 µL of tracer stock solution into 4.5 mL of PCB assay buffer. Use within one hour of preparation.
2. Prepare the PCB antibody solution by diluting 50 µL of PCB antibody stock solution in 1.5 mL of PCB assay buffer per strip of wells used. Use within one hour of preparation.
3. Place the required number of microtitration strips in a strip frame. Wash the strips using the "PREWASH" program of the plate washer. Tap the strips upside-down gently on a paper towel to blot away any excess wash solution that may remain in the wells.
4. Pipet 100 µL of the diluted PCB antibody solution into each well.
5. Pipet 4 µL of each control or sample into a well using the sequence shown in Table 3. It is recommended that columns 1 and 2 on each strip of wells be used for controls.

Table 3. Recommended Sequence for Well Use

Row	Well											
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
A	Control	Control	1st Unk	1st Unk	2nd Unk	2nd Unk	3rd Unk	3rd Unk	4th Unk	4th Unk	5th Unk	5th Unk
B	Control	Control	6th Unk	6th Unk	7th Unk	7th Unk	Etc.[a]					

Unk = unknown sample

[a] The plate is a 12 by 8 well configuration. Each of the 8 rows holds one strip that can contain two controls and five samples run in duplicate. The user can run one to eight strips at a time, for a maximum of 40 samples.

6. Shake the wells for 15 min using an automated shaker.
7. Wash the strips using the "3 WASHES" program on the plate washer. Tap the strips upside-down gently on a paper towel to blot away any excess wash solution that may remain in the wells.
8. Pipet 100 µL of the diluted PCB tracer solution into each well.
9. Shake the wells for 5 min.
10. Repeat step 8.
11. Add 150 µL of enhancement solution to each well.
12. Select "PCB Quant" from the list of protocols in the time-resolved fluorometer and measure the fluorescence in each well. The protocol will automatically shake the wells for 1 min and calculate the concentration of PCB in the extracts. The amount of PCB in the sample must be correlated using the sample processing concentration factor or dilution factor.

A summary protocol sheet is presented in Table 4.

Table 4. Summary Protocol Sheet

Task		Action
1	Prepare PCB tracer solution	50 µL tracer per 1.5 mL assay buffer per microtitration strip
2	Prepare PCB antibody solution	50 µL antibody per 1.5 mL assay buffer per microtitration strip
3	Prewash strips	"PREWASH" program
4	Add antibody solution	100 µL
5	Add control and samples	4 µL
6	Incubate	Shake for 15 min
7	Wash	"3 WASHES" program
8	Add tracer solution	100 µL
9	Incubate	Shake for 5 min
10	Wash	"3 WASHES" program
11	Enhance	150 µL
12	Incubate and count	Use a "PCB Quant" protocol to shake for 2 min and measure fluorescence

Section 3 — Verification Test Design

Objective

The purpose of this section is to describe the verification test design. It is a summary of the test plan (ORNL 2000).

Testing Location and Conditions

The verification of field analytical technologies for PCBs was conducted at ORNL's Building 5507, in Oak Ridge, Tennessee. Testing activities occurred at two sites: a natural outdoor environment (the outdoor site) and inside a controlled environmental atmosphere chamber (the chamber site). The temperature and relative humidity (RH) were monitored during testing. Over the two days of outdoor testing, the average temperature was 86ºF and ranged from 63 to 98ºF. The average relative humidity was 50% and ranged from 27 to 85%.

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. 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. During the two days of testing in the controlled atmosphere, the chamber conditions were set to 55°F and 50% RH and were maintained at those conditions with little variation.

What Are PCBs?

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 (Erickson 1997). 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%).

Soil Sample Descriptions

The samples used in this study were shipped to the testing location for evaluation by the vendor. PCB-contaminated soils from Kentucky, Ohio, and Tennessee were used in this verification. Because samples were obtained from multiple U.S. Department of Energy (DOE) sites, the samples represented a reasonable cross section of the population of PCB-contaminated matrices, such that the versatility of the field technology could be evaluated. 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 verification test. More specific details about the samples are presented below.

Sources of Samples

Oak Ridge, Tennessee

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 National Security Complex (formerly known as the Oak Ridge Y-12 Plant), and East Tennessee Technology Park (ETTP). Chemical processing and warhead component production have occurred at Y-12, 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. Excavation activities occurred between 1991 and 1995. The Oak Ridge samples were composed 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). The PCB concentrations in these samples ranged from approximately 0.5 to 300 ppm.

Portsmouth, Ohio

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. The PCB concentrations in these samples ranged from approximately 1 to 700 ppm.

Paducah, Kentucky

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. The PCB concentrations in these samples ranged from approximately 1 to 500 ppm.

Performance Evaluation Samples

Samples of Tennessee reference soil (Maskarinec 1992) served as the blanks. Preprepared certified performance evaluation (PE) samples were obtained from Environmental Resource Associates (ERA) of Arvada, Colorado, and from 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 EPA samples were also spiked with target pesticides [benzenehexachloride (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 vendor and reference laboratory analyses as received. The PCB concentrations in PE soils ranged from 2 to 50 ppm.

Soil 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. 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 and then poured into a plastic-lined 5-gal container. All samples were subjected to radiological screening and were determined to be nonradioactive. Soil samples were collected from 55-gal drums stored at Paducah in a similar fashion and were shipped to ORNL in lined 5-gal containers.

Soil Sample Preparation

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 10-mesh screen (2-mm particle size). Last, the soil was thoroughly mixed with a spatula. A comparison of dried and undried soils showed that a minimal amount of PCBs (<20%) was lost during sample drying, making this procedure suitable for use in the preparation of the soil

samples. The Paducah samples, because of their sandy characteristics, required only the sieving and mixing preparation steps.

To provide the vendors with soils contaminated at higher PCB concentrations, some of the environmental soils were spiked with additional PCBs. Spiked soil 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 10-mesh screen (2-mm particle size). Approximately 1500 g of the sieved soil was 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 verification test. Soil sample homogeneity was confirmed by extracting 3–5 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 EPA's SW-846 dual-column Method 8081 (EPA 1994).

Extract Sample Description

Extract samples were prepared by making solutions of PCBs in methanol at two concentration levels (10 and 100 μg/mL). Aroclor 1242 was used to prepare the 10-μg/mL samples, and Aroclor 1254 was used for the 100-μg/mL samples. Multiple aliquots of each sample were analyzed using the Method 8081 to confirm the accurate preparation of the samples with respect to PCB concentration.

Sample Randomization

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 vendor. The samples were randomized in two stages. First, the order in which the filled jars were distributed was randomized so that the same vendor did not always receive the first jar filled for a given sample set. Second, the order of analysis was randomized so that each participant analyzed the same set of samples, but in a different order. Each jar was labeled with a sample number. Replicate samples were assigned unique (but not sequential) sample numbers. Spiked materials and blanks were labeled in the same manner, such that these quality control (QC) samples were indistinguishable from other samples. All samples were analyzed blindly by both the vendor and the reference laboratory.

Summary of Experimental Design

The distribution of samples from the various sites is shown in Table 5. A total of 208 soil samples were analyzed, with approximately 70% of the samples

Table 5. Summary of PCB Verification Test Design

Sample source	Number of samples	
	Outdoor site	Chamber site
Oak Ridge soil	48	0
Portsmouth soil	0	48
Paducah soil	20	20
Spiked soil	32	32
Blank soil	4	4
Spiked extract	8	8
Blank extract	4	4
Total	116	116

being naturally contaminated environmental soils and the remaining 30% being spikes and blanks. Twenty-four extract samples were also analyzed, for a grand total of 232 samples in the verification test, with 116 samples analyzed at each of the two sites. Four replicates were analyzed for each sample type. For example, 48 samples were analyzed from the Oak Ridge site, indicating that 12 different original samples were used in the study. As Table 5 indicates, the Paducah, PE, and extract samples were analyzed at both the outdoor and chamber sites so that performance under different environmental conditions could be evaluated. Table 6 contains a characterization summary of the environmental samples.

Description of Performance Factors

In Section 5, technology performance is described in terms of precision, accuracy, completeness, and comparability, which are indicators of data quality (EPA 1996). False positive and negative results, sample throughput, and ease of use are also described. Each of these performance characteristics is defined in this section.

Precision

Precision is the reproducibility of measurements under a given set of conditions. Standard deviation (SD) and relative standard deviation (RSD) for replicate results are used to assess precision, using the following equation:

$$RSD = (SD/\text{average concentration}) \times 100\% \quad . \qquad \text{(Eq. 1)}$$

The overall RSD is characterized by three summary values:

- 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
- range — i.e., the highest and lowest RSD values that were reported.

The average RSD may not be the best representation of precision, but it is reported for convenient reference. RSDs greater than 100% should be viewed as indicators of large variability and possibly non-normal distributions.

Accuracy

Accuracy represents the closeness of the technology's measured concentrations to known (in this case, PE) values. Accuracy is assessed in terms of percent recovery, calculated by the following equation:

$$\%\ recovery = (\text{measured concentration}/\text{known concentration}) \times 100\% \quad . \qquad \text{(Eq. 2)}$$

As with precision, the overall percentage of recovery is characterized by three summary values: mean, median, and range.

False Positive/False Negative Results

A false positive (fp) result is one in which the technology detects PCBs in the sample when there actually are none (Berger, McCarty, and Smith 1996). A false negative (fn) result is one in which the technology indicates that no PCBs are present in the sample when there actually are (Berger, McCarty, and Smith 1996). The evaluation of fp and fn results is influenced by the actual concentration in the sample and includes an assessment of the reporting limits of the technology.

False positive results are assessed in two ways. First, the results are assessed relative to the blanks (i.e., the technology reports a detected value when the sample is a blank). Second, the results are assessed on environmental and spiked samples where the analyte was not detected by the reference laboratory (i.e., the reference laboratory reports a

Table 6. Range of Characterization Values by Sample Source

Sample source	Composition (%)			Total organic carbon (mg/kg)	pH
	Gravel	Sand	Silt + clay		
Oak Ridge	0–2.3	85.6–99.3	0.2–14.4	5,384–38,907	7.1–7.7
Paducah	0–0.4	83.6–93.7	5.8–16.3	1,296–6,097	7.4–7.7
Portsmouth	0–1.3	65.8–87.1	12.9–34.2	1,328–10,687	7.6–7.9

nondetect and the field technology reports a detection).

False negative results, also assessed for environmental and spiked samples, indicate the frequency with which the technology reported a nondetect (i.e., less than reporting limits) and the reference laboratory reported a detection.

The reference laboratory results were validated by ORNL so that fp/fn assessment would not be influenced by faulty laboratory data. The reporting limit is considered in the evaluation. For example, if the reference laboratory reported a result as 0.9 ppm, and the technology's paired result was reported as below reporting limits (<1 ppm), the technology's result was considered correct and not a false negative result.

Completeness

Completeness is defined as the percentage of measurements that are judged to be usable (i.e., the result is not rejected). The acceptable completeness is 95% or greater.

Comparability

Comparability refers to how well the field technology and reference laboratory data agree. The difference between accuracy and comparability is that accuracy is judged relative to a known value, and comparability is judged relative to the results of a standard or reference procedure, which may or may not report the results accurately. The reference laboratory result is not assumed to be the "correct" result. This evaluation is performed to compare the result from the field analytical technology with what a typical fixed analytical laboratory might report for the same sample. A one-to-one sample comparison of the technology results and the reference laboratory results is performed in Section 5.

A correlation coefficient quantifies the linear relationship between two measurements (Draper and Smith 1981). The correlation coefficient, denoted by the letter *r*, ranges in value from –1 to +1, where 0 indicates the absence of any linear relationship. The value $r = -1$ indicates a perfect negative linear relation (one measurement decreases as the second measurement increases); the value $r = +1$ indicates a perfect positive linear relation (one measurement increases as the second measurement increases).

The slope of the linear regression line, denoted by the letter *m*, is related to *r*. Whereas *r* represents the linear association between the vendor and reference laboratory concentrations, *m* quantifies the amount of change in the vendor's measurements relative to the reference laboratory's measurements. A value of +1 for the slope indicates perfect agreement. (It should be noted that the intercept of the line must be close to zero [i.e., not statistically different from zero], in order for the slope value of +1 to indicate perfect agreement.) Values greater than 1 indicate that the vendor results are generally higher than those of the reference laboratory, while values less than 1 indicate that the vendor results are usually lower than the values from the reference laboratory.

In addition, a direct comparison between the field technology and reference laboratory data is performed by evaluating the percent difference (%D) between the measured concentrations, defined as

$$\%D = ([field\ technology] - [ref\ lab])/(ref\ lab) \times 100\% . \quad \text{(Eq. 3)}$$

The range of %D values is summarized and reported in Section 5.

Sample Throughput

Sample throughput is a measure of the number of samples that can be processed and reported by a technology in a given period of time. This is reported in Section 5 as number of samples per hour or day times the number of analysts.

Applicability to Regulatory Decision-Making

The concentration level of regulatory concern for PCBs is 50 ppm. When the level of contamination is above 50 ppm, the material must be managed according to Toxic Substances Control Act (TSCA) regulations. To address this issue, the performance of the technology for samples that fall in the range of 40 to 60 ppm is independently evaluated. Precision, accuracy, and comparability to the reference laboratory are assessed specifically for this concentration range in Section 5.

Ease of Use

A significant factor in purchasing an instrument or a test kit is how easy the technology is to use. Several factors are evaluated and reported on in Section 5:

- What is the required operator skill level (e.g., technician or advanced degree)?
- How many operators were used during the test? Could the technology be run by a single person?
- How much training would be required in order to run this technology?
- How much subjective decision-making is required?

Cost

Another important factor in the consideration of whether to purchase a technology is cost. Costs involved with operating the technology and the standard reference analyses are estimated in Section 5. To account for the variability in cost data and assumptions, the economic analysis is presented as a list of cost elements and a range of costs for sample analysis. Several factors affect the cost of analysis. Where possible, these factors are addressed so that decision makers can independently complete a site-specific economic analysis to suit their needs.

Miscellaneous Factors

Any other information that might be useful to a person who is considering purchasing the technology is documented in Section 5. Examples of information that might be useful to a prospective purchaser are the amount of hazardous waste generated during the analyses, the ruggedness of the technology, the amount of electrical or battery power necessary to operate the technology, and aspects of the technology or method that make it user-friendly or user-unfriendly.

Section 4 — Reference Laboratory Analyses

Reference Laboratory Selection

The verification process is based on the presence of a statistically validated data set against which the performance of the technology may be compared. The choice of an appropriate reference method and reference laboratory are critical to the success of the verification test. To assess the performance of the PCB field analytical technology, the data obtained from verification test participants were compared with data obtained using conventional analytical methods.

The first evaluation of PCB detection technologies under the ETV program occurred in 1997. LAS Laboratories, of Las Vegas, Nevada, was selected as the reference laboratory for that study. A readiness review conducted by ORNL confirmed the selection of LAS as the reference laboratory. Acceptance of the reference laboratory was finalized by satisfactory performance in a predemonstration study. ORNL contracted LAS to provide full data packages for the verification study sample analyses within 30 days of sample shipment. An on-site audit of LAS occurred August 11–12, 1997, during the analysis of the verification samples. This surveillance focused specifically on the procedures that were currently in use for the analysis of the verification samples. The audit 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.

A sample holding time study performed by ORNL in April 2000 indicated that the concentration of PCBs in the samples had not changed significantly. Therefore, archived soil samples and the reference laboratory data generated in 1997 were used for comparison with the vendor results for the 2000 verification test.

Reference Laboratory Method

The reference laboratory's analytical method, presented in the technology test plan, followed the guidelines established in EPA SW-846 Method 8081 (EPA 1994). (Note that since the time of the original PCB analyses, Method 8081 was updated to Method 8082 for PCB analyses.) According to LAS procedures, 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 on the basis of the initial calibration of the primary column.

Reference Laboratory Performance

ORNL validated all of the reference laboratory data according to the procedure described in the test plan (ORNL 2000). During the validation, the following aspects of the data were reviewed: completeness of the data package, adherence to holding time requirements, correctness of the data, correlation between replicate sample results, evaluation of QC sample results, and evaluation of spiked sample results. Each of these categories is described in detail in the test plan. 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. Approximately 8% of the data had correctable errors (e.g., transcription, calculation, and interpretation errors). A small portion of the sample results (5%) were considered suspect because the reference laboratory did not report a quantitative result or because the result was significantly different from replicate results. The reference laboratory's performance was evaluated with and without the suspect values to represent, respectively, the worst- and best-case scenarios.

The performance of the reference laboratory was evaluated by statistical analysis of the data. Table 7 provides a summary of the performance of the

Table 7. Summary of the Reference Laboratory Performance

Sample matrix	Sample type	Number of samples	Precision (av % RSD)	Accuracy (av % recovery)
Blank	Soil	8	n/a [a]	All samples were
	Extract	16		reported as nondetects.
Environmental soil	Sample no. 110	4	n/a [a]	All samples were
with interferences	Sample no. 112	4		reported as nondetects.
Soil: best case	PE	63	18	101
(excluding suspect	Environmental			
data)	<125 ppm	107	23	n/a[b]
	>125 ppm	17	19	n/a[b]
	All samples	187	21	101
Soil: worst case	PE	64	21	105
(including suspect	Environmental			
data)	<125 ppm	108	26	n/a[b]
	>125 ppm	20	56	n/a[b]
	All samples	192	28	n/a[b]
Extract	10 ppm of Aroclor 1242	16	19	104
	100 ppm of Aroclor 1254	16	8	64
	All samples	32	14	84

[a] Because the results were reported as nondetects, precision assessment is not applicable.
[b] n/a = not applicable; accuracy assessment calculated for samples of known concentration only.

reference laboratory for the analysis of all sample types used in the technology verification study.

As shown in Table 7, the precision for the PE soils was comparable to that for the environmental soils. A weighted average, based on the number of samples, gave a best-case precision (i.e., excluding suspect values) of 21% and a worst-case precision (i.e., including suspect values) 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 (which ranged from 0 to 50 ppm PCBs) was 101% for the best case (which excluded the suspect value) and 105% for the worst case (which included the suspect value). These results indicate that the reference laboratory results were unbiased estimates of the certified PE concentrations.

The 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 nondetects but had difficulty with two soil samples that contained chemical interferences (Oak Ridge 2, samples 4 and 6, see Appendix A). Overall, it was concluded that the reference laboratory results were acceptable for comparison with the field analytical technology.

Section 5 — Technology Evaluation

Objective and Approach

The purpose of this section is to present a statistical evaluation of the DELFIA PCB Assay data and determine the technology's ability to measure PCBs in contaminated soil and extract samples. This section includes an evaluation of comparability through a one-to-one comparison with the reference laboratory data. Other aspects of the technology (such as cost, sample throughput, hazardous waste generation, and logistical operation) are also evaluated in this section. Appendix A contains the raw data provided by the vendor during the verification test that were used to assess the performance of the DELFIA PCB Assay. During the verification test, Hybrizyme was provided with information as to which Aroclor or Aroclors were present in the sample based on what was reported by the reference laboratory. Hybrizyme used this information to determine the final sample results. In Appendix B, a data quality objective (DQO) example of how the data in this report might be used in a real-world application is presented.

Precision

Precision is the reproducibility of measurements under a given set of conditions. Precision was determined by examining the results of blind analyses for four replicate samples. Data were evaluated only for those samples where all four replicates were reported as a detection. For example, N_R = 43 (43 sets of four replicates) represents a total of 172 individual sample analyses. A summary of the overall precision of the DELFIA PCB Assay for the soil and extract sample results is presented in Table 8. The mean RSDs for the soil and extract samples were comparable at 20% and 15%, respectively. The technology's precision was statistically the same for both outdoor and chamber conditions.

Accuracy

Accuracy represents the closeness of the DELFIA PCB Assay's measured concentrations to the known content of spiked samples. A summary of the assay's overall accuracy for the soil results is presented in Table 9. The percent recoveries were significantly different for data generated under the outdoor and chamber conditions. The results were biased high (mean % recovery = 124%) under the outdoor conditions and biased low (mean % recovery = 72%) under the chamber conditions. Based on the performance acceptance ranges shown in Table 10, which are the guidelines established by the provider of the spiked materials to gauge acceptable analytical results, 78% of the results (25 of 32) met the acceptance criteria under the outdoor conditions, while 88% (28 of 32 of the results) met the criteria under the chamber conditions. The accuracy of the extract samples is shown in Table 11. Most of the extract results were biased high, with larger bias observed under the outdoor conditions.

False Positive/False Negative Results

Table 12 shows the DELFIA PCB Assay performance for false positive results for blank samples. No fp results were reported for the soil and extract samples. Table 13 summarizes the assay's fp and fn results relative to the reference laboratory results. (See Section 3 for a more detailed discussion of this evaluation.) For the environmental

Table 8. Summary of the DELFIA PCB Assay Precision

Statistic	RSD (%)[a]	
	Soil samples (N_R = 43[b])	Extract samples (N_R = 4[b])
Mean	20	15
Median	14	12
Range	3–99	8–26

[a] Calculated only from those samples where all four replicates were reported as a detect.
[b] N_R = number of replicate sets.

Table 9. Summary of the DELFIA PCB Assay Accuracy for Soils

Statistic	% recovery		
	Outdoor conditions (N = 32)	Chamber conditions (N = 32)	All data (N = 64)
Mean	124	72	98
Median	109	68	87
Range of results	81–387	36–188	36–387

Table 10. Number of DELFIA PCB Assay Results within Acceptance Ranges for Spiked Soils

Spike concentration (ppm)	Outdoor conditions		Chamber conditions	
	Acceptance range (ppm)	No. of results within range	Acceptance range (ppm)	No. of results within range
2	0.7–2.2	3 of 4	0.7–2.2	4 of 4
20	11.4–32.4	4 of 4	11.4–32.4	0 of 4
5	2.1–6.2	1 of 4	2.1–6.2	4 of 4
50	19.7–63.0	4 of 4	19.7–63.0	4 of 4
10.9	4.0–12.8	1 of 4	4.0–12.8	4 of 4
50	11.9–75.9	4 of 4	11.9–75.9	4 of 4
2	0.9–2.5	4 of 4	0.9–2.5	4 of 4
49.8	23.0–60.8	4 of 4	23.0–60.8	4 of 4
Total		25 of 32 results		28 of 32 results

Table 11. Summary of DELFIA PCB Assay Accuracy for Extracts

Statistic	% recovery		
	Outdoor conditions (N = 8)	Chamber conditions (N = 8)	All data (N = 16)
Mean	300	145	222
Median	284	153	238
Range of results	267–359	76–208	76–359

Table 12. Summary of DELFIA PCB Assay False Positive Performance on Blank Samples

Statistic	Soil samples	Extract samples
Number of data points	8	8
Number of fp results	0	0
% of fp results	0	0

Table 13. Summary of the DELFIA PCB Assay Detect/ Nondetect Performance Relative to the Reference Laboratory Results for Soil Samples (N = 192)

Statistic	No.	%
False positive (fp) results	0	0
False negative (fn) results	4	2

Note: The reference laboratory did not analyze the extract samples, so fp/fn relative to the reference laboratory results could not be evaluated.

Of 208 samples, this evaluation excludes the 8 blanks and 8 reference laboratory results for which a results could not be generated. (See Section 4 for more information on these suspect samples.) All remaining 192 samples were reported as detects.

and spiked soils, none of the PCB results were reported as false positives relative to the reference laboratory results because the laboratory did not report any of the 192 samples as a nondetect. Four of 192 samples—2% of the results—were false negatives, where the laboratory reported a detection but Hybrizyme reported a nondetect. For those four samples, Hybrizyme reported each as <0.6 ppm, while the reference laboratory reported values between 1.0 and 1.6 ppm. The fp/fn evaluation could not be performed for the extract samples because the reference laboratory did not analyze these samples.

Completeness

Completeness is defined as the percentage of measurements that are judged to be usable (i.e., the result was not rejected). The DELFIA PCB Assay obtained valid results for all 208 soil samples and 24 extract samples. Therefore, completeness was 100%.

Comparability

Comparability refers to how well the DELFIA PCB Assay and reference laboratory data agreed. In this evaluation, the laboratory results are not presumed to be the "correct" answers. Rather, these results represent what a typical fixed laboratory would report for these types of samples. A one-to-one sample comparison of the DELFIA PCB Assay results and the reference laboratory results was performed for all environmental and spiked samples that were reported as a detection (N = 170). (See Appendix A to review the raw data and Section 4 for a complete evaluation of the reference laboratory results.) Table 14 presents the comparability of the results in terms of correlation coefficients (*r*) and slopes (*m*). As shown in Table 14, a few suspect values (two for the reference laboratory and four for Hybrizyme) influence both the correlation coefficient (0.50 vs 0.89) and the slope (0.20 vs 0.78). Figure 1 is a plot of the DELFIA PCB Assay results versus those for the reference laboratory for all results (N = 164), excluding the Hybrizyme and reference laboratory suspect values. As this figure illustrates, Hybrizyme's results generally agreed with those of the reference laboratory.

Another metric of comparability is the percent difference (%D) between the reference laboratory and the DELFIA PCB Assay results (see Section 3). The ranges of %D values for the PCB results are presented in Figure 2. Acceptable %D values would be between –25% and 25%, or near the middle of the *x*-axis of the plots. Approximately 45% of the results are between –25% and 25%.

Comparison of Performance under Different Environmental Conditions

The Paducah and PE soil samples were analyzed under both the outdoor and the chamber conditions so that the performance of the DELFIA PCB Assay could be assessed under different environmental conditions. When the performance of the DELFIA PCB Assay is compared with that of the reference laboratory for these samples, there is no statistical difference between the data set that was generated outdoors and that generated in the chamber. The data sets overlap and are statistically indistinguishable. However, as shown in Tables 9 and 10, when DELFIA's results are compared with the nominal concentrations of the spiked PE samples, there is a statistical difference between the results generated outdoors and those generated in the chamber. The comparison with the reference laboratory results did not show statistical differences because of more uncertainty (i.e., variability) in these two data sets.

Table 14. DELFIA PCB Assay Correlation with Reference Data

Description of sample set	Number of samples	Correlation coefficient *(r)*	Slope (*m)*
All values where a detection was reported	170	0.50	0.20
Excluding reference suspect values	168	0.50	0.20
Excluding Hybrizyme suspect values	166	0.81	0.61
Excluding reference and Hybrizyme suspect values	164	0.89	0.78

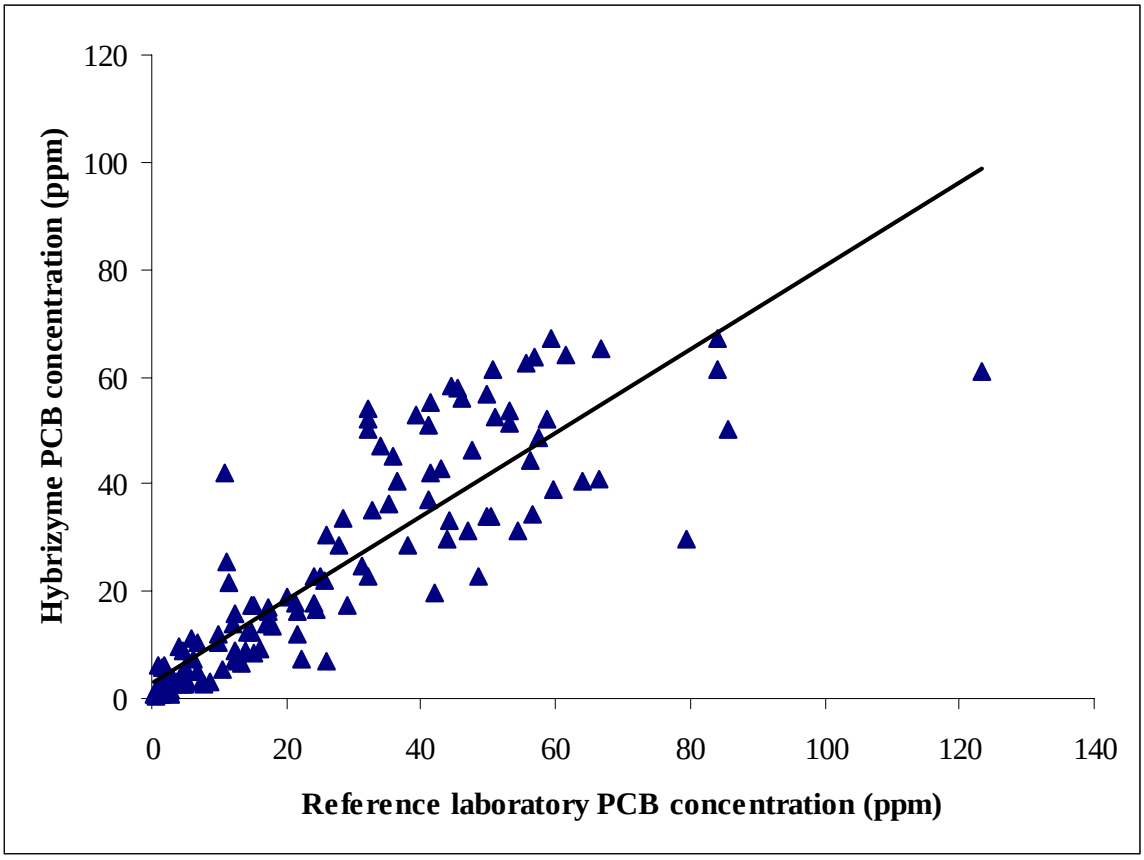

Figure 1. Comparison of Hybrizyme and reference laboratory PCB results, excluding nondetects and suspect values (N = 164). The slope of the linear regression line is 0.78 and the intercept is 2.6 ppm.

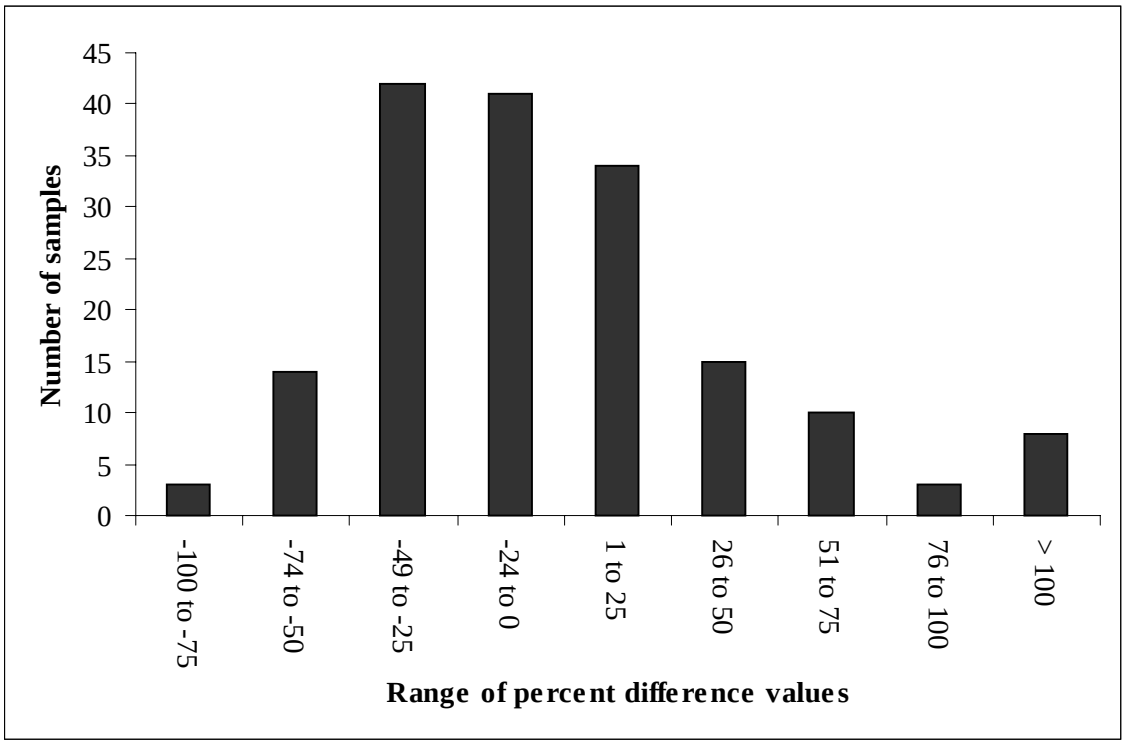

Figure 2. Range of percent difference values.

Application to Regulatory Decision-Making

One of the objectives of this verification test was to assess the technology's ability to perform at regulatory decision-making levels for PCBs—specifically, to detect PCBs at a level >50 ppm in soils. The technology's performance in detecting PCBs ranging in concentration from 40 to 60 ppm in PE and environmental soil samples were used to assess this ability. The performance of the DELFIA PCB Assay for this concentration range, as shown in Table 15, was precise (mean RSD = 14%), unbiased (mean % recovery = 94%), and comparable to the performance of the reference laboratory (mean of the absolute value of %D = 27%).

Table 15. Performance of DELFIA PCB Assay on Regulatory Sample PCB Concentrations (40–60 ppm)

Statistic	% RSD	% recovery	% D (absolute value)
Mean	14	94	27
Median	13	99	24

Sample Throughput

Sample throughput is representative of the estimated amount of time required to prepare and analyze the sample and perform the data analysis. Operating in both the field and the chamber, the two-person Hybrizyme team accomplished a sample throughput rate of approximately six samples per hour for the 208 soil and 24 extract samples.

Ease of Use

Two operators were used for the test because of the number of samples and working conditions, but the technology can be operated by a single person. Users unfamiliar with immunoassay techniques may need approximately one-half day of additional training to operate the instrument. No particular level of educational training is required for the operator.

Cost Assessment

The purpose of this economic analysis is to estimate the range of costs for analysis of PCB-contaminated soil samples using the DELFIA PCB Assay and a conventional analytical reference laboratory method. The analysis was based on the results and experience gained from this verification test, costs provided by Hybrizyme, and representative costs provided by the reference analytical laboratories that offered to analyze these samples. To account for the variability in cost data and assumptions, the economic analysis is presented as a list of cost elements and a range of costs for sample analysis by the DELFIA PCB Assay instrument and by the reference laboratory.

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

- sample shipment costs,
- labor costs, and
- equipment costs.

Each of these cost factors is defined and discussed and serves as the basis for the estimated cost ranges presented in Table 16. This analysis assumed that the individuals performing the analyses were fully trained to operate the technology. Costs for sample acquisition and pre-analytical sample preparation, which are tasks common to both methods, were not included in this assessment.

DELFIA PCB Assay Costs

The costs associated with using the DELFIA PCB Assay instrument included labor, equipment, and waste disposal costs. No sample shipment charges were associated with the cost of operating the instrument because the samples were analyzed on-site.

Labor

Labor costs included mobilization and demobilization, travel, per diem expenses, and on-site labor.

- *Mobilization and demobilization*. This cost element included the time for one person to prepare for and travel to each site. This estimate ranged from zero (if the analyst is located on site) to 5 h, at a rate of $50/h.
- *Travel*. This element was the cost for the analyst(s) to travel to the site. If the analyst is located at the site, the cost of commuting to the site would be zero. The estimated cost of an

Table 16. Estimated Analytical Costs for PCB-Contaminated Samples

Analysis method: DELFIA PCB Assay **Analyst/manufacturer:** Hybrizyme **Sample throughput:** 6 samples/h		**Analysis method:** EPA SW-486 Method 8081 **Analyst/manufacturer:** Reference laboratory **Typical turnaround:** 14–30 working days	
Cost category	**Cost ($)**	**Cost category**	**Cost ($)**
Sample shipment	0	**Sample shipment**	
		Labor	100–200
		Overnight shipping	50–150
Labor		**Labor**	
Mobilization/demobilization	0–250	Mobilization/demobilization	Included[a]
Travel	0–1,000 per analyst	Travel	Included
Per diem expenses	0–150/day per analyst	Per diem expenses	Included
Rate	30–75/h per analyst	Rate	44–239 per sample
Equipment		**Equipment**	Included
Mobilization/demobilization	0–150		
Instrument purchase price	30,000		
Instrument lease price	500 per week		
Reagents/supplies	22.50 per sample		

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

analyst traveling to the site for this verification test ($1000) included the cost of airline travel and rental car fees.

- *Per diem expenses*. This cost element included food, lodging, and incidental expenses. The estimate ranged from zero (for a local site) to $150/day for each analyst.
- *Rate*. The cost of the on-site labor was estimated at a rate of $30–75/h, depending on the required expertise level of the analyst. This cost element included the labor involved with the entire analytical process, comprising sample preparation, sample management, analysis, and reporting.

Equipment

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

- *Mobilization and 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 verification test, the cost of shipping equipment and supplies was estimated at $150.
- *Instrument purchase/lease*. The time-resolved fluorometer can be purchased for $30,000. The instrument can also be leased on a weekly basis for $500 per week.
- *Reagents and supplies*. Hybrizyme PCB DELFIA Reagent Kit provides 40 sample analysis. The retail price is $22.50 per sample (which includes duplicates and controls).

Reference Laboratory Costs

Sample Shipment

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

- *Labor*. This cost element 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. The estimate to complete this task ranged from 2 to 4 h at $50/h.
- *Overnight shipping*. The overnight express shipping service cost was estimated to be $50 for one 50-lb cooler of samples.

Labor, Equipment, and Waste Disposal

The labor bids from commercial analytical reference laboratories that offered to perform the reference analysis for this verification test ranged from $44 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. This rate was a fully loaded analytical cost that included equipment, labor, waste disposal, and report preparation.

Cost Assessment Summary

An overall cost estimate for use of the DELFIA PCB Assay instrument versus use of the reference laboratory was not made because of the extent of variation in the different cost factors, as outlined in Table 16. The overall costs for the application of any technology would 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's providing immediate answers versus the reference laboratory's provision of reporting data within 30 days of receipt of samples.

Miscellaneous Factors

The following are general observations regarding the field operation and performance of the DELFIA PCB Assay instrument:

- The system included a time-resolved fluorometer that was transportable by one person; however, it is rather large instrument (41.5 kg) that requires 110 V of electrical power.
- During outdoor tests, the Hybrizyme team used a portable air conditioner to cool their tent setup. Because the tent was not air-tight, the temperature inside the tent was not much cooler than the outdoor temperature.
- The Hybrizyme technology allowed the processing of 40 samples at one time.
- All 208 soil samples and 24 extracts were initially analyzed using a protocol to detect 1 ppm PCBs (a range of 0.5 to 3.2 ppm). Sample dilution and additional analyses were required to detect PCB concentrations from 3.2 ppm to >150 ppm. In all, the Hybrizyme team performed 436 analyses over the four days of testing.
- Hybrizyme used information on which Aroclors were in the samples to determine the final sample result (based on instrumental response for each Aroclor). If the Aroclor had been unknown, Hybrizyme would have used the calibration curve for Aroclor 1248.
- Tests with the Hybrizyme assay generated the following wastes: 13 L of soil/methanol mixture (classified as RCRA/TSCA waste), 95 L of TSCA-regulated solids (glass, paper, plastic, etc.), and 6.8 L of PCB-detectable, non-TSCA aqueous waste.

Summary of Performance

A summary of the performance of DELFIA PCB Assay is presented in Table 17. Precision, defined as the mean RSD, was 20% for soils and 15% for extracts. Accuracy, defined as the mean percent recovery relative to the spiked concentration, was 124% under the outdoor conditions (biased high) and 72% under the chamber conditions (biased low). There was a statistical difference between the data generated under the outdoor and chamber conditions. For the extracts, most of the sample results were biased high. No false positives were reported for the soil and extract blanks. Additionally, false positive and false negative results were determined by comparing the DELFIA PCB Assay result to the reference laboratory result for the environmental and spiked samples. None of the results were reported as false positives, but 2% were false negatives. A subset of the data was evaluated to assess the technology's ability to detect PCB contamination at levels that are of regulatory concern (i.e., >50 ppm). The technology was precise (14% RSD), accurate (94% recovery), and comparable to the reference laboratory (27% absolute value of %D) for this soil concentration range.

The verification test found that the DELFIA PCB Assay instrument was relatively simple for a trained analyst to operate in the field, requiring less than an hour for initial setup. The sample throughput of the DELFIA PCB Assay was six samples per hour. Two operators analyzed samples during the verification test, but the technology can be run by a single trained operator. The overall performance of the DELFIA PCB Assay for the analysis of PCBs in soil and solvent extracts was characterized as biased (dependent on environmental conditions) but precise.

Table 17. Performance Summary for the DELFIA PCB Assay

Feature/parameter	Performance summary
Precision	**Mean RSD** Soil: 20% Extract: 15%
Accuracy	**Mean recovery** (significantly different for the two conditions) *Soil* Outdoor: 124% Chamber: 72% *Extract* Outdoor: 300% Chamber: 145%
False positive results on blank samples	Soil: none Extract: none
False positive results relative to reference laboratory results	None
False negative results relative to reference laboratory results	2% (4 of 192 samples)
Comparison with reference laboratory results (all data, excluding suspect values)	*r* / *m* / **Median absolute % D** All values: 0.50 / 0.20 / 29% Excluding suspect values: 0.89 / 0.78 / 29%
Regulatory decision-making (40 to 60 ppm soil)	RSD: 14% % recovery: 94% Abs %D: 27%
Completeness	100% of 208 soil samples and 24 extract samples
Weight of time-resolved fluorimeter	41.5 kg
Sample throughput (2 operators)	6 samples/h
Power requirements	110 V
Training requirements	One-half day technology-specific training
Cost	Instrument purchase: $30,000 Instrument lease: $500 per week Reagents/supplies: $22.50 per sample
Waste generated	13 L of soil/methanol mixture (classified as RCRA/TSCA) 95 L of TSCA-regulated solids (glass, paper, plastic, etc.) 6.8 L of PCB-detectable, non-TSCA aqueous waste (Total number of samples analyzed: 232)
Overall evaluation	Precise Biased high for outdoor conditions Biased low for chamber conditions

Section 6 — Technology Update and Representative Applications

In this section, the vendor (with minimal editorial changes by ORNL) provides information regarding new developments with its technology since the verification activities. In addition, the vendor provides a list of representative applications in which its technology has been used.

Temperature Control

The Hybrizyme assay system is designed for laboratory or mobile laboratory use. For applications beyond the normal temperature variations that occur indoors, the Victor™ Time-Resolved Fluorometer can be equipped with temperature control. In addition, calibrators included within each sample batch can be used to automatically compensate for extreme temperature conditions. The data contained within this ETV report was obtained without controlling for temperature fluctuations.

Food Test Validation

Hybrizyme's DELFIA PCB assay has been validated for testing food products by the European Commission's Joint Research Centre, Institute for Health and Consumer Protection, Food Products Unit, Ispra, Italy. A report on the validation results, entitled "Use of an immunoassay as a means to detect polychlorinated biphenyls in animal fat," by S. Jaborek-Hugo et al., has been accepted for publication in *Food Additives & Contaminants*, ed. John Gilbert (Taylor & Francis Ltd., London).

Section 7 — References

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Appendix A

Hybrizyme's DELFIA PCB Assay Results Compared with Reference Laboratory Results

Location	Sample site or type	Sample no.	Sample replicate	Total PCB conc. (ppm)		Hybrizyme analysis order [a]
				DELFIA	Reference	
Outside	Oak Ridge 1	1	1	1.0	0.6	1091
Outside	Oak Ridge 1	1	2	0.6	0.4	1025
Outside	Oak Ridge 1	1	3	0.8	0.5	1063
Outside	Oak Ridge 1	1	4	0.5	0.5	1056
Outside	Oak Ridge 1	2	1	2.5	2.2	1001
Outside	Oak Ridge 1	2	2	3.6	2.1	1062
Outside	Oak Ridge 1	2	3	2.5	1.7	1085
Outside	Oak Ridge 1	2	4	3.2	2.5	1059
Outside	Oak Ridge 1	3	1	3.9	3.0	1094
Outside	Oak Ridge 1	3	2	3.7	2.4	1015
Outside	Oak Ridge 1	3	3	6.0	2.0	1020
Outside	Oak Ridge 1	3	4	5.7	1.6	1027
Outside	Oak Ridge 1	4	1	10.6	6.8	1058
Outside	Oak Ridge 1	4	2	11.2	6.0	1070
Outside	Oak Ridge 1	4	3	12.3	14.8	1082
Outside	Oak Ridge 1	4	4	10.5	9.9	1054
Outside	Oak Ridge 1	5	1	56.6	49.7	1098
Outside	Oak Ridge 1	5	2	61.3	84.1	1013
Outside	Oak Ridge 1	5	3	61.5	50.6	1017
Outside	Oak Ridge 1	5	4	51.2	53.2	1076
Outside	Oak Ridge 1	6	1	>150	269.6	1030
Outside	Oak Ridge 1	6	2	>150	255.9	1009
Outside	Oak Ridge 1	6	3	>150	317.6	1053
Outside	Oak Ridge 1	6	4	>150	649.6	1103
Outside	Oak Ridge 2	1	1	1.2	1.0	1022
Outside	Oak Ridge 2	1	2	1.3	1.6	1074
Outside	Oak Ridge 2	1	3	2.8	1.2	1100
Outside	Oak Ridge 2	1	4	1.1	1.2	1101

Location	Sample site or type	Sample no.	Sample replicate	Total PCB conc. (ppm)		Hybrizyme analysis order [a]
				DELFIA	Reference	
Outside	Oak Ridge 2	2	1	1.6	1.7	1057
Outside	Oak Ridge 2	2	2	1.5	2.0	1023
Outside	Oak Ridge 2	2	3	1.5	1.7	1081
Outside	Oak Ridge 2	2	4	1.8	1.9	1061
Outside	Oak Ridge 2	3	1	2.2	1.5	1031
Outside	Oak Ridge 2	3	2	1.9	2.1	1087
Outside	Oak Ridge 2	3	3	2.2	1.8	1044
Outside	Oak Ridge 2	3	4	1.9	2.4	1084
Outside	Oak Ridge 2	4	1	30.9	<490	1037 [b]
Outside	Oak Ridge 2	4	2	20.9	<99	1093 [b]
Outside	Oak Ridge 2	4	3	32.2	<66	1008 [b]
Outside	Oak Ridge 2	4	4	37.2	<98	1032 [b]
Outside	Oak Ridge 2	5	1	58.3	44.5	1099
Outside	Oak Ridge 2	5	2	45.2	36.0	1066
Outside	Oak Ridge 2	5	3	52.9	39.3	1014
Outside	Oak Ridge 2	5	4	36.3	35.1	1072
Outside	Oak Ridge 2	6	1	139.0	<66	1086 [b]
Outside	Oak Ridge 2	6	2	129.0	<200	1083 [b]
Outside	Oak Ridge 2	6	3	128.0	<130	1007 [b]
Outside	Oak Ridge 2	6	4	158.0	<200	1034 [b]
Outside	Paducah	1	1	1.1	0.7	1065
Outside	Paducah	1	2	1.0	1.1	1041
Outside	Paducah	1	3	1.0	0.6	1090
Outside	Paducah	1	4	1.0	1.9	1067
Outside	Paducah	2	1	1.1	1.1	1026
Outside	Paducah	2	2	1.1	1.2	1010
Outside	Paducah	2	3	0.8	1.3	1052
Outside	Paducah	2	4	1.1	1.7	1033
Outside	Paducah	3	1	17.2	14.9	1028
Outside	Paducah	3	2	16.0	12.4	1080
Outside	Paducah	3	3	17.3	15.0	1073
Outside	Paducah	3	4	13.7	16.9	1006

Location	Sample site or type	Sample no.	Sample replicate	Total PCB conc. (ppm)		Hybrizyme analysis order [a]
				DELFIA	Reference	
Outside	Paducah	4	1	42.2	41.4	1078
Outside	Paducah	4	2	37.0	41.2	1075
Outside	Paducah	4	3	22.8	48.5	1029
Outside	Paducah	4	4	47.1	34.0	1002
Outside	Paducah	5	1	>150	431.6	1024
Outside	Paducah	5	2	>150	406.3	1102
Outside	Paducah	5	3	>150	304.7	1096
Outside	Paducah	5	4	>150	392.8	1092
Outside	Spike/PE	1	1	1.8	2.1	1046
Outside	Spike/PE	1	2	2.3	1.9	1097
Outside	Spike/PE	1	3	1.7	0.7	1051
Outside	Spike/PE	1	4	1.9	1.6	1048
Outside	Spike/PE	2	1	17.9	21.2	1047
Outside	Spike/PE	2	2	16.1	17.2	1060
Outside	Spike/PE	2	3	17.1	17.4	1036
Outside	Spike/PE	2	4	16.6	24.4	1055
Outside	Spike/PE	3	1	8.7	4.5	1071
Outside	Spike/PE	3	2	9.6	4.0	1035
Outside	Spike/PE	3	3	7.5	6.3	1079
Outside	Spike/PE	3	4	5.7	5.0	1050
Outside	Spike/PE	4	1	52.1	58.7	1064
Outside	Spike/PE	4	2	62.6	55.7	1089
Outside	Spike/PE	4	3	53.6	53.2	1043
Outside	Spike/PE	4	4	52.6	50.9	1003
Outside	Spike/PE	5	1	14.0	12.2	1077
Outside	Spike/PE	5	2	42.2	10.9	1040
Outside	Spike/PE	5	3	21.6	11.3	1016
Outside	Spike/PE	5	4	11.8	10.0	1069
Outside	Spike/PE	6	1	67.1	59.2	1012
Outside	Spike/PE	6	2	63.5	56.9	1049
Outside	Spike/PE	6	3	65.4	66.8	1039
Outside	Spike/PE	6	4	48.5	57.5	1095

Location	Sample site or type	Sample no.	Sample replicate	Total PCB conc. (ppm)		Hybrizyme analysis order [a]
				DELFIA	Reference	
Outside	Spike/PE	7	1	2.4	1.8	1045
Outside	Spike/PE	7	2	2.0	1.4	1005
Outside	Spike/PE	7	3	2.2	1.9	1042
Outside	Spike/PE	7	4	2.1	1.8	1038
Outside	Spike/PE	8	1	54.0	32.0	1018
Outside	Spike/PE	8	2	55.0	41.3	1068
Outside	Spike/PE	8	3	56.0	46.0	1088
Outside	Spike/PE	8	4	52.1	32.2	1004
Outside	Soil Blank	1	1	<0.5	<0.1	1011
Outside	Soil Blank	1	2	<0.5	<0.1	1021
Outside	Soil Blank	1	3	<0.5	<0.2	1019
Outside	Soil Blank	1	4	<0.5	<1.3	1104
Outside	Extract Blank	1	1	<0.5	n/a [c]	1116
Outside	Extract Blank	1	2	<0.5	n/a [c]	1106
Outside	Extract Blank	1	3	<0.5	n/a [c]	1111
Outside	Extract Blank	1	4	<0.5	n/a [c]	1108
Outside	Extract	1	1	28.4	n/a [c]	1113
Outside	Extract	1	2	28.4	n/a [c]	1112
Outside	Extract	1	3	27.9	n/a [c]	1105
Outside	Extract	1	4	35.9	n/a [c]	1115
Outside	Extract	2	1	267.0	n/a [c]	1109
Outside	Extract	2	2	271.0	n/a [c]	1110
Outside	Extract	2	3	342.0	n/a [c]	1107
Outside	Extract	2	4	311.0	n/a [c]	1114
Chamber	Paducah	1	1	0.8	1.0	2020
Chamber	Paducah	1	2	<0.6	1.0	2052
Chamber	Paducah	1	3	0.7	1.1	2059
Chamber	Paducah	1	4	0.7	0.6	2048
Chamber	Paducah	2	1	0.8	1.4	2079
Chamber	Paducah	2	2	<0.6	1.6	2066
Chamber	Paducah	2	3	<0.6	1.2	2099
Chamber	Paducah	2	4	<0.6	1.5	2017

Location	Sample site or type	Sample no.	Sample replicate	Total PCB conc. (ppm)		Hybrizyme analysis order [a]
				DELFIA	Reference	
Chamber	Paducah	3	1	9.0	14.0	2096
Chamber	Paducah	3	2	8.1	12.8	2053
Chamber	Paducah	3	3	9.2	16.2	2102
Chamber	Paducah	3	4	7.5	12.4	2022
Chamber	Paducah	4	1	42.7	43.1	2057
Chamber	Paducah	4	2	58.0	45.3	2103
Chamber	Paducah	4	3	51.0	41.0	2067
Chamber	Paducah	4	4	46.4	47.7	2031
Chamber	Paducah	5	1	>150	3305.0	2098
Chamber	Paducah	5	2	>150	538.7	2078
Chamber	Paducah	5	3	>150	457.0	2080
Chamber	Paducah	5	4	>150	483.3	2011
Chamber	Portsmouth 1	1	1	0.9	2.9	2076
Chamber	Portsmouth 1	1	2	0.8	1.1	2028
Chamber	Portsmouth 1	1	3	1.0	1.1	2047
Chamber	Portsmouth 1	1	4	1.1	2.5	2004
Chamber	Portsmouth 1	2	1	13.5	17.8	2039
Chamber	Portsmouth 1	2	2	12.5	14.3	2007
Chamber	Portsmouth 1	2	3	16.3	21.6	2026
Chamber	Portsmouth 1	2	4	12.0	21.6	2005
Chamber	Portsmouth 1	3	1	19.8	42.0	2033
Chamber	Portsmouth 1	3	2	28.7	27.7	2100
Chamber	Portsmouth 1	3	3	22.9	24.0	2070
Chamber	Portsmouth 1	3	4	33.5	28.4	2063
Chamber	Portsmouth 1	4	1	35.1	32.7	2032
Chamber	Portsmouth 1	4	2	29.6	79.3	2094
Chamber	Portsmouth 1	4	3	25.6	11.0	2069
Chamber	Portsmouth 1	4	4	28.7	37.9	2025
Chamber	Portsmouth 1	5	1	61.0	123.2	2101
Chamber	Portsmouth 1	5	2	64.1	61.5	2071
Chamber	Portsmouth 1	5	3	67.1	84.1	2006
Chamber	Portsmouth 1	5	4	50.2	85.5	2081

Location	Sample site or type	Sample no.	Sample replicate	Total PCB conc. (ppm)		Hybrizyme analysis order [a]
				DELFIA	Reference	
Chamber	Portsmouth 1	6	1	124.0	387.8	2015
Chamber	Portsmouth 1	6	2	>150	581.4	2092
Chamber	Portsmouth 1	6	3	>150	330.0	2073
Chamber	Portsmouth 1	6	4	>150	318.7	2012
Chamber	Portsmouth 2	1	1	2.9	3.8	2087
Chamber	Portsmouth 2	1	2	2.6	3.9	2010
Chamber	Portsmouth 2	1	3	3.0	4.3	2008
Chamber	Portsmouth 2	1	4	6.0	0.8	2002
Chamber	Portsmouth 2	2	1	4.9	6.9	2058
Chamber	Portsmouth 2	2	2	3.2	7.3	2061
Chamber	Portsmouth 2	2	3	2.7	7.8	2049
Chamber	Portsmouth 2	2	4	5.5	10.5	2104
Chamber	Portsmouth 2	3	1	30.3	26.0	2097
Chamber	Portsmouth 2	3	2	21.9	25.6	2093
Chamber	Portsmouth 2	3	3	17.4	29.1	2019
Chamber	Portsmouth 2	3	4	18.8	20.2	2077
Chamber	Portsmouth 2	4	1	22.9	25.1	2036
Chamber	Portsmouth 2	4	2	17.9	24.1	2035
Chamber	Portsmouth 2	4	3	3.1	26.2	2050
Chamber	Portsmouth 2	4	4	24.8	31.2	2060
Chamber	Portsmouth 2	5	1	35.5	151.6	2030
Chamber	Portsmouth 2	5	2	31.1	47.0	2056
Chamber	Portsmouth 2	5	3	31.3	54.3	2091
Chamber	Portsmouth 2	5	4	40.5	64.0	2089
Chamber	Portsmouth 2	6	1	>150	886.7	2074
Chamber	Portsmouth 2	6	2	>150	549.8	2014
Chamber	Portsmouth 2	6	3	3.0	542.8	2045
Chamber	Portsmouth 2	6	4	>150	1913.3	2021
Chamber	Spike/PE	1	1	1.4	2.8	2038
Chamber	Spike/PE	1	2	1.3	2.4	2084
Chamber	Spike/PE	1	3	2.0	2.6	2040
Chamber	Spike/PE	1	4	1.4	2.6	2023

Location	Sample site or type	Sample no.	Sample replicate	Total PCB conc. (ppm)		Hybrizyme analysis order [a]
				DELFIA	Reference	
Chamber	Spike/PE	2	1	7.5	22.4	2024
Chamber	Spike/PE	2	2	7.1	26.0	2042
Chamber	Spike/PE	2	3	37.6	29.4	2034
Chamber	Spike/PE	2	4	8.4	15.2	2027
Chamber	Spike/PE	3	1	3.1	8.5	2018
Chamber	Spike/PE	3	2	2.6	4.9	2016
Chamber	Spike/PE	3	3	2.8	4.7	2088
Chamber	Spike/PE	3	4	3.0	5.2	2083
Chamber	Spike/PE	4	1	22.8	32.0	2062
Chamber	Spike/PE	4	2	33.3	44.1	2085
Chamber	Spike/PE	4	3	29.7	43.8	2090
Chamber	Spike/PE	4	4	38.9	59.6	2003
Chamber	Spike/PE	5	1	6.7	13.2	2082
Chamber	Spike/PE	5	2	8.8	12.4	2001
Chamber	Spike/PE	5	3	6.9	12.7	2051
Chamber	Spike/PE	5	4	7.3	12.7	2043
Chamber	Spike/PE	6	1	34.2	56.6	2013
Chamber	Spike/PE	6	2	34.1	50.3	2046
Chamber	Spike/PE	6	3	33.8	49.9	2075
Chamber	Spike/PE	6	4	40.8	66.4	2064
Chamber	Spike/PE	7	1	1.3	2.2	2037
Chamber	Spike/PE	7	2	1.5	1.2	2065
Chamber	Spike/PE	7	3	1.6	1.4	2041
Chamber	Spike/PE	7	4	1.7	2.1	2068
Chamber	Spike/PE	8	1	44.2	56.4	2072
Chamber	Spike/PE	8	2	40.4	36.5	2086
Chamber	Spike/PE	8	3	50.2	32.1	2029
Chamber	Spike/PE	8	4	37.4	146.0	2095
Chamber	Soil Blank	1	1	<0.5	<0.1	2009
Chamber	Soil Blank	1	2	<0.5	<0.8	2044
Chamber	Soil Blank	1	3	<0.6	<0.1	2054
Chamber	Soil Blank	1	4	<0.6	<0.1	2055

Location	Sample site or type	Sample no.	Sample replicate	Total PCB conc. (ppm)		Hybrizyme analysis order [a]
				DELFIA	Reference	
Chamber	Extract Blank	1	1	<0.5	n/a [c]	2111
Chamber	Extract Blank	1	2	<0.5	n/a [c]	2113
Chamber	Extract Blank	1	3	<0.5	n/a [c]	2112
Chamber	Extract Blank	1	4	<0.5	n/a [c]	2114
Chamber	Extract	1	1	20.8	n/a [c]	2106
Chamber	Extract	1	2	17.2	n/a [c]	2115
Chamber	Extract	1	3	18.5	n/a [c]	2105
Chamber	Extract	1	4	19.0	n/a [c]	2109
Chamber	Extract	2	1	83.8	n/a [c]	2107
Chamber	Extract	2	2	76.3	n/a [c]	2116
Chamber	Extract	2	3	111.0	n/a [c]	2108
Chamber	Extract	2	4	133.7	n/a [c]	2110

[a] Indicates order of analysis by Hybrizyme; for example, 1001 was analyzed first, then 1002, etc.
[b] Reference laboratory had trouble analyzing these samples. See Section 4 for more details.
[c] Reference laboratory did not analyze these extract samples.

Appendix B

Data Quality Objective (DQO) Example

Disclaimer

The following hypothetical example demonstrates how the information provided in this report may be used in the data quality objective (DQO) process. While this example illustrates the application of quantitative DQOs to a decision process, it cannot attempt to provide a thorough education in this topic. Please refer to other educational or technical resources for further details (e.g., ASTM 1997a, b; EPA 1996). In addition, because the focus of this report is on the analytical technology, this example makes simplifying assumptions (such as that the sample is homogeneous and that the reference laboratory results represent the true concentration) that may not be valid in the real world.

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 Hybrizyme's DELFIA PCB Assay 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 ≥50 ppm ("hot"). A concentration of 50 ppm is the TSCA regulatory threshold (RT) for this environmental problem. Those drums with PCB concentrations <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 < 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

The DQO team's primary goal was to calculate how many samples would need to be analyzed by the DELFIA PCB Assay in order to confidently make a decision about remediating the processed soil, given the uncertainties of the technology's results. The worst possible mistake would be to send a drum to the landfill with PCB concentrations exceeding 50 ppm. The error rate of this false-rejection decision would serve as the primary determinant for the number of samples measured. A secondary decision error would be to unnecessarily send an excessive number of drums to the incinerator if the average PCB concentration was <50 ppm. This decision error would be a false-acceptance decision error. Both the false-rejection decision error and the false-acceptance decision error were taken into account to determine the final sampling plan.

EPA required that a sufficient number of samples be measured from each drum so that the false-rejection error rate (FR) for the decision rule was 0.05 or less if the true drum concentration was ≥50 ppm. This DQO goal represents a 5% chance of sending to a landfill those drums with PCB concentrations >50 ppm.

The DQO team did not want to send an excessive number of drums to the incinerator if the average PCB concentration was <50 ppm because of the expense. In this situation, a false-acceptance decision is made when it is concluded that a drum is "hot" when, in actuality, the drum contains soil with PCB contamination

<50 ppm. Therefore, the DQO team recommended that the false-acceptance decision error rate (FA) be 0.10 if the true PCB concentration is 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 is 40 ppm.

Permissible FR and FA Error Rates and Critical Decision Points

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

FA: 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 was considering the use of the Hybrizyme's DELFIA PCB Assay, 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 DELFIA PCB Assay's analytical method, which is determined by precision studies.

2. *What is the appropriate action level (AL)* for using the Hybrizyme's DELFIA PCB Assay 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 DELFIA PCB Assay, 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.

Hybrizyme's DELFIA PCB Assay Accuracy

The ETV verification test results indicated that the DELFIA PCB Assay's accuracy for soil samples showed a statistically significant difference between data generated under the outdoor and chamber conditions. The results were biased slightly high (mean % recovery = 124%) under the outdoor conditions, and biased slightly low (mean % recovery = 72%) under the chamber conditions. For this example, the testing will occur during warm temperatures similar to the outdoor test runs. Colder temperatures would be similar to the chamber conditions. Average replicate PCB concentrations determined by the DELFIA PCB Assay in outdoor conditions showed a strong linear correlation ($R^2 = 0.96$) with the certified values for the performance evaluation samples. This correlation is represented by a line fitted to the data that predicts the expected DELFIA PCB Assay's concentration from the certified PE value. Figure B-1 shows this linear relationship with the PCB concentrations plotted against the certified PCB values for the PE samples, which included the concentration range of 0 to 50 ppm. The arrow on the plot in Figure B-1 demonstrates a method to quickly estimate a corrected PCB concentration from a DELFIA PCB Assay measurement. For example, a DELFIA PCB Assay concentration of 50 ppm would correspond to a certified PCB concentration of 44 ppm. The equation for the PCB prediction line is

$$Delfia\ Result = 1.65 + 1.10 \times (Certified\ PE\ Value) \quad \text{(Eq. B-1)}$$

The critical decision points, 40 ppm and 50 ppm, correspond to DELFIA PCB Assay results of 45.7 ppm and 56.7 ppm, respectively. The DQO team knew that if they selected the DELFIA PCB Assay for this project, they would have to compensate for the bias. Compensation may be performed either by a graphical method using a calibration line such as Figure B-1 or by a calibration equation such as B-1.

Determining the Number of Samples

With the critical decision points selected, the DQO 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 DELFIA PCB Assay's replicate results for each sample from the ETV verification test established that the standard deviation for PE samples could be approximated by a linear model within the concentration range of 0 to 50 ppm (see Figure B-2). The equation for the line is

DELFIA SD = 2.80 + 0.05 × (Certified PE Value) (Eq. B-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 DQO goals for FR and FA error rates. A formula is provided in EPA's *Guidance for Data Quality Assessment* (EPA 1996, pp. 3.2-3, Box 3.2-1) that can be adapted to this example for calculating the number of samples required to meet the FR and FA requirements:

$$N = \frac{S^2\left(Z_{1-FR} + Z_{1-FA}\right)^2}{\left(RT - C_{FA}\right)^2} + (0.5)Z_{1-FR}^2 \quad , \qquad \text{(Eq. B-3)}$$

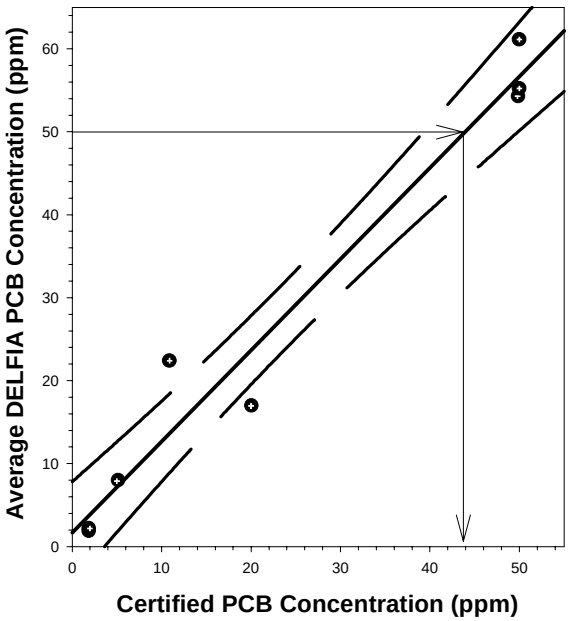

Figure B-1. A linear model for predicting DELFIA PCB Assay concentrations from certified PCB concentrations with 95% confidence intervals (dashed lines).

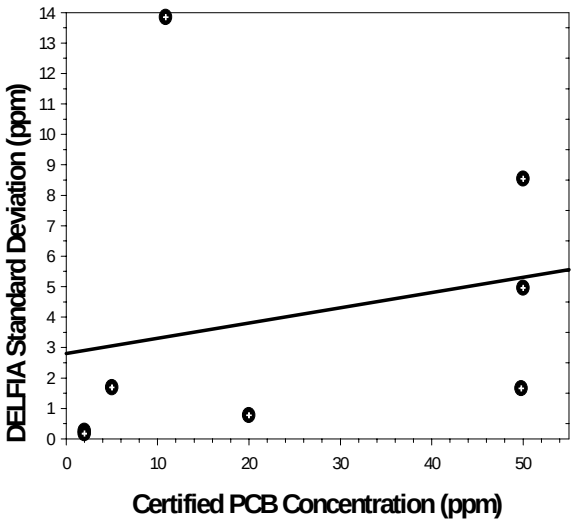

Figure B-2. A linear model fitted to DELFIA PCB Assay standard deviation versus certified PCB concentration.

where

- **N** = number of samples from a drum to be measured
- S^2 = variance for the measurement [e.g., $S^2 = (2.80 + 0.05 \times \text{Certified PE Value})^2$]
- RT = regulatory threshold (e.g., $RT = 50$ ppm)
- C_{FA} = concentration at which the FA is specified (e.g., $C_{FA} = 40$ ppm)
- FR = false-rejection decision error rate (e.g., $FR = 0.05$)

FA = false-acceptance decision error rate (e.g., $FA = 0.10$)
Z_{1-p} = the $(1 - p)^{th}$ percentile of the standard normal distribution (see EPA 1996, Appendix A, Table A-1) (e.g., $Z_{(1-FR)} = Z_{0.95} = 1.645$).

Incorporating the appropriate values for the DELFIA PCB Assay into Eq. B-3 gives

$$N = \frac{(2.80 + 0.05 \times 50)^2 (1.645 + 1.282)^2}{(50 - 40)^2} + (0.5)(1.645)^2 = 3.76 \approx 4 \quad . \qquad \text{(Eq. B-4)}$$

Therefore, four samples from each drum would be analyzed by Hybrizyme's DELFIA PCB Assay to meet the criteria established by the DQO process. Note that, to be conservative, one would evaluate the standard deviation at 50 ppm and round the sample size up to the next integer. These four samples are averaged (by taking the arithmetic mean) to produce an DELFIA PCB Assay value for a drum's PCB concentration. As discussed earlier, this DELFIA PCB Assay value can then be converted to a corrected average drum concentration by using a graph such as Figure B-1 or an equation for the PCB prediction line such as Eq. B-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 AL is the decision criterion (or "cut-off" value) that will be compared with 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 the basis of controlling the FR established in the DQO process. Recall that the team set the permissible FR error rate at 5%.

The formula to compute the action level (EPA 1996) is

$$AL = RT - Z_{1-FR} \times \frac{S}{\sqrt{n}} \quad . \qquad \text{(Eq. B-5)}$$

Computing the AL in this instance, we find the following:

$$AL = 50\,\text{ppm} - (1.645) \times \frac{2.80 + 0.05 \times 50}{\sqrt{4}} = 45.6\,\text{ppm} \quad . \qquad \text{(Eq. B-6)}$$

To summarize, four random samples from each drum are analyzed, and the biased results are corrected. The four corrected results are averaged to produce the average PCB concentration for the drum, which is then compared to the AL for the decision rule (45.6 ppm). Therefore, the decision rule using the DELFIA PCB Assay to satisfy a 5% FR and a 10% FA (after correcting the results for bias) is as shown in the box below.

Decision Rule for 5% FR and 10% FA

If the corrected average PCB concentration of four random soil samples from a drum < 45.6 ppm, then send the drum to the landfill.

If the corrected average PCB concentration of four random soil samples from a drum ≥ 45.6 ppm, then send the drum to the incinerator.

The decision performance curve (see EPA 1996, pp. 34–36) calculates the probability of sending a drum to the incinerator for different values of true PCB concentration in a drum. Figure B-3 shows that the decision performance curve has the value of Pr[Take Drum to Incinerator] = 0.965 for True = 50 ppm. This indicates that the decision rule meets the DQO team's FR percentage of 5%. The Pr[Take Drum to Incinerator] = 0.009 for True = 40 ppm, which is better (at 0.9%) than the FA percentage 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.

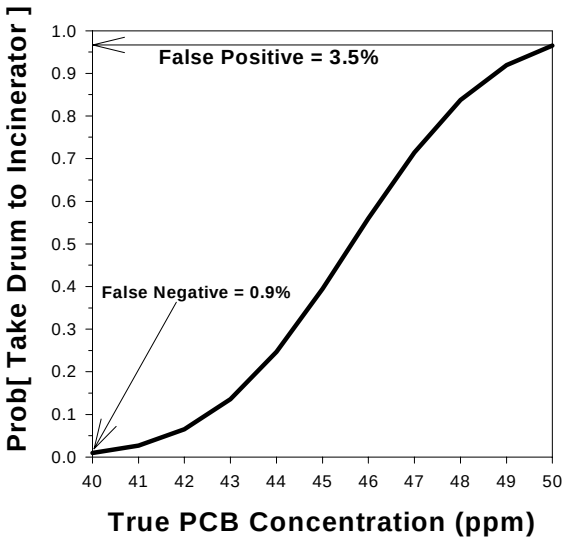

Figure B-3. Decision performance curve for PCB drum example.

Alternative FR 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% FR) 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 FR requirement from 5% to 1% would affect the decision rule.

Using FR = 0.01, the sample size is calculated to be seven and the action level is calculated to be 45.3 ppm. The decision performance curve has the value of Pr[Take Drum to Incinerator] = 0.995 for True = 50 ppm. This indicates that the decision rule meets the DQO team's FR of 1%. The Pr[Take Drum to Incinerator] = 0.002 for True = 40 ppm is better than the FA percentage 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 FR would be as shown below.

Decision Rule for FR = 1% and FA = 10%

If the corrected average PCB concentration of seven random soil samples from a drum < 45.3 ppm, then send the drum to the landfill.

If the corrected average PCB concentration of seven random soil samples from a drum ≥ 45.3 ppm, then send the drum to the incinerator.

Comparison with Reference Laboratory

A statistical analysis of the results from the reference laboratory over the range 0 to 60 ppm gave a linear approximation to the standard deviation of $S_{ref} = 0.14 + 0.134 \times$ (Certified PE Value). Decision rules can be calculated on the basis of this standard deviation. Table B-1 compares the decision rules for Hybrizyme's DELFIA PCB Assay with those of the reference laboratory.

Table B-1. Comparison of Decision Rules for DELFIA PCB Assay Measurements and Reference Laboratory Measurements

Analysis Method	FR = 5% and FA = 10%		FR = 1% and FA = 10%		Cost per sample	Turnaround time
	N	AL (ppm)	N	AL (ppm)		
DELFIA	4	45.6	7	45.3	$22.50 [a]	6 samples/hr
Reference Lab	6	45.4	9	44.7	$144	14–30 working days

[a] Plus instrument purchase or rental cost (see Table 16).